United States Patent

Moorman et al.

[15] **3,673,405**

[45] **June 27, 1972**

[54] GAS INLET SYSTEM FOR A MASS SPECTROMETER

[72] Inventors: **Charles J. Moorman; Fred A. Reuter,** both of Cincinnati, Ohio

[73] Assignee: **The Bendix Corporation**

[22] Filed: **Jan. 14, 1971**

[21] Appl. No.: **106,576**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 812,582, March 28, 1969, abandoned.

[52] **U.S. Cl.** .....**250/41.9 S,** 250/41.9 SB, 250/41.9 TF

[51] **Int. Cl.**.....**H01j 39/34**

[58] **Field of Search**.....250/41.9 G, 41.9 SB, 41.9 S, 250/41.9 TF; 313/63, 230

[56] **References Cited**

UNITED STATES PATENTS

2,569,032	9/1951	Washburn	250/41.9
2,583,541	1/1952	Berry	250/41.9
3,142,752	7/1964	Hamer et al.	250/41.9
2,775,707	12/1956	Benapfl	250/41.9
3,500,040	3/1970	Padrta	250/41.9

OTHER PUBLICATIONS

" The Encyclopedia of Spectroscopy," Edited B. G. L. Clark, Published by Reinhold Publishing Corp., New York, 1960, pages 636- 639.

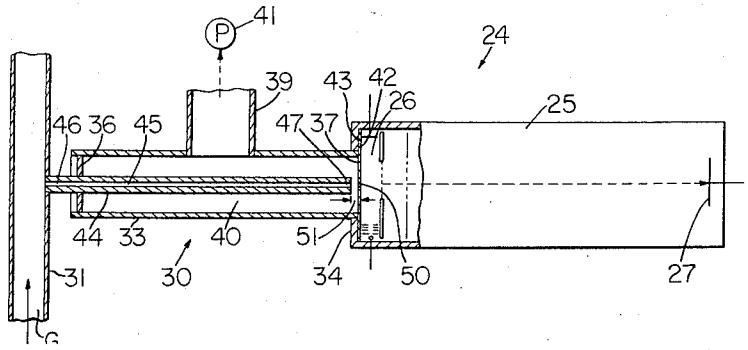
Primary Examiner—William F. Lindquist

Attorney—Raymond J. Eifler and Plante, Hartz, Smith and Thompson

[57] **ABSTRACT**

A mass spectrometer having an improved inlet system which assures that there is a minimum time lag, generally of the order of milliseconds, between changes in the composition of a material being analyzed and the analysis of corresponding changes in the associated spectra. The inlet system includes a primary leak directly opposite and closely spaced to a secondary leak leading into an ionization chamber so that changes in the composition of a gas leaving the primary leak are more rapidly communicated to the ionization chamfer for faster analysis by the mass spectrometer.

11 Claims, 4 Drawing Figures



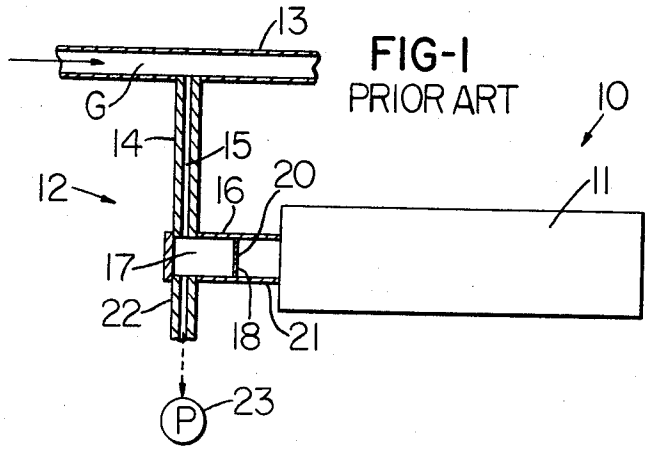


FIG-1
PRIOR ART

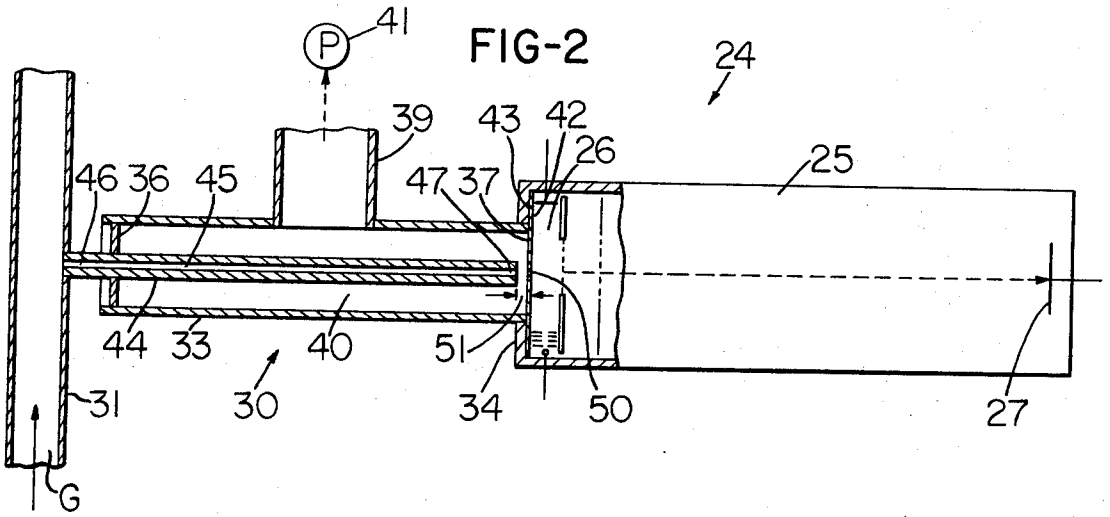


FIG-2

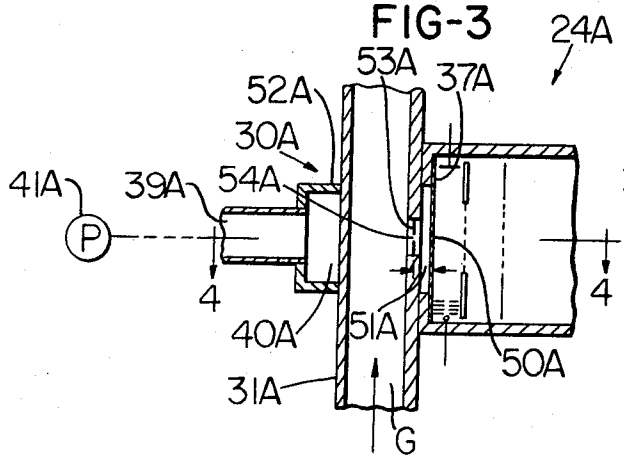


FIG-3

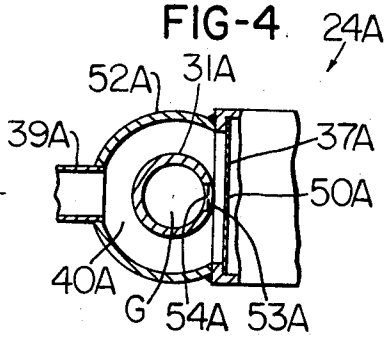


FIG-4

INVENTORS
CHARLES J. MOORMAN
FRED A. REUTER
BY Ernest J. Hoy
THEIR ATTORNEY

GAS INLET SYSTEM FOR A MASS SPECTROMETER

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 812,582 filed Mar. 28, 1969 now abandoned.

BACKGROUND OF THE INVENTION

There are many devices and techniques in present use for introducing a material such as a fluid sample, for example, into the ionization chamber of a mass spectrometer. Present devices respond comparatively slowly to changes in the composition of such fluid and many of such devices have response time which range from several seconds to several minutes. In applications where speed of response is not important, these present devices may be acceptable; however, in applications such as on-stream applications, where the spectrometer is used to monitor a continuous process, speed of response is of utmost importance and time-of-flight spectrometers, with their inherent high speed scanning capability, are of particular value. Accordingly, it is necessary that the inlet system for such high speed spectrometers be capable of continuously providing fresh samples of the spectrometer in a minimum of time.

SUMMARY OF THE INVENTION

This invention provides an improved mass spectrometer, and a simple and economical inlet system therefor, which operates with a minimum time lag generally of the order of milliseconds between changes in the composition of a material being analyzed and the analysis of corresponding changes in the associated spectra.

The invention is characterized by a mass spectrometer inlet system having the outlet of a primary leak located directly opposite and spaced in the range of 1/32 to 13/32 of an inch from the inlet of a secondary leak which is located in a wall of the ionization chamber of a mass spectrometer. Further, the volume of the ionization chamber with the above spacing should be 1 cubic inch or less.

Other details, uses and advantages of this invention will become apparent as the following description of the exemplary embodiments thereof presented in the accompanying drawing proceeds.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing shows a typical prior art device and present exemplary embodiments of this invention in which:

FIG. 1 illustrates a typical prior art inlet system for a mass spectrometer.

FIG. 2 illustrates one exemplary embodiment of this invention.

FIG. 3 illustrates another exemplary embodiment of this invention.

FIG. 4 is a view taken essentially on the line 4—4 of FIG 3.

DESCRIPTION OF ILLUSTRATED EMBODIMENTS

Reference is now made to FIG. 1 of the drawing which schematically illustrates a mass spectrometer **10**, which may be of any type well known in the art, having an ionization chamber and drift tube assembly **11** and a typical prior art inlet system. The inlet system **12** comprises a conduit **13** which contains a fluid, such as gas G, which is to be analyzed and the gas in conduit **13** may be a moving stream of such gas. A tube **14** having a small diameter bore **15** is provided and one end of tube **14** is attached to the conduit **13** with the opposite end of tube **14** being attached to a tubular housing **16** which defines a chamber **17** of comparatively large volume whereby gas may be bled from the conduit **13** into the chamber **17** through the bore **15**.

The housing **16** has an inner wall **18** which has an orifice **20** provided therein and the orifice **20** places the chamber **17** in flow communication with a tube **21** of comparatively large

cross-sectional area which communicates with the ionization and drift tube assembly **11**. Another tube **22** is provided and has one end thereof in fluid flow communication with the chamber **17** and its opposite end is connected to a suitable vacuum pump **23** which is capable of providing a high degree of evacuation and in a known manner.

The bore **15** defines what is commonly referred to as a "primary leak" between the fluid source, i.e., the gas flowing through conduit **13**, and the chamber **17**. The orifice **20** defines what is commonly referred to as a "secondary leak" between the chamber **17** and the ionization chamber and drift tube assembly **11**.

With the prior art inlet system **12** a sample of the gas G which is to be analyzed is drawn from the conduit **13** into the chamber **17** through the primary leak **15**. Molecules of the gas G are then passed by molecular effusion from chamber **17** through the secondary leak **20** into the tube **21** which conveys such molecules to the ionization chamber and drift tube assembly **11**.

The construction and arrangement of inlet system **12** is such that the outlet of the primary leak or bore **15** is spaced a considerable distance from, and is generally at right angles to the wall **18** which has the secondary leak or orifice **20** provided therein. With this construction, it will be seen that an appreciable volume of gas may accumulate in the chamber **17** which may result in an appreciable delay between the time gas having a changed composition enters chamber **17** and the time it moves adjacent the secondary leak. In addition, the typical prior art inlet system **12** is such that the ionization chamber of the spectrometer **10** may be spaced from the secondary leak a distance ranging between roughly a few centimeters and several feet, whereby a considerable volume may be provided by the tube **21**. Thus, with the typical inlet system **12** it may take from several seconds to several minutes, as previously indicated, for new molecules of the gas being analyzed to be moved from the conduit **13** to the ionization chamber of the spectrometer **10**, whereby such inlet system is obviously not satisfactory for use in applications where samples must be analyzed rapidly.

In the exemplary embodiment of this invention illustrated in FIG. 2 of the drawing a time-of-flight mass spectrometer **24** is illustrated and comprises an ionization chamber and drift tube assembly **25** which has an ionization chamber **26** provided at one end thereof and typical ion collector **27** provided at its opposite end. The spectrometer **24** has an inlet system **30** which enable high speed and efficient introduction of gas molecules into the ionization chamber **26** which are converted to ions in a known manner by electron bombardment.

The ions are periodically forced out of the ionization chamber **26** and through the drift tube portion of the assembly **25** toward the collector **27** by one or more electrical fields established between appropriate grids provided in the assembly **25**. The ions are propelled toward the collector **27** as a function of their mass-to-charge ratios whereby they are separated into groups or bunches with the lightest group reaching the collector **27** first followed by successively heavier groups. Suitable electrical circuitry is provided and connected to the collector **27** and may be made to show a complete mass spectrum of the gas molecules ionized in the ionization chamber **26**. The volume of the ionization chamber **26**, i.e., the volume between the diaphragm **37** and the grid closest to the diaphragm, should be less than one cubic inch and is preferably 0.03 of a cubic inch (0.005 of a liter).

The spectrometer **24** has its inlet system **30** operatively connected to a source of fluid or gas which is also designated by the reference letter G and is to be continuously analyzed and such gas is provided in a conduit **31** which may be considered a part of such inlet system. The inlet system includes a tubular housing **33** which has its inner end fixed in sealed (vacuum-tight) relation to an end wall **34** of the assembly **25** and the housing **33** has an end plate **36** fixed to its outer end. A think wall in the form of a diaphragm **37** is fixed in a sealed manner to the inner end of tubular wall **33**. The walls **33** and **34**

cooperate with the diaphragm 37 to define a chamber 40 which will be referred to as the second or evacuated chamber. The second chamber 40 has an outlet 39, communicating with a suitable pump 41, such as a diffusion pump or molecular pump, which is capable of providing a high degree of evacuation in said second chamber.

The diaphragm 37 comprises a substantially planar member which has opposed surfaces 42 and 43, with surface 42 comprising enclosure means in the form of one wall for the ionization chamber 26 and the surface 43 comprising an end wall of the evacuated chamber 40. Thus, the diaphragm 37 defines a common wall for the evacuated chamber 40 and the ionization chamber 26.

The inlet system 30 has a capillary tube 44 which extends in sealed relation through end wall 36. The tube 44 has a passage 45 extending therethrough and the tube 44 is fixed to the conduit 31 so that one end 46 of the passage 45 is in flow communication with the conduit 31 and the opposite or inner end 47 of the passage 45 is in flow communication with the evacuated chamber 40. In this embodiment of the invention, the passage 45 defines what is commonly referred to as the primary leak from the conduit 31 into the evacuated chamber 40.

The capillary tube 44 is in the form of a tube having the inner end 47 of its passage 45 arranged adjacent to and aligned directly opposite an orifice 50 which may be provided substantially centrally in the diaphragm 37. The orifice 50 defines what is commonly referred to as the secondary leak from the evacuated chamber 40 into the ionization chamber 26. The inner end 47 of the tube 44 (primary leak) is arranged directly opposite the orifice 50 (secondary leak) so as to provide a convection in the region of the secondary leak which removes the remaining portion of a sample once it is no longer present in the sample of gas leaving the passage 45. It is common in the art of mass spectrometry to have a differential in pressure between the ionization chamber 26 and the analyzer chamber. For a discussion of quasi steady-state pressure characteristics of an inlet system for mass spectrometers see "-Mass Spectroscopy," by M. G. Ingram and R. J. Hayden published by the National Academy of Sciences-National Research Council, Washington, D.C. The inner end 47 of the tube 44 is spaced a distance 51 from the orifice 50. For this type of inlet system the response of the mass spectrometer to changes in the composition of the sample gas is optimized if the controlled distance 51 is greater than 1/32 of an inch but less than 13/32 of an inch. Preferably, the distance 51 is one-sixteenth of any inch.

With the inlet system 30 the gas being analyzed flows through the primary leak, i.e., passage 45, into the evacuated chamber 40 and molecules thereof pass through the orifice 50 into the ionization chamber 26. By providing the diaphragm 37 so that it defines a common wall between the chamber 40 and the ionization chamber 26, it will be seen that molecules are introduced directly from chamber 40 into chamber 26 in a minimum of time and with no time delay being due to travel between the secondary leak and the ionization chamber as is required in systems proposed heretofore. It will also be appreciated that by aligning the inner end 47 of the passage 45 so that it is directly opposite the secondary leak or orifice 50 new gas molecules from the conduit 31 are introduced through the secondary leak and into the ionization chamber 26 with optimum efficiency.

The diaphragm 37 may be of any suitable thickness and good results have been obtained with diaphragms having thicknesses generally of the order of 0.0001 inch and even less. It has also been found that diaphragms having thicknesses ranging between 0.0001 and 0.005 inch are comparatively easy to install and use and provide satisfactory results. Further, the size of the secondary or molecular leak,as it is often called, is such that is assures effusion of gas molecules therethrough and such size is determined by well known techniques.

Thus, it is seen that when primary leak 45 is arranged opposite of and in the range of 7/32 to 1/32 of an inch from the secondary leak 50 leading into the ionization chamber 26 the spectrometer 24 has a small response time generally of the order of milliseconds. In particular, it has been found that by utilizing the construction and arrangement of components essentially as presented in FIG. 2 of the drawing, the spectrometer 24 has a response time not exceeding approximately 30 milliseconds. This response time was verified in laboratory tests wherein the volume of the ionization chamber 26 was 0.03 of a cubic inch (approximately 0.005 of a liter) and the pumping speed out of the ionization chamber 26 was one liter per second making the time required to pump out the ionization region 0.005 of a second. When a gas sample was admitted to the inlet system 30 the pressure fell to one-tenth of its value (a 90 per cent change) in about 0.015 of a second. This response time is in sharp contrast to the comparatively slow response times ranging between roughly several seconds and several minutes obtained by present spectrometers using inlet systems of the types proposed heretofore.

Another exemplary embodiment of this invention is illustrated in FIGS. 3 and 4 of the drawings. The spectrometer 24 illustrated in FIGS. 3 and 4 is very similar to the spectrometer 24; therefore, such spectrometer will be designated generally by the reference number 24A and parts of the spectrometer 24A which are very similar to corresponding parts of the spectrometer 24 will be designated by the same reference numerals as in the spectrometer 24 also followed by the letter designation A and not described again. Only those component parts which are substantially different from corresponding parts of the spectrometer 24 will be designated by new reference numerals each followed by the letter designation A and described in detail.

The main difference between the spectrometer 24A and the spectrometer 24 is in the means utilized in the inlet system 30A to provide the primary leak from the sample stream or conduit means 31A to the evacuated chamber 40A. In particular, it will be seen that the conduit means or conduit 31A extends in a sealed (vacuum-tight) relation through a housing 52A defining the outer portion of chamber 40A and conduit 31A is arranged adjacent the common wall means or diaphragm 37A. The conduit 31A has a thin-walled flat insert disc 53A fixed in sealed vacuum-tight relation therein and the insert 53A has an aperture 54A provided therein which defines the primary leak and is arranged directly opposite the secondary leak or orifice 50A with a distance 51A in the range of 1/32 to 3/16 of an inch provided therebetween. Preferably, the distance 51A in this embodiment is one-sixteenth of an inch. The distance 51A, like the distance 51, may be optimized within their given ranges depending in part on the characteristics of the gas G which is to be analyzed and which is contained in the conduit 31A.

The aperture 54A has an effective area which is controlled so that, in essence, it provides the equivalent pressure drop that is provided by the passage 45 in the capillary tube 44, yet it will be appreciated that the distance that the gas must travel from the conduit 31A to the secondary leak is substantially reduced whereby the inlet system 30A and its mass spectrometer 24A will have a more rapid response time than the spectrometer 24. For a more detailed discussion of the required pressure differentials, see the aforementioned article on "Mass Spectroscopy" by Ingram and Hayden.

The inlet system 30A has another advantage in that it enables the conduit 31A to extend through the evacuated chamber 40A whereby that inlet system 30A in addition to providing faster response times is also more compact.

It should again be emphasized that in both exemplary embodiments of this invention presented in this specification the secondary or molecular leak is defined in a common wall between the evacuated chamber and the ionization chamber and such wall is of minimum thickness which may be as small as approximately 0.0001 inch. This arrangement assures that time delays which might be encountered (in previous inlet systems) by molecules traveling from the secondary leak to the ionization chamber are substantially eliminated. In addi-

tion, it will be appreciated that with this invention the cooperating arrangement of the various components of the spectrometer is such that there is little likelihood that a gas sample being analyzed will dwell for an appreciable time in the evacuated chamber before being either rapidly removed therefrom or molecules thereof effused directly into the ionization chamber.

The pressures at various points in each exemplary inlet system of this invention may vary within predetermined limits. In an exemplary operating condition, gas at the source or sample stream may be at a normal atmospheric pressure. The operation of the vacuum pump associated with the evacuated chamber is such that the pressure in such chamber is generally of the order of 100 to 500 microns of mercury and the pressure in the ionization chamber is generally of the order of 10^{-5} – 10^{-7} mm of mercury.

Reference has been made throughout this specification to minimum response time and it should be understood that the response time referred to is defined as that time increment which elapses from the time gas first enters the primary leak until the spectrometer has reached 90 percent of its final output performance.

While present exemplary embodiments of this invention, and methods of practicing the same, have been illustrated and described, it will be recognized that this invention may be otherwise variously embodied and practiced by those skilled in the art.

Having described the invention, what is claimed is:

1. In combination with a mass spectrometer of the type having an ionization chamber for ionizing gas, said ionization chamber including a grid that periodically forces said ionized gas molecules into an analyzing region wherein said ionized gas molecules are separated according to their mass-to-charge ratio, the improvement comprising:

a second chamber having an orifice in one wall, an orifice in another wall opposite said one wall, and an outlet disposed in said second chamber between said walls, said outlet adapted to be connected to a means for evacuating said second chamber, one of said second chamber walls, having an orifice, forming a common wall between said second chamber and said ionization chamber;

a tube disposed within said second chamber, said tube having one end spaced in the range of 13/32 to 1/32 of an inch from the orifice in said common wall between said ionization chamber and said second chamber, the other end of said tube extending through the orifice in the other wall of said second chamber and in fluid communication with said gas to be ionized so that said gas may rapidly travel into said ionization chamber from said tube.

2. The combination recited in claim 1 wherein the volume of said ionization chamber is less than 1 cubic inch.

3. The combination as recited in claim 2 wherein said end of said tube, spaced from said orifice in said common wall, is located directly opposite said orifice in said common wall.

4. The combination as recited in claim 3 wherein the thickness of said common wall between said ionization chamber and said second chamber is between 0.0001 inch and 0.005 inch.

5. The combination as recited in claim 2 wherein the thickness of said common wall between said ionization chamber and said second chamber is between 0.0001 inch and 0.005 inches.

6. The combination as recited in claim 1 wherein the thickness of said common wall between said ionization chamber and said second chamber is between 0.0001 inch and 0.005 inch.

7. The combination as recited in claim 1 wherein said end of said tube, spaced from said orifice in said common wall, is located directly opposite said orifice in said common wall.

8. An inlet system for a mass spectrometer having an ionization chamber for ionizing a sample of gas to be analyzed, said ionization chamber including an aperture for receiving said gas sample and a grid for periodically accelerating said ionized gas molecules into an analyzing region wherein said ionized gas molecules are separated according to their mass-to-charge ratio, said inlet system comprising:

a second chamber in vacuum-tight relationship with said ionization chamber with the wall of said ionization chamber having said aperture therein forming a common wall with said second chamber and with outlet means adapted to be connected to a means for evacuating said second chamber and

gas feed means extending through a wall in said second chamber, said gas feed means having an outlet spaced in the range of 7/32 to 1/32 of an inch from said aperture in said common wall so that gas samples can be rapidly passed through said feed means, a part of said second chamber and said aperture in said common wall to said ionization chamber.

9. The combination as recited in claim 8 wherein the volume of said ionization chamber is less than 1 cubic inch.

10. The combination as recited in claim 9 wherein the thickness of said common wall between said ionization chamber and said second chamber is between 0.0001 inch and 0.005 inch.

11. The combination as recited in claim 8 wherein the thickness of said common wall between said ionization chamber and said second chamber is between 0.0001 inch and 0.005 inch.

* * * * *