

Sept. 25, 1951

H. W. WASHBURN

2,569,032

CONSTANT PRESSURE INLET FOR MASS SPECTROMETERS

Filed April 30, 1948

FIG. 1.

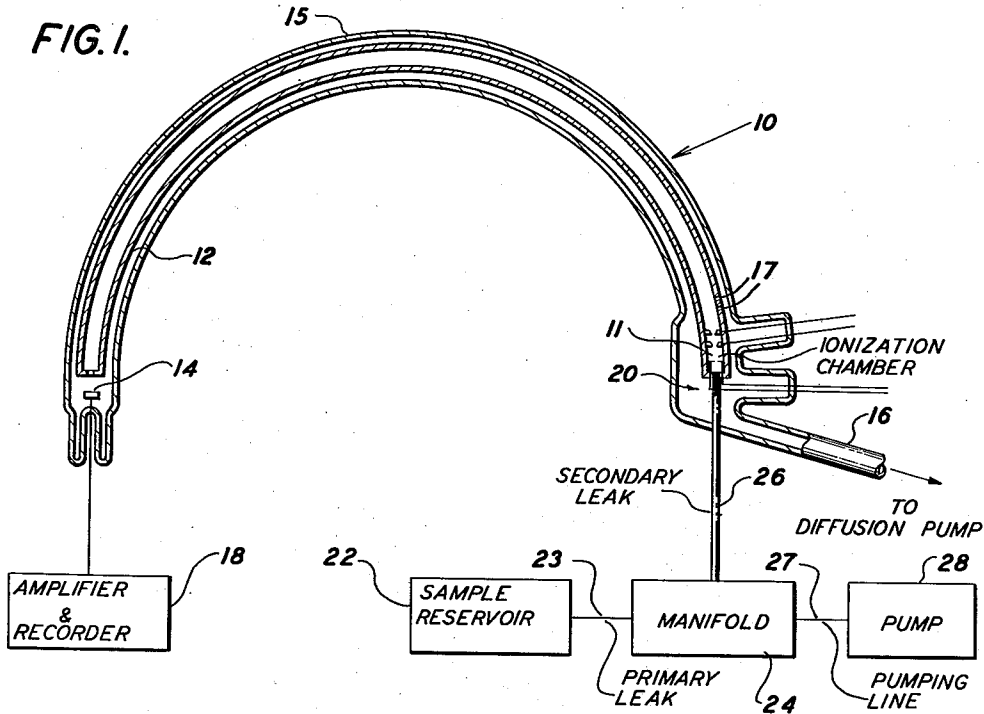
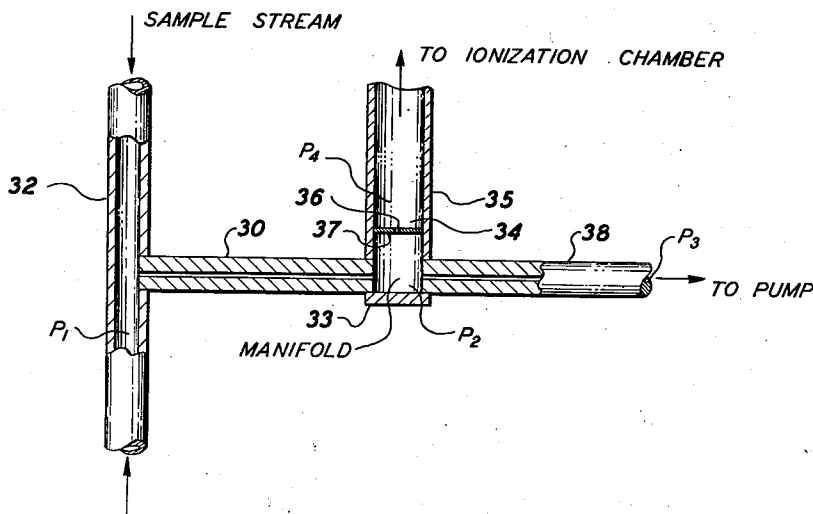


FIG. 2.



INVENTOR.  
HAROLD W. WASHBURN

BY

*James B. Christie*  
ATTORNEY

## UNITED STATES PATENT OFFICE

2,569,032

## CONSTANT PRESSURE INLET FOR MASS SPECTROMETERS

Harold W. Washburn, Pasadena, Calif., assignor to Consolidated Engineering Corporation, Pasadena, Calif., a corporation of California

Application April 30, 1948, Serial No. 24,334

11 Claims. (Cl. 250—41.9)

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The invention is concerned with mass spectrometers and particularly with a system employed for introducing a gas sample to be analyzed in such instruments. The invention is particularly related to apparatus for continuous introduction of the gases to be analyzed when the mass spectrometer is used for "monitoring," i. e. for substantially continuous analysis of a variable sample stream.

A mass spectrometer is an apparatus employed for sorting ions. Ordinarily it includes an ionization chamber in which molecules of the material to be analyzed are bombarded by a stream of electrons and thereby converted into ions. These ions are propelled into and through an analyzer chamber where they are acted upon by a magnetic or an electrical field or both and separated according to their mass-to-charge ratios, i. e. their specific masses, into a plurality of diverging ion beams having different specific masses, with each beam composed of ions of the same specific mass. The diverging beams are successively focused on and discharged at an ion collector and the current thus produced from each ion beam is indicative of the amount of ions in that beam, and may be a measure of the partial pressure of the molecules (from which the ions were derived) present in the material undergoing analysis.

The ionization chamber and the analyzer chamber should be operated at a low pressure of the order of 0.1 and .001 micron, respectively so that the mean free path of the ions is sufficiently large compared to the physical dimensions of the apparatus that collisions of the ions with neutral molecules will not scatter the ions and interfere with sharp focusing.

Conveniently, the required low pressures are obtained by enclosing the ionization chamber and the analyzing chamber in a sealed envelope and evacuating the envelope through a conduit connected to a vacuum pump. Various types of pumps, such as diffusion pumps or molecular pumps that are capable of accomplishing this high degree of evacuation may be employed and are well known.

The sample admitted to the ionization chamber should bear a definite relationship to the mixture to be analyzed. As indicated above, the ion source in an analytical mass spectrometer usually operates at a gas pressure of  $10^{-4}$  to  $10^{-6}$  mm. of mercury. The sample to be analyzed, on the other hand, is almost always provided in the form of a gas at a pressure greater than 1 cm. of mercury or in the form of a liquid in

which the least volatile component has a vapor pressure in the neighborhood of 1 mm. of mercury or above. It is therefore necessary to reduce the sample pressure before admitting the sample to the ion chamber.

In providing means for accomplishing this pressure reduction it is necessary to take into consideration the evacuating system associated with the ion chamber and the analyzer chamber. The geometry and operating pressures of the system are generally such that the gas flow out of the ion chamber is by molecular diffusion rather than by viscous flow. If independent flow of the components of a mixture to the ionization chamber is to be obtained, it is necessary that the flow of gaseous or vaporous sample from the manifold into the ionization chamber likewise be by molecular diffusion. This independent flow is highly desirable for certain applications of the mass spectrometer. In order to achieve molecular flow into the ionization chamber, it is necessary that the opening between a so-called "sample manifold" and the ionization chamber be small as compared with the mean free path of the gas in the sample manifold. Since this mean free path is inversely proportional to a function of the pressure within the manifold, it is necessary in order to permit use of an opening of practical dimensions, to maintain the gas in the sample manifold at a pressure below a few millimeters of mercury and preferably below 1 mm. of mercury. Thus means must be provided for admitting a sample into the sample manifold in such a manner as to hold the manifold pressure at the desired low value and at the same time to insure the introduction of a representative sample into the manifold. The present invention is directed to this end.

If the mass spectrometer is to be used for continuous monitoring for controlling a process, it is desirable that the sample be delivered to the sample manifold in a continuous manner rather than as discrete amounts periodically introduced. It has been proposed heretofore to introduce the gas continuously through a "primary leak" between the sample source and a "secondary leak," and into the ionization chamber through the "secondary leak." Many "leaks" or "capillary leaks," as they are often referred to, have been developed for this and similar purposes.

I have now found that in many applications analytical inaccuracies result from the use of a primary and secondary leak system such as that described above. The origin and cause of such inaccuracies may be explained as follows.

In a sample under a pressure higher than 1 or 2 cm. of mercury, the gas flow through a leak of practical dimensions will be viscous. Since most plant processes, etc., are carried out at pressures above this range, the sample source, at least in continuous monitoring applications, generally operates above this pressure. It follows that the gas flow through the primary leak from the sample source to the sample manifold will be by viscous flow. Now, if the composition and hence the viscosity of the gas changes, the rate of gas flow (viscous flow) through the primary leak connecting the source and the manifold will change proportionately. At the same time the rate of gas flow (viscous, molecular, and intermediate between viscous and molecular) through the secondary leak between the manifold and the ionization chamber may either increase or decrease or remain constant for the same manifold pressure. The rate of flow of gas through the secondary leak shows no constant dependence on the viscosity of the gas in question since its flow is determined by the effusion properties of the gas as well as its viscosity. Since under these conditions the rate of influx and efflux will differ, a change in manifold pressure will result.

Consider, in relation to the foregoing discussion, an analytical operation in which a mass spectrometer is being used to monitor one or less than all of the gases in the sample mixture; the effect of the change in total sample manifold pressure will be the same as the effect of a corresponding change in the partial pressure of the gas or gases being monitored, although this latter change may not in fact, have taken place. For purposes of illustration assume a gas sample comprising the components A, B and C in which the component A is being monitored. If the relative proportions of B and C are varied, the viscosity of the gas may, and in fact usually will, vary. This will result, as described above, in a change in the total sample manifold pressure and in an apparent analytical change in the partial pressure of A which in fact may not have changed.

The apparatus of the present invention provides means for maintaining sample manifold pressures substantially constant in spite of variation in the composition and viscosity of the sample being monitored. In one embodiment, the apparatus comprises a sample source or reservoir connected through a so-called primary leak to a sample manifold, a secondary leak linking the sample manifold to the ionization chamber of a mass spectrometer, and a vacuum pump connected to the sample manifold through a separate pumping line. As will be more apparent from the following detailed description, the proportioning of the primary leak and the pumping line so that flow therethrough is controlled substantially by viscosity, and the proportioning of the secondary leak so that flow therethrough is by molecular diffusion results in the maintenance of a substantially constant manifold pressure regardless of variation in sample composition. Such constancy in manifold pressure will result, with reference to the example given above, in a true analysis of the partial pressure of component A regardless of changes in the relative proportions of components B and C.

The invention will be more clearly understood from the following description taken in relation to the accompanying drawing in which:

Fig. 1 illustrates schematically a mass spectrometer equipped with one form of sample intro-

ducing system in accordance with the invention; and

Fig. 2 is a sectional view of an alternative embodiment of sample introducing system adapted for connection to a mass spectrometer such as the spectrometer shown in Fig. 1.

Referring to Fig. 1, it will be observed that it shows a mass spectrometer 10 comprising an ionization chamber 11, an analyzer tube 12, and an ion collector 14 disposed within an envelope 15 which must be kept at low pressure during operation. An exhaust line 16 connects the envelope 15 with an evacuating system (not shown) whereby the pressure within the envelope, analyzer tube and ionization chamber can be maintained at the low values necessary. The analyzer tube and ionization chamber are evacuated through pumping holes 17 in the wall of the analyzer tube. The evacuating system normally includes a mercury diffusion pump or a molecular pump associated with a mechanical vacuum pump. The evacuating system may be of any appropriate design but conveniently is constructed as disclosed in U. S. Patent No. 2,431,351, issued to Harold W. Washburn and entitled Evacuating System for Mass Spectrometry.

An amplifier and measuring or recording system 18 associated with the ion collector 14, and a sample introducing system 20, serve to complete the apparatus as shown diagrammatically in Fig. 1.

The sample introducing system 20 as shown in Fig. 1 includes a sample reservoir 22, a primary leak 23, a sample manifold 24, a secondary leak 26, a pumping line 27, and a vacuum pump 28. The primary leak 23 permits passage of gas from the reservoir to the manifold, the secondary leak 26 provides means for gas passage from the manifold to the ionization chamber 11 of the mass spectrometer, and the pumping line 27 provides means for gas passage from the manifold to the pump. The primary leak 23 is of such dimensions as to permit the sample of gas to flow through it at an appropriate rate. If the rate of gas consumption by the ion source is  $g$ , the rate of gas flow through the primary leak is  $kg$  where  $k$  is greater than 1. As above indicated, substantially all of the flow resistance in the primary leak will be due to viscous resistance. The fraction due to viscous resistance may be designated as  $\gamma$  and the fraction of resistance due to molecular diffusion as  $1-\gamma$ . The secondary leak 26 through which the rate of flow is  $g$  is so proportioned that the flow therethrough occurs by means of molecular diffusion. The flow through the pumping line 27 will thus be  $(k-1)g$ . The pumping line 27 is of such dimensions that, of the total pressure drop between the sample manifold and the pump, the fraction  $\beta$  is due to viscous flow and the fraction  $1-\beta$  is due to molecular diffusion. The pump 28 is of sufficient size and capacity to maintain essentially zero pressure at the pump end of the line 27. For the purposes of this invention pressure less than  $1/100$  of the pressure in the sample manifold is considered to be essentially zero.

Considering the operation of the device from a mathematical standpoint, it can be shown by elementary considerations that where the viscosity  $\eta$  of a mixture is an arbitrary function of the composition, and the effective molecular weight  $\mu$  of the mixture, which governs its resistance to flow by molecular effusion, is another arbitrary function of the composition, and where  $k$  is sufficiently large that  $1/k$  is a negligibly small quantity of

the order of  $1/10$  to  $1/1000$ , the steady state pressure in the sample manifold M of the system described may be made independent of the nature of the gas flowing into the system by suitable adjustment of  $\beta$  and  $\gamma$ . The constancy of the pressure in the sample manifold improves as the function  $1/k$  becomes small and as  $\beta$  approaches  $\gamma$ , and the manifold pressure approaches complete independence of the nature of the gas admitted as  $1/k$  approaches zero when  $\beta=\gamma$ . In a practical situation however, it is difficult to maintain gamma independent of the nature of the gas when gamma is fractional so that practically it is most desirable simply to design the pumping line 27 of such shape and dimensions that the gas flow through it is viscous; that is, so that gamma approaches 1 and beta approaches 1. In one particular apparatus of the type described the primary leak 23 consisted of a 1 cm. length of 0.1 mm. bore tubing, the sample manifold 24 had a volume of approximately 80 cc., and the pumping line 27 consisted of 12 feet of 0.15 inch bore copper tubing having a slight constriction at the pump end. In this particular apparatus the steady-state pressure in the manifold changed less than 2% when the gas admitted was changed from air to methane.

Another embodiment of the invention, illustrated in section in Fig. 2, is designed to sample a stream containing a gas or vapor mixture so that the partial pressure of each gas in the sample manifold will be proportional to the partial pressure of that gas in the sample stream and substantially independent of the composition of the remainder of the mixture. This apparatus comprises a small bore tube 30 through which gas may be bled from a pipe 32. Gas passes through the tube 30 into a manifold 33. A tube 35 connects the manifold with the ionization chamber of a mass spectrometer such as that shown diagrammatically in section in Fig. 1. The tube 35 contains an orifice 36 which may consist of a hole formed in a sheet of metal foil 37 or the like disposed across the tube. A second tube 38 connects the manifold 33 with a vacuum pump (not shown). In this embodiment the dimensions of the tubes 30 and 38 are so made that the flow throughout the entire length is substantially viscous. In this respect the tubes 30 and 38 are similar to the primary leak 23 and the pumping line 27 respectively of the embodiment shown in Fig. 1.

The dimension of the orifice 36 in the metal foil diaphragm 37 is such that it is small as compared with the mean free path of the molecules in the gas sample at the pressure existing within the manifold 33. This will insure gas passage through the orifice by molecular effusion rather than by viscous flow. For example, at a manifold pressure of 1 mm. of mercury the orifice 36 could be approximately  $2 \times 10^{-4}$  in diameter, although a somewhat larger hole may work satisfactorily. As in the foregoing embodiment of the invention, the overall design should be such that the flow through the tubes 30 and 38 is several times the flow through the orifice 36. This will reduce the error in sampling caused by removing gases through the orifice in different relative proportions than the proportions in which they may be admitted to the manifold. Further the volume of the chamber 34 in which the diaphragm 37 is located should be as small as possible in order to keep the time constant in the system low. Representing the pressure in the sample pipe 32 as  $P_1$ , the pressure in the manifold  $P_2$ , the pressure in the chamber 34 on the spectrometer side of the

orifice 36 as  $P_4$  and pressure at the pump end of the line 38 as  $P_3$  typical values for these pressures are as follows:

- $P_1=760$  mm. of mercury
- $P_2=1$  mm. of mercury
- $P_3=10^{-2}$  mm. of mercury
- $P_4=10^{-4}$  mm. of mercury

Embodiments of the invention shown in Figs. 1 and 2 are somewhat similar in construction and functioning; that shown in Fig. 1 being particularly adapted to intermittent sample introduction and that shown in Fig. 2 being particularly adapted to continuous sample introduction. It is to be understood that the specific dimensions and pressures outlined above are only intended to be illustrative of specific embodiments of the invention and do not represent limitation in the apparatus. Having in mind the time factor, i. e. the lag between withdrawal of a sample from a sample stream or reservoir and the time of analysis of that particular sample, the dimensions of the various parts of the apparatus are comparatively flexible. Providing that the primary leak and the pumping lines are of such size as to permit viscous flow therethrough and the secondary leak (Fig. 1) or orifice (Fig. 2) is of such size as to permit substantially only molecular diffusion therethrough the apparatus will function satisfactorily, providing further that the pressure at the pump end of the pumping line is considerably lower than that in the sample manifold.

I claim:

1. A constant pressure gas inlet system for introducing gas into an evacuated chamber which comprises a sample source, a sample manifold, a vacuum pump, a primary leak connecting the source and manifold, a secondary leak connecting the manifold and the chamber, and a gas flow line connecting the manifold and the pump, the primary leak and gas flow line being of such size that substantially the entire flow resistance therein is viscous resistance.
2. A constant pressure gas inlet system for introducing gas into an evacuated chamber which comprises a sample reservoir, a sample manifold, a vacuum pump, a primary leak connecting the reservoir and manifold, a secondary leak connecting the manifold and the chamber, and a gas flow line connecting the manifold and the pump, the primary leak and gas flow line being of such size that substantially the entire flow resistance therein is viscous resistance.
3. A constant pressure gas inlet system for introducing gas into an evacuated chamber which comprises a sample reservoir, a sample manifold, a vacuum pump, a primary leak connecting the reservoir and manifold, a secondary leak connecting the manifold and the chamber, and a gas flow line connecting the manifold and the pump, the primary leak and gas flow line being of such size that substantially the entire flow resistance therein is viscous resistance and the secondary leak being of such size that gas flow therethrough is by molecular effusion at the pressure subsisting in the manifold.
4. Apparatus according to claim 3 wherein the gas flow line has a larger cross sectional area than the primary leak.
5. A constant pressure gas inlet system for introducing gas into an evacuated chamber comprising a sample reservoir, a sample manifold, a tube having approximately a 0.1 mm. bore connecting the reservoir and manifold, a vacuum

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pump, a tube having a bore of approximately  $15/100''$  connecting the manifold and the vacuum pump, and a tube connecting the manifold and the chamber.

6. A constant pressure gas inlet system for introducing gas into an evacuated chamber comprising a sample reservoir, a sample manifold, a tube having approximately a 0.1 mm. bore connecting the reservoir and manifold, a vacuum pump, a tube having a bore of approximately  $15/100''$  connecting the manifold and the vacuum pump, and a tube connecting the manifold and the chamber, said last named tube being of such size that gas flow therethrough is by molecular diffusion at the pressure subsisting in the manifold.

7. A constant pressure system for continuously bleeding a small amount of gas from a gas stream into a chamber connected with an evacuating system, which comprises the combination of a sample manifold, a pump connected to the manifold by a gas flow line, a second line connecting the gas stream and manifold, and a third line connecting the manifold and the chamber, an orifice in the third line of such size that gas flow therethrough is by molecular diffusion at the subsisting pressure of the manifold, and the first and second lines being of such size that gas flow therethrough is by viscous flow.

8. A constant pressure system for continuously bleeding a small amount of gas from a gas stream into a chamber connected with an evacuating system, which comprises the combination of a sample manifold, a pump connected to the manifold by a gas flow line, a second line connecting the gas stream and manifold, and a third

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line connecting the manifold and the chamber, the first and second lines being of such size that gas flow therethrough is by viscous flow.

9. Apparatus according to claim 8 wherein the pump maintains a pressure in the manifold of about 1 mm. of mercury and the orifice is approximately  $2 \times 10^{-4}''$  in diameter.

10. A constant pressure gas inlet system for introducing gas into an evacuated chamber which comprises a sample source, a sample manifold, a vacuum pump, a primary leak connecting the source and the manifold, the resistance to gas flow in the primary leak including the fraction  $\gamma$  due to viscous resistance, a secondary leak connecting the manifold and the chamber, and a gas flow line connecting the manifold and the vacuum pump, the resistance to gas flow in the gas flow line including the fraction  $\beta$  due to viscous resistance where  $\gamma$  and  $\beta$  are substantially equal.

11. Apparatus according to claim 10 where  $\gamma$  and  $\beta$  are each substantially equal to 1.

HAROLD W. WASHBURN.

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