March 4, 1969 R. F. CREE 3,430,417

GAS SAMPLE ENRICHMENT DEVICE

Filed June 15, 1966

FIG. 1.

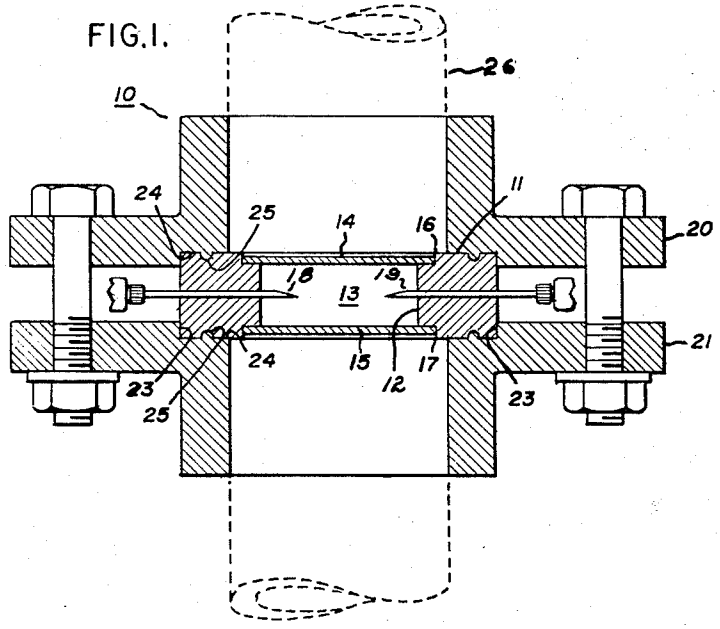
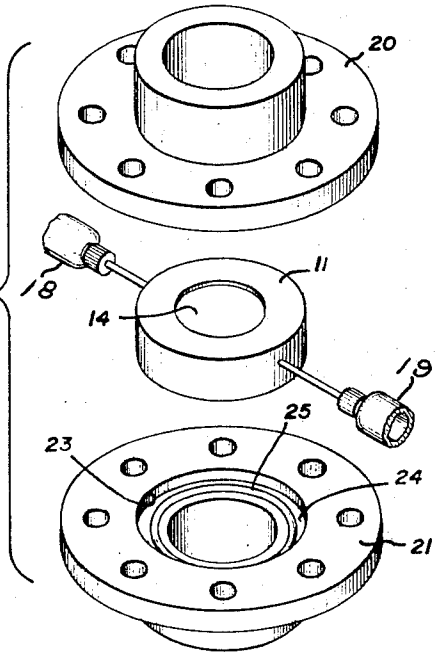


FIG. 2.



INVENTOR:
ROBERT F. CREE,

BY James J. Tickiello
HIS ATTORNEY.

United States Patent Office 3,430,417
Patented Mar. 4, 1969

3,430,417

GAS SAMPLE ENRICHMENT DEVICE

Robert F. Cree, Ballston Lake, N.Y., assignor to General Electric Company, a corporation of New York

Filed June 15, 1966, Ser. No. 557,683
U.S. Cl. 55—16 3 Claims
Int. Cl. B01d 59/12

ABSTRACT OF THE DISCLOSURE

Device and method for removing a carrier gas from the effluent of a gas separation apparatus and for providing an enriched sample of the gas to be analyzed. A pair of membrane gas filters are positioned on opposite sides of a metallic annular member to form a chamber into which the effluent gas, comprising the carrier gas and the gas to be analyzed, is introduced under pressure. The carrier gas flows through the filters and the resulting enriched sample of the gas to be analyzed is removed from the chamber at a point generally opposite from the point of entry of the effluent.

This invention relates to a gas sample enrichment device and more particularly to a gas sample enrichment device which operates to remove a carrier gas from the effluent of a gas separation apparatus to facilitate more accurate analysis and identification of effluent gases.

Certain well known devices such as gas chromatographs and mass spectrometers are widely utilized in gas analysis and control equipment. The gas chromatograph and the mass spectrometer operate on different principles in that the gas chromatograph usually involves the principle of selective absorption of one or more gases from a mixture, while the mass spectrometer involves the analysis or identification of gas ions based upon a predetermined trajectory of gas ions through electric and/or magnetic fields. In many instances it is quite desirable to couple a mass spectrometer directly to a gas chromatograph so that the gas chromatograph separates certain gases and the mass spectrometer identifies the separated gas. See Analytical Chemistry, vol. 36, April 1964, pp. 759–764; vol. 37, #7, June 1965, pp. 844–851.

However, the gas chromatograph ordinarily operates at atmospheric pressure at its exit while the mass spectrometer operates at internal pressures as low as 10^{-8} torr. Consequently an inlet means or device is necessary which will permit acquisition of a sample of gas separated by the chromatograph at atmospheric pressure and delivery of this sample to the mass spectrometer inlet at very low pressures. Additionally, the sample delivered to the mass spectrometer must be in good analytical condition, i.e., have good enrichment in the particular gas which is to be analyzed or identified. This enrichment represents a difficult problem because the effluent from a gas chromatograph ordinarily includes a large amount of a carrier gas which is used to increase the efficiency of a gas chromatograph, and large amounts of gas other than the gas to be identified affects the sensitivity of detection in the identifying apparatus such as a mass spectrometer. It is therefore desirable to have a gas sampling inlet device which will also function to remove significant quantities of carrier gas from the gas sample.

Further information concerning gas chromatograph may be found in U.S. Patent 3,140,598 Dunham and the references therein, and for mass spectrometers U.S. Patent 2,699,305 Usher and the references therein.

Accordingly, it is an object of this invention to provide an improved gas enrichment means.

It is a further object of this invention to provide an improved mass spectrometer gas enrichment inlet device.

It is yet another object of this invention to provide

an improved high temperature bakable gas enrichment device for a mass spectrometer inlet.

It is another object of this invention to provide a gas enrichment sample device adapted for connection between a gas chromatograph and a mass spectrometer inlet to provide an enriched gas sample to the mass spectrometer.

It is still another object of this invention to provide a gas inlet enrichment sample device for a mass spectrometer in the form of a short cylindrical device adapted to be placed between vacuum conduit flanges.

Briefly described, this invention in one of its preferred forms includes a gas sample enrichment or separation device in the form of a relatively thick, disk-like, hollow housing defining a central gas chamber and adapted to interconnect a mass spectrometer inlet and a gas chromatograph exit so that a predetermined amount of a sample gas may flow from the gas chromatograph into the mass spectrometer. The disk-like device is also adapted to be positioned coaxially between mating conduit flanges in a vacuum conduit so that filter interaction means separate the defined chamber in the disk housing from the vacuum conduit. Additional transverse port means in the disk housing provide for a flow of gas from the gas chromatograph transversely through the defined chamber in the disk housing to the mass spectrometer. The separation device provides a removal of carrier gas from the chromatograph gas flowing through the port means by selective removal from the defined chamber of the carrier gas through the filter interaction means.

This invention will be better understood when taken in connection with the following description and the drawings in which:

FIG. 1 is a cross sectional view of one preferred embodiment of this invention;

FIG. 2 is an exploded view of the embodiment of FIG. 1.

Referring now to FIG. 1, there is shown a gas sample enrichment separator device **10** in accordance with one preferred embodiment of this invention. Separator device **10** comprises a body section or member **11** which may be conveniently in the form of an annular or short cylindrical disk-like configuration to define a concentric axial opening **12** therethrough. The opening **12** defines a central chamber **13** which is closed on opposite sides thereof by means of selective gas filters **14** and **15**. Filters **14** and **15** are preferably in sheet or disk form and are sealed to member **11** in countersinks **16** and **17** respectively by suitable vacuum bonding materials such as for example a silicone rubber glue or cement. Filters **14** and **15**, however, may be sealed directly to the side surfaces of member **11** or otherwise suitably attached thereto by mechanical or chemical means. Separator device **10** in one form is adapted to be inserted in a vacuum conduit so that low pressure or vacuum conditions exist adjacent filters **14** and **15**, and by this means a selected gas is removed from chamber **13** through filters **14** and **15**. Accordingly, filters **14** and **15** are chosen to be of a predetermined material and porosity properly correlated with adjacent low pressure conditions acting thereon to selectively pass substantially more of a specific carrier gas for example than of the sample gas to be analyzed.

Chamber **13** is adapted to contain therein a sample of a gas taken from for example the effluent of a gas chromatograph, and to deliver at least a part of this sample to an analyzer device such as a mass spectrometer. Therefore, dual and cross flow conditions are established through device **10**, one for the sample gas entering and exiting from chamber **13** and the other to remove a carrier gas from the sample gas in chamber **13**. One preferred arrangement utilizes transverse cross flow conditions as illustrated in FIG. 1 by opposed transverse inlet and exit

port means **18** and **19** respectively. Port means **18** and **19** may take the form of suitable control valves or, in one preferred form, as calibrated orifices or needles properly correlated to provide predetermined quantities of gas entering and exiting from chamber **13**. The correlation must provide balanced flow conditions with the entering quantity providing the desired amount at the desired pressure of an enriched sample at the exit, in view of the amount of carrier gas being removed through the filters **14** and **15** and the high pressure at the inlet to chamber **13**.

The foregoing system may be described as an intersecting or transverse crossflow system where there is a gas flow through chamber **13** in two channels along intersecting perpendicular axes. However, other flow systems including counterflow and parallel flow systems may be employed with good results whether or not the invention is utilized in disk form and flange mounted.

The body member **11** may be utilized as a vacuum gasket itself, by being of a suitable vacuum gasket material including metals and non-metals. For example, body member **11** of oxygen-free (OHFC) copper has been employed with good results in this invention. When utilized as a gasket member, body member **11** is positioned between for example the mating vacuum flanges **20** and **21** of a vacuum conduit. However, member **11** may also be a separate structural member utilized in conjunction with other structures or gasket assemblies.

As illustrated in FIG. 1, axially spaced flanges **20** and **21** are adapted to bear directly on member **11**. For example these flanges **20** and **21** may be of the kind described and disclosed in copending application S.N. 295,120 Kearns assigned to the same assignee as the present invention, and now abandoned. Accordingly, each of the flanges, for example flange **21**, includes an annular concentric channel, groove or depression **23** in the face thereof. From the bottom surface **24** of the channel **23** there projects a small concentric ridge or bead **25**. Each of the flanges **20** and **21** is provided with identical channels and ridges so that when placed in abutting relationship the ridges **25** engage annular member **11** therebetween to be impressed therein to provide a vacuum seal. The flange arrangement is an advantageous one because it retains an all metal system which is not fragile, as in the case of glass systems, and provides for an expedient and more desirable metal-to-metal seal rather than glass-to-glass or metal-to-glass seals. The all metal system as disclosed is readily bakable at high temperatures in excess of for example 300° C.

In the illustrated arrangement of FIG. 1 a gas in chamber **13** is exposed by means of filters **14** and **15** to low pressure or vacuum conditions in the conduit **26**. Accordingly, by the predetermined selectivity characteristics of the material and porosity of filters **14** and **15**, a further selected or predetermined gas in chamber **13** such as a carrier gas is caused to proceed through filters **14** and **15** and to be carried away by conduit **26** which may be connected to the same vacuum pumping source as the mass spectrometer. The gases to be removed from chamber **13** are generally those carrier gases associated with gas chromatography which include, primarily, helium or such other gases as hydrogen, nitrogen, et cetera, which also may be employed as carrier gases. Most of the effluent from a gas chromatograph is in the form of a carrier gas such as helium, a substantial portion of which must be removed prior to admittance to a mass spectrometer for increased instrument sensitivity. It has been found that removal of a carrier gas from the sample being admitted to the mass spectrometer may increase the sensitivity of detection in the mass spectrometer by a factor of 50 to 100.

The quantity of effluent gas from a gas chromatograph is usually in excess of that which the mass spectrometer is capable of handling. For example, mass spectrometers are ordinarily limited to an inlet flow of about 0.1 milliliter per minute while the effluent gas or outflow from a gas chromatograph may exceed 500 times this amount. Therefore, only a small part of the effluent from a gas chromatograph is admitted to the mass spectrometer. The apparatus of the present invention may be suitably connected in bypass arrangement in a system for either continuous or intermittent use, and the flow therethrough may be a continuous monitoring flow which is utilized as a suitable process control signal means.

In one preferred form of this invention calibrated orifices **18** and **19** in the form of stainless steel hypodermic needles were employed. These needles are commercially available in a wide range of inside diameters so that suitable needles may be employed to provide the required gas flow into and out of the chamber **13**. These needles are inserted in suitable openings in annular member **11** and may be sealed thereto by a vacuum bonding means or other vacuum connections which facilitate removal and replacement. In one form of this invention where the pressure at the gas chromatograph exit was atmospheric and the inlet pressure at the mass spectrometer was about 7×10^{-7} torr, exemplary needle sizes were about 0.1 minimum bore size at the outlet for the mass spectrometer and a standard #24 needle at the inlet from the gas chromatograph.

Filters **14** and **15** may be commercially available filters of numerous materials including metals and non-metals, for example silver, glass frits, et cetera. In one preferred form of this invention these filters were commercially available silver membrane filters which are available in many diameters and are obtainable with porosities ranging from about 15 microns to about 0.2 micron. These filters are about 0.002 inch thickness and have approximately 80% free space through the membrane. In one operative embodiment of this invention as described above, two silver membrane filters of 47 millimeters diameter were sealed by means of SR82 silicone resin on opposite sides of an oxygen-free (OHFC) copper gasket member **11** of 4 millimeters thick. The silver filters are produced from fine particle metallic silver which is sintered to provide the desired form and porosity. This porosity entails gas molecular flow in the pores as compared to viscous flow through orifices **18** and **19**.

Member **11** was mounted between two 3⅜ inch vacuum conduit flanges which were bored to accept a 1 inch vacuum exhaust line. The resulting volume of chamber **13** was about 5.0 cc. The flange mounting arrangement provides for extreme flexibility of this device in that it may be employed with any number of instruments where fixtures are not standard. All that is required in a preferred form of this invention is a pair of mating flanges in a vacuum line. The invention may thus be provided from a range of readily available parts such as orifices, filters, housing, et cetera, to provide a gas sample enrichment device for differing instruments or widely different applications.

FIG. 2 illustrates the embodiment of FIG. 1 in an exploded view and exemplifies the simplicity of the arrangement for flange mounting. Housing **11** may be of a convenient size to fit a number of different flange or conduit sizes. Furthermore, housing **11** may be conveniently rotated so that orifices **18** and **19** project in the desired directions.

In the usual application, the conduit diameter is smaller than the diameter of chamber **13**. Therefore, in order to provide better gas conductance the flange members **20** and **21** may be suitably recessed on each side of filters **14** and **15** to create a larger volume space which is connected to the vacuum conduit.

While this invention has been described with reference to particular and exemplary embodiments thereof, it is to be understood that numerous changes can be made by those skilled in the art without actually departing from the invention as disclosed, and it is intended that the appended claims include all such equivalent variations as come within the true spirit and scope of the foregoing disclosure.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A gas enrichment device adapted to interconnect a gas separator and a gas analyzer to deliver a predetermined quantity of an enriched gas from said separator to said analyzer comprising in combination:

(a) a relatively thick metallic annular member defining a coaxial central aperture therethrough,

(b) a thin disk-like replaceable membrane filter positioned coaxially on each side of said annular member to cover said aperture and define a central chamber,

(c) a pair of replaceable calibrated orifice means sealed into said annular member transversely thereof to provide entrance and exit means for said chamber,

(d) said entrance orifice being larger than said exit orifice each to provide viscous flow of gas mixture therethrough,

(e) said filters passing a molecular flow therethrough consisting substantially of one gas of said gas mixture,

(f) said orifice means and said filters being predeterminedly correlated to provide a predetermined removal of a gas from said mixture while a measured amount of the remaining gas is delivered to said analyzer at a lower pressure.

2. A gas sampling apparatus adapted to remove a carrier gas from a gas sample from a gas separator and to admit an enriched sample to a gas analyzer comprising in combination:

(a) oppositely disposed conduit flange members adapted for connection to a low pressure region,

(b) a relatively thick annular metallic member adapted to be positioned concentrically between flanges to define a central chamber therein,

(c) said flanges bearing against said annular member to provide a vacuum tight seal,

(d) separate membrane gas filters disposed and sealed transversely across each side of said annular member and coaxially with said flanges to enclose said chamber,

(e) opposite separate orifice means sealed to and projecting transversely into said annular member to provide a measured amount of gas flow therethrough,

(f) whereby gas at a high pressure enters one of said orifice means and said filter removes carrier gas from the gas in said chamber, and exit orifice means remove a gas sample of predetermined enrichment at a predetermined low pressure into said analyzer.

3. A method of enriching a gas sample as effluent gas from a gas chromatograph for admittance to a mass spectrometer comprising in combination:

(a) introducing a gas sample including a carrier gas into a defined chamber through entrance orificial means at a predetermined pressure and rate,

(b) exposing opposite sides of said chamber transversely to said orifice means to low pressure conditions through selective filter means to remove carrier gas from said gas sample by molecular flow,

(c) removing an enriched gas sample from said chamber through exit orifice means at a location opposite to that of said entrance orifice means at a lower predetermined pressure,

(d) maintaining a correlation between said orifices and said filters so that a gas sample continuously exits from said chamber at a predetermined enrichment at a lower pressure than the gas entering said chamber.

References Cited

UNITED STATES PATENTS

2,045,379	6/1936	Bennett	55—158
2,824,620	2/1958	De Rosset	55—16
3,244,763	4/1966	Cahn	55—16
3,246,450	4/1966	Stern et al.	55—16

REUBEN FRIEDMAN, *Primary Examiner.*

C. N. HART, *Assistant Examiner.*

U.S. Cl. X.R.

55—67; 73—23.1