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SAMPLE INTRODUCTION SYSTEM FOR MASS SPECTROMETER ANALYSIS

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Figure 1

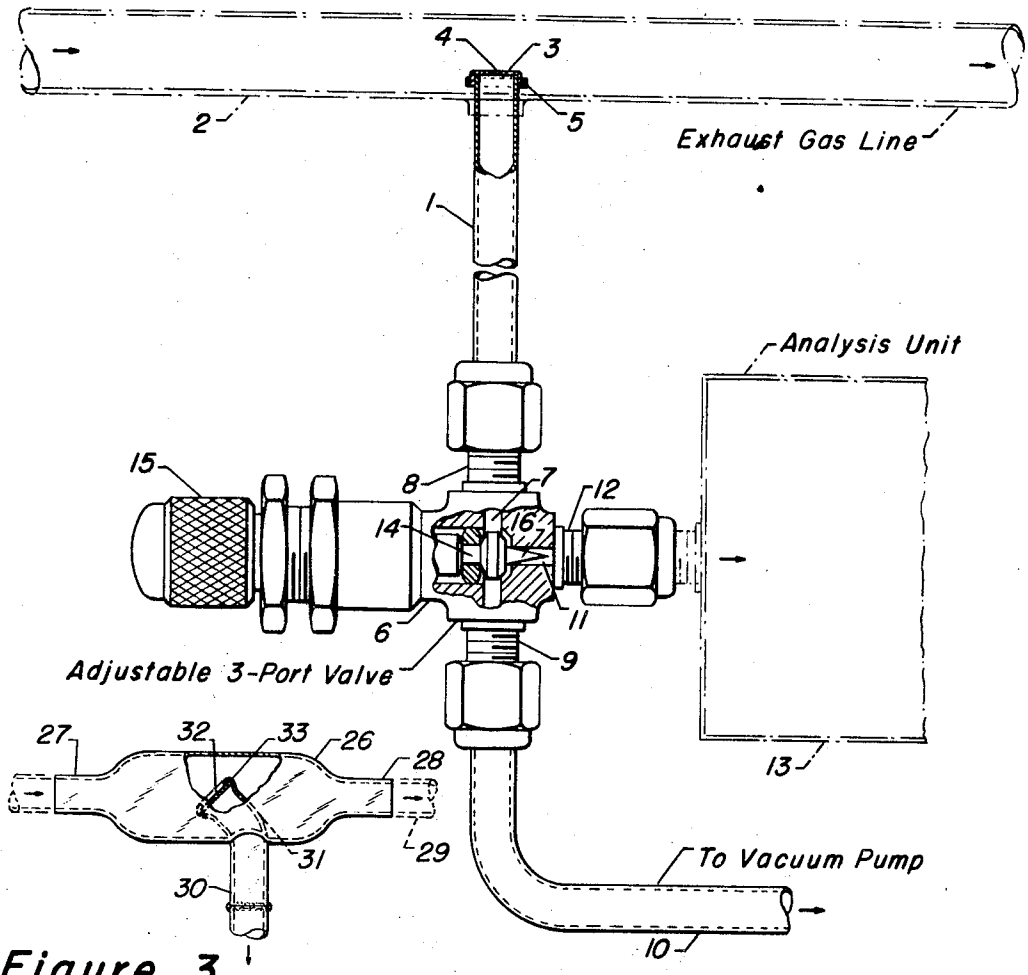


Figure 3

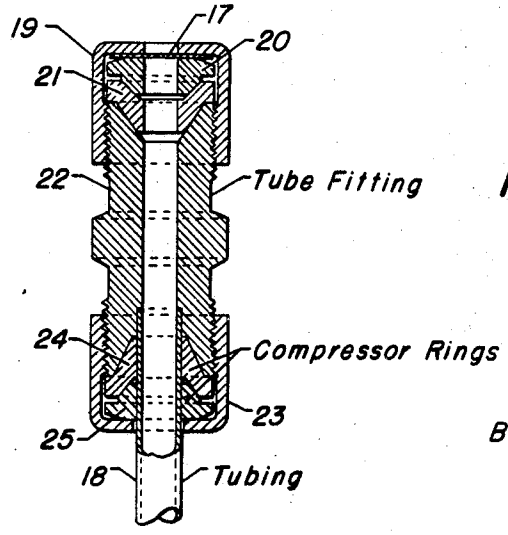


Figure 2

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SAMPLE INTRODUCTION SYSTEM FOR MASS SPECTROMETER ANALYSIS

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U.S. Cl. 250—41.9 5 Claims

ABSTRACT OF THE DISCLOSURE

A sample introducing system for a mass spectrometer utilizing a short length of tubing with a molecular leak inlet section of a thin diaphragm having central opening means of the order of about .004" in diameter and an adjustable splitter valve member providing two outlet means from the tubing. One outlet is adapted to connect with a vacuum pump and the other to cause a fractional portion of the withdrawn gaseous sample stream to be shunted to the mass spectrometer.

This application is a continuation-in-part of my previously filed application Ser. No. 654,773, filed July 20, 1967, which is now abandoned.

The present invention relates to an improved arrangement for effecting the rapid introduction of a gaseous sample into a mass spectrometer analysis unit. More particularly, the invention is directed to a special tubular sample inlet system which, in part, utilizes an orifice type molecular leak means as an inlet section and a stream splitting gas distribution means that cooperates in providing a continuous fast transfer of a sample stream to the analysis unit.

The usual types of sample withdrawal means for a mass spectrometer, whether periodic or continuous, utilize a capillary tube inlet section so that merely a small portion of the material to be analyzed from a process or product stream will be withdrawn for transfer to the particular analysis unit. However, the capillary tube arrangement results in a slow, large surface area transfer passageway such that a portion of the stream, or condensate therefrom may be adsorbed on the wall of the tubing. Alternatively, highly reactive components can undergo undesired reactions with other accompanying constituents during the time period required to effect the transfer through the capillary tubing. For instance, in attempting to carry out the continuous sampling of an auto engine exhaust stream for the monitoring of entrained nitric oxide (NO) in a mass spectrometer unit, it is necessary to obtain a fast sampling operation to minimize adsorption of entrained hydrocarbons to the tube wall, as well as necessary to minimize the reaction of the nitric oxide with oxygen and other constituents in the stream. Preferably the sampling is to be attained in a period of time of less than about 3 seconds. Also, it may be pointed out that an automotive exhaust stream is continually changing with varying operating speeds and conditions and rather continuous sampling is needed to obtain a proper analysis of any one component in such an exhaust stream.

This usual mass spectrometer, including those for nitric oxide monitoring, provides a vacuum for the sample intake so that, for the present type of sample introduction system used with auto exhaust gases, there is a pressure differential involved of from about 1 atmosphere in the exhaust line to a vacuum of about 10^{-5} millimeters of mercury as provided by the analysis unit. However, since the gaseous flow in the auto exhaust line may vary in pressure, a preferred system provides for a vacuum pump connection to bring the sample stream to the zone of the analyzer at uniform conditions.

Along with the use of capillary tube type inlet means for usual sampling systems, there have been used glass frit discs, and the like, directly ahead of the analysis unit so as to limit or proportion the sample stream flow to such unit. However, systems using frits have no adjustability and tend to have operating difficulties because of dirt accumulations, particularly with auto exhaust gas streams which can provide carbon particles and condensation of hydrocarbons. Also, it has been found that certain frits, such as of sintered silicon carbide may tend to initiate or enter into a chemical reaction with certain of the exhaust constituents and thus provide still further difficulties in obtaining accurate analysis for nitric oxide or for any other particular component.

It may be considered a principal object of the present invention to utilize a gas sample introduction system for an analysis unit which provides for rapid withdrawal and shunting of a sample portion of a gaseous stream to the analyzer.

It may be considered a further object of this invention to provide a compact sample introduction system particularly adapted to effect the monitoring of the NO content in an exhaust gas stream by eliminating long tubular means and any materials which tend to enter into reaction with such gas stream.

In a broad aspect, the present invention provides a sample introduction system for a mass spectrometer which is particularly adapted to effect rapid sampling of a gaseous stream and preclude reaction of an entrained highly reactive material with other accompanying constituents, which comprises in combination, a molecular leak inlet section connective with a sample receiving tube, with such leak section comprising a thin diaphragm member having at least one small opening, with open area being less than about 7.0×10^{-6} square inches, and an adjustable outlet means from said sample tube providing two outlet passageways therefrom, whereby a vacuum source may pull a sample stream to the zone of said outlet passageways and then a fractional portion shunted therefrom to said mass spectrometer.

A preferred design utilizes a thin foil membrane, as of gold, for the thin diaphragm member having the orifice opening to provide in effecting "molecular leak." Actually, the entire introduction system is preferably of glass or stainless steel or other smooth substantially nonactive type of material such that there will be a minimum of adsorption or retention of particulates or of any entrained gaseous components passing through the system. Also, as will be set forth more fully hereinafter, the outlet passageway means preferably utilizes an adjustable three-port valve where there is a means for accurately adjusting the outlet flow from at least one of the outlet ports. Generally, in a conventional "splitter" valve, or three-port valve, there will be a straight through passageway for continuous flow of at least a portion of the fluid stream and an adjustable tapered plug in a needle valve design from the second of the outlet ports of the valve unit.

Reference to the accompanying drawing and the following description thereof will serve to more clearly illustrate one embodiment of the improved sample introduction system for a mass spectrometer unit, as well as point out additional advantageous features which are obtained through the use of such specially constructed system.

DESCRIPTION OF THE DRAWING

FIGURE 1 of the drawing is a diagrammatic eleva-

tional type view indicating the arrangement for the rapid transfer of a sample stream through the improved introduction system to an analysis unit.

FIGURE 2 of the drawing indicates in a sectional view one means for attaching a thin gold foil membrane to the end of a tubular member so as to provide a molecular leak inlet section thereto.

FIGURE 3 of the drawing illustrates another form of molecular leak inlet section constructed of glass and adopted for direct insertion into a glass line carrying the gaseous stream to be analyzed.

Referring now particularly to FIGURE 1 of the drawing, there is shown a sample withdrawal tube **1** connecting to and projecting slightly interiorly of a line **2** which is carrying a stream that is to be analyzed for at least one entrained gaseous component. The inlet end of the sample withdrawal tube **1** is provided with a thin diaphragm member **3** having a small orifice opening **4** and clamp means **5**. The latter is merely indicated diagrammatically and may constitute any suitable holding or clamping means that is capable of attaching the diaphragm member **3** to the end of the tube member **1**. The diaphragm **3** is preferably very thin and in the nature of gold foil or other equivalent noble metal foil, whereby the depth of the passageway provided by orifice **4** is almost negligible.

For continuous sampling of a particular gaesous component, as for example nitric oxide in an automotive exhaust gas stream, the size of a single orifice will be about .003" in diameter and in the range of .0008" to .004" whereby only a very small fractional portion of the continuously flowing exhaust gas stream will be taken into the sample introduction system. With two orifices, each will be about .002" in diameter. With other gas analysis operations the leak may be of a slightly different size and thus be within the range of from about 0.5×10^{-6} to about 7.0×10^{-6} square inches.

The tubing **1** is preferably kept relatively short in length, generally less than about 1 foot long, and preferably only about 3" long when using Pyrex glass tubing which is of the order of 5 millimeter inside diameter. As pointed out hereinbefore, preferably the tubing is supplied of glass, stainless steel, or other smooth and chemically inert type of material and will be of a small diameter ⅛" to ⅜". At least the material shall be non-reactive with the particular component to be analyzed in the mass spectrometer or other analyzer unit.

In the present drawing, the tubing **1** is shown connecting with one form of adjustable three-port valve unit **6**, which again is preferably of stainless steel, glass, or the like. The valve **6** is provided with a straight through passageway **7** suitable for carrying gas or fluid from an inlet port section **8** to an outlet port **9** and thence into tubing **10**, as well as suitable for effecting the shunting of a fractional portion of the stream through a small port **11** communicating with an outlet connection **12**, in turn carrying to an analysis unit **13**. The adjustable feature of valve **6** provides a turnable valve stem section **14** connecting between an exterior grip section **15** and an internal needle-like valve plug or projection **16**. The latter moves within the outlet orifice opening **11** and meters the flow therethrough into the analysis unit **13**. Although not shown in the drawing, a preferred form of device will have heating means, such as resistance coil wrapping, around that portion of the device illustrated by numerals **1** through **14**, except for tube **10**. The heating is needed to prevent condensation of any of the constituents gases flowing to the analysis instrument.

In the present operation for effecting the rapid withdrawal of a sample gas stream and its introduction into a mass spectrometer type of unit, there will be a vacuum pump connection to line **10** and valve at port **9** such that there is a positive withdrawal and flow of a sample of gas through the inlet end of the system at the leak section **4**. The withdrawn gas sample stream is thus continuously carried down into the straight through passageway **7** of valve **6** whereby a major portion of a stream will carry on to the vacuum pump means and a fractional portion shunted through the metered passageway **11** and outlet port **12** to be then introduced into analysis unit **13**.

Where desired, there may be adjustment of the flow through port **11** by means of the moving stem **14** and needle valve means **16**. Generally, an analyzer unit of the mass spectrometer type, will operate under a vacuum, such as about 10^{-6} millimeters of mercury; however, as noted hereinbefore, where the gas stream being transferred in line **2** is under a low pressure, or at least under varying pressure conditions, there is preferably used a vacuum pump connection to line **10** in order to insure a uniform continuous gas flow down into the flow splitting arrangement for tube **1**, as provided by the three-port valve means **6**.

In FIGURE 2 of the drawing there is shown the utilization of standard tube fitting means for attaching a diaphragm or thin foil molecular leak member, such as **17**, to the end of a sample withdrawal tube, being indicated as **18**. The arrangement is, of course, of advantage in providing a simple means for having a removable screw cap member **19** effect the holding of an insertable diaphragm or leak member **17**. In this case, the latter is clamped between the underside of cap member **19** and above compressor rings **20** and **21**, with the latter in turn being designed to fit against the inwardly sloping end of a standard tube connector fitting **22**. The latter, in turn, is shown connecting to the tube **18** by means of an internally threaded member **23** which bears against internal compression ring members **24** and **25** encompassing the end of tubing **18** within the end of tube fitting **22**.

In FIGURE 3 of the drawing there is shown still another form of inlet or molecular leak section, where such entire section is of glass and is adapted to be inserted directly into a glass tube line which is carrying at least a portion of the gaseous stream to be analyzed. In other words, the enlarged section **26** has end portions **27** and **28** which can be sealed into a glass tube gas conducting line, indicated as **29**. Connecting to the side of section **26** is a short glass tube section **30** which extends into the interior of the enlarged portion at **31** and holds a transverse thin diaphragm or gold foil member **32** in a crimped end portion **33**. The diaphragm or foil member **32**, as noted with the other embodiments, shall have at least one small "molecular" sized opening to restrict the gas flow to the analyzer zone. For NO analysis, the leak opening will be of the order of .003" diameter, or two openings of the order of .002" diameter to provide an area of about 0.628×10^{-6} square inches.

The glass tube **30** may connect directly to a valve unit, such as **6** in FIGURE 1, or be sealed and joined to a different short length of tubing which will have the same coefficient of expansion as glass, such as Kovar metal tubing. The latter will then connect to the valve unit. In any case, the tubing length will be short, with the total being less than one foot and preferably only 3" or 4". Also, the entire glass section and the valve section will be suitably heated, by electric resistance heating, or otherwise, to preclude condensation problems.

It is, of course, not intended to limit the present invention to any one means for holding a diaphragm member and small molecular sized orifice leak across the end of a tube in order to provide the inlet to the latter, inasmuch as various clamping or sealing means will be obvious to those skilled in the art of working with tubular equipment. It is, however, the principal feature of the present invention to obtain a rapid transfer of the withdrawn sample stream into the inlet system through a small sized orifice that has a minimum of depth or length, versus utilizing a long piece of capillary tubing.

In addition, modified means, such as various sized molecular leaks, may be used for fixed designs in pro-

viding the bypassing of a portion of the sample stream into the analyzer unit **13** may be provided other than through the use of an adjustable three-port valve, such as **6**. However, the latter means is of particular advantage in giving an adjustable control through a small open orifice and precludes the difficulties that are frequently obtained through the use of some other means, such as frits or other porous types of membranes which may be readily clogged by dirt or condensate. The adjustable feature of the valve means is also of advantage, as noted hereinbefore, in obtaining a desired controlled flow into an analysis unit which is to be continuously monitoring a flow stream.

I claim as my invention:

1. A sample introduction system for a mass spectrometer which is particularly adapted to effect rapid sampling of a gaseous stream and preclude reaction of an entrained highly reactive material with other accompanying constituents, which comprises in combination, a molecular leak inlet section connective with a sample withdrawal tube as an inlet means thereto, with said leak member comprising a thin diaphragm having at least one opening and the open area being less than about 7.0×10^{-6} square inches, and an adjustable outlet means from said sample tube providing two outlet passageways therefrom, whereby a vacuum source may pull a sample stream to the zone of said outlet means and then a fractional portion shunted therefrom to said mass spectrometer.

2. The system of claim **1** further characterized in that said thin diaphragm comprises a gold foil.

3. The system of claim **1** further characterized in that said adjustable outlet means from the withdrawal tube comprises an adjustable metering three-port valve unit whereby a metered flow may be provided from at least one of the outlet ports at the valve unit.

4. The system of claim **1** further characterized in that the inlet means, tubular means and outlet means from the tube are of a material which provides substantially smooth interior passageway means and is a substantially inert non-reactive type of material.

5. The system of claim **1** further characterized in that said molecular leak inlet section is connective with a glass tubing as said sample withdrawal tube and the latter, together with said adjustable outlet means, is encompassed with electrical resistance heating means.

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