Dec. 10, 1946. H. W. WASHBURN 2,412,236

MASS SPECTROMETRY

Filed Dec. 9, 1943 2 Sheets-Sheet 1

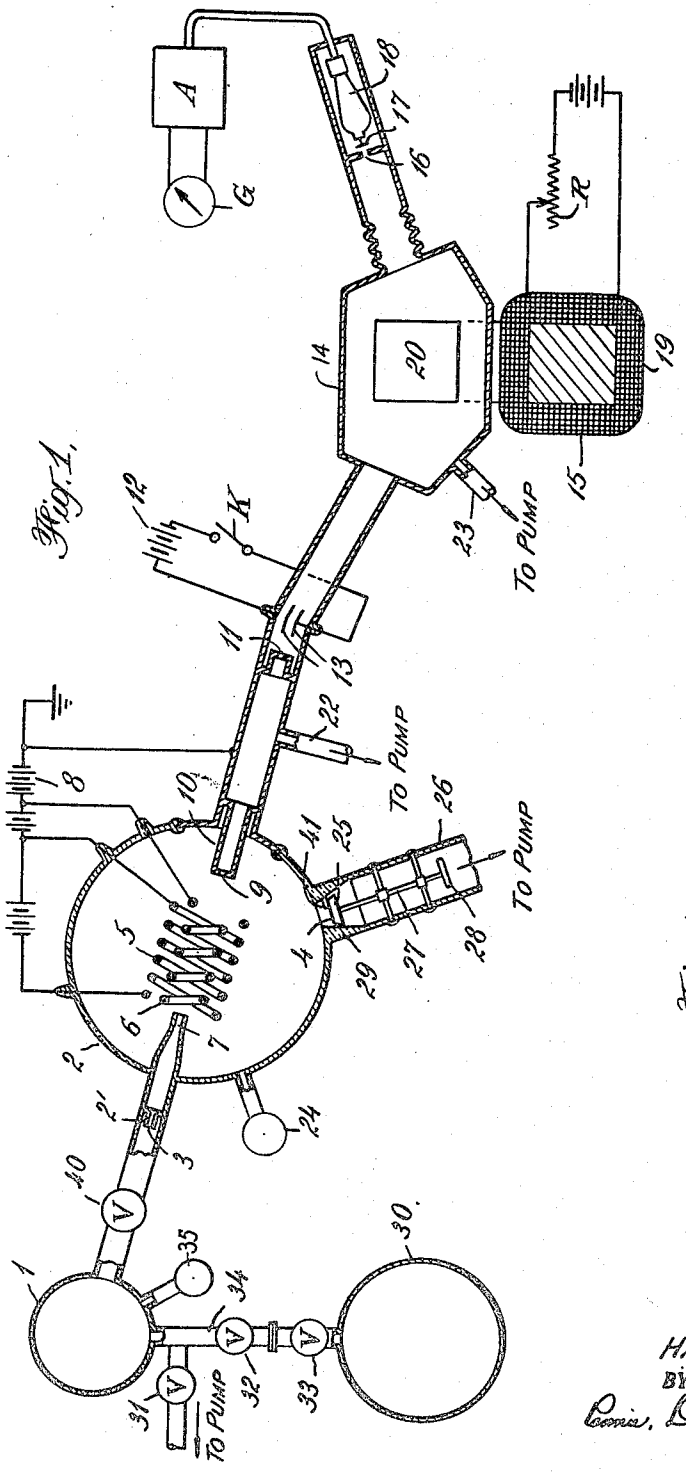


Fig. 1.

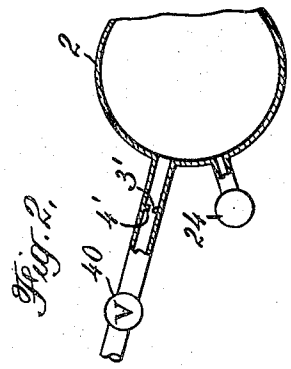


Fig. 2.

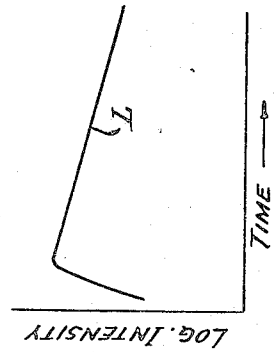


Fig. 3.

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Filed Dec. 9, 1943 2 Sheets-Sheet 2

Fig. 4,

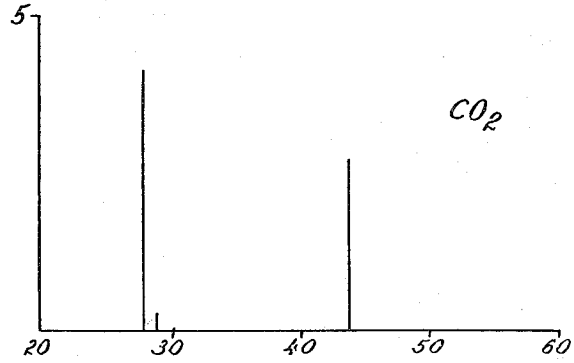


Fig. 5,

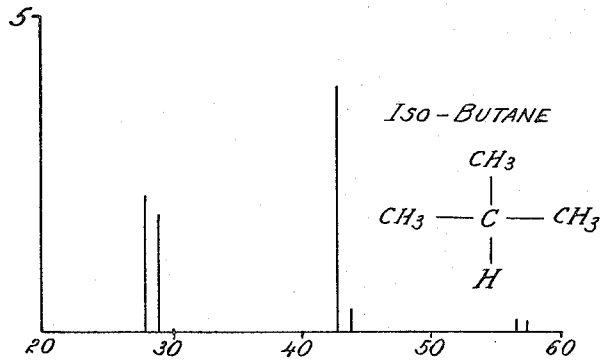
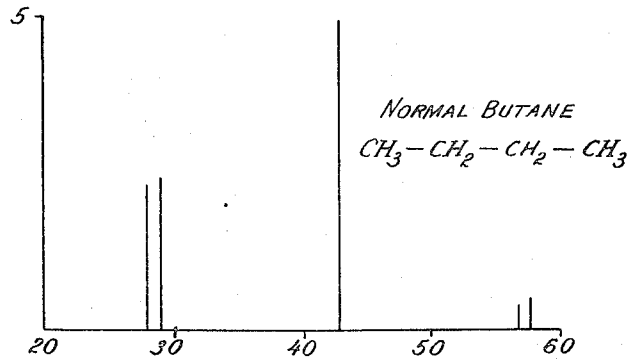


Fig. 6,



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MASS SPECTROMETRY

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Application December 9, 1943, Serial No. 513,526

20 Claims. (Cl. 73—18)

1

This invention relates to gas analysis and particularly to quantitative analysis of gaseous mixtures by mass spectrometry.

This application is a continuation in part of my co-pending application Serial No. 320,802, filed February 26, 1940.

A mass spectrometer is an apparatus employed for producing and sorting ions. One known form of mass spectrometer comprises a sample chamber, an ionization chamber, an analyzer, and a collector. A gas mixture to be analyzed is introduced from the sample chamber through an orifice into the ionization chamber and is there bombarded by electrons emitted by a filament, so that molecules in the mixture become positive ions. As a result of their charge, the positive ions are accelerated toward an exit slit in the ionization chamber. After passing through this slit the ions are accelerated further toward a second slit, which is kept at a large negative potential with respect to the first slit. Hence the positive ions pass through the second slit at high velocity and enter the analyzer, where they are subjected to the action of a magnetic field that causes them to pursue a curved path. The radius of curvature of this path for a given accelerating voltage depends upon the ratio of the charge on the ion to its mass or atomic weight, which ratio is hereinafter sometimes referred to as "specific mass." In consequence, the ions of low mass follow a path of short radius in the analyzer, while those of larger mass follow a path of greater radius.

At the exit end of the analyzer there is an exit slit, and by proper adjustment of the magnetic field or the accelerating voltage or both, the radius of path for ions of a given mass can be adjusted so that these ions are directed at the split, pass through it and strike a collector, where their quantity is measured, for example by a galvanometer connected to the collecter through a suitable vacuum tube amplifier.

By varying the magnetic field or the accelerating voltage, the diverging ion beams of different specific mass formed from the gas molecules in the mixture can be brought successively through the exit slit and discharged to produce a series of ion currents which represent the mass spectrum. If a quantitative relationship can be found between the molecular components of the mixture and the ions formed therefrom, the mass spectrum becomes a means for the quantitative analysis of the mixture.

As the result of my investigation, I have found that it is possible to establish and maintain a

2

simple quantitative relationship between the composition of the mixture to be analyzed and the various ions formed therefrom in the mass spectrometer. Thus I have found that, if the pressure in the sample chamber from which the gas mixture is admitted into the ionization chamber is sufficiently low the various components of a gaseous mixture to be analyzed will flow into the ionization chamber at mutually independent rates, i. e. the rate of flow of each component will be in accordance with the partial pressure of the component in the mixture and independent of the partial pressures of the other components. Hence the portion of the mixture which enters the ionization chamber will be quantitatively as well as qualitatively representative of the mixture.

The pressure in the sample chamber should be reduced so far that the mean free path of the molecules in the region of the conduit through which the mixture is admitted into the ionization chamber is large compared to the least cross sectional dimension of this conduit. It appears that optimum results are obtained if the pressure in the sample chamber is so low that the mean free path of each type of molecule present is at least twice the least cross section dimension of the conduit. However, irrespective of the particular ratio between the mean free path of the molecules and the cross section of the conduit through which they enter the ionization chamber, the fact remains that in any instance the pressure in the sample chamber can be reduced to a point below which the molecules will flow from sample chamber to ionization chamber at mutually independent rates, and that when this condition prevails it becomes much simpler to determine the quantitative composition of the gas mixture from its spectrum. In short, conditions of "molecular flow" into the ionization chamber can be obtained by reducing the pressure in the sample chamber and when molecular flow is established quantitative analysis with a mass spectrometer becomes relatively simple. In order to obtain a uniform mixture within the sample chamber, the diffusion within the latter must be rapid, which is the case when the pressure is low and the shape of the chamber is appropriate, i. e., relatively wide in proportion to its length.

In summary, my invention contemplates flowing the mixture (preferably by pressure) from the sample chamber into the ionization chamber while maintaining the pressures in both chambers so low that each component flows into the

ionization chamber at a rate dependent on the partial pressure of that component in the mixture and independent of the partial pressure of any other component. Moreover, the net withdrawal of each component from the ionization region by the pumping system (taking into account that there is some diffusion of the components in the opposite direction) should be independent of the partial pressures of other components present. This can be accomplished (*a*) by having a pumping speed of the system employed to exhaust the ionization chamber high (as compared with the pumping speed of the exhaust port of the ionization chamber) and (*b*) by introducing a "bottle neck" between the pump and the chamber, so that a high pumping speed in the pump (as compared with the bottle neck) is obtained. In such case, each component flows through the ionization chamber at the rate it would have if it alone were present.

The pressure in the ionization chamber should fulfill another requirement, in that it should be such that the number of ions derived from an individual component in the ionization step varies in accordance with the partial pressure of that component and independently of the partial pressures of other components, intermolecular collisions being minimized by the low pressure. Again, pressure should be so low that ionization of each component proceeds independently of the presence of other components.

Molecular flow through the conduit probably arises under these conditions because the molecules in passing through the conduit into the ionization chamber strike the walls of the conduit to a much greater extent than they strike each other. The molecules, upon striking the walls of the conduit, rebound with a velocity which is controlled primarily by the character and temperature of the conduit surface and is independent of the original velocity of the molecule striking the wall. Moreover, since the molecules do not collide with each other to a substantial extent, if at all, in the conduit, fast-moving molecules have little or no opportunity to impart their velocity characteristics to slow-moving molecules. The result of the collision with the conduit wall and the lack of collision between the molecules themselves is that each kind of molecule flows through the conduit at a rate which is dependent only upon the temperature and nature of the conduit surface, and upon the molecular weight and partial pressure of that kind of molecule.

In any event, and whatever be the explanation, the fact remains that under the conditions specified above, each kind of molecule (i e. each component) flows into the ionization chamber at an independent rate. This phenomenon coupled with other conditions discussed hereinafter can be employed to establish a linear relation between the mass spectrum of the gas mixture and the mass spectra of any of the individual components obtained under similar conditions. And this linear relation greatly simplifies quantitative analysis with a mass spectrometer, especially of gas mixtures containing components which crack under the conditions prevailing in the ionization chamber.

The establishment of the required linear relationship is further aided if, during the analysis period, the contents of the sample chamber is agitated with a view to maintaining it homogeneous throughout and so that the portion of the sample immediately adjacent the conduit is

quantitatively and qualitatively the same as that in any other portion of the chamber. However, the rates of diffusion of the components of gas sample at those temperatures and pressures which I prefer to maintain in the chamber usually are such that an adequate degree of homogeneity is obtained without agitation.

Another factor which aids in establishment of the required linear relationship of the mass spectrum of the gas mixture to the mass spectra of its pure components obtained under similar conditions is the maintenance of a pressure in the ionization chamber such that each component is ionized to the same extent in the same manner that it would be ionized if it alone were present. In other words, the pressure in the ionization region (i. e. in the space in which the ions are formed and through which they travel until they enter the analyzer) should be so low that the ions formed do not collide substantially with each other or with uncharged particles. By avoiding such collisions in this region, interchange of charge between particles, secondary ionization of particles by the original ions, and combination of ions with other particles, are prevented. In other words, the possibility of collision in the ionization chamber may be minimized by making the mean free path of each and every type of ion present greater than the distance to be travelled by these ions from their point of formation to the point at which they enter the analyzer.

Thirdly, in order to obtain the desired linear relationship between the spectrum of the mixture and the several spectra of its individual components, collision between ions and uncharged molecules should be avoided in the analyzer and this requires that the pressure prevailing in the analyzer be so low that the mean free path of the ions at the prevailing pressure in the analyzer is greater (and preferably much greater) than the distance travelled by the ions from the point of ionization to the point of collection. At the same time, the space charge and interior surface effects in the ionization chamber should be kept low, and electron emission should be kept uniform.

These and other features of my invention will be more thoroughly understood in the light of the following detailed description taken in conjunction with the accompanying drawings in which:

Fig. 1 is a schematic diagram, partly in cross-section, showing a gas analysis apparatus including a mass spectrometer, which may be operated in accordance with my invention;

Fig. 2 illustrates a modified form of the inlet system of the mass spectrometer of Fig. 1;

Fig. 3 represents graphically the time decay curve of ion currents produced by the ionization of a sample of pure gas in the mass spectrometer of Fig. 1; and

Figs. 4, 5 and 6 represent graphically the intensities of certain ion currents measured under standard conditions for CO_2, iso-butane, and normal butane, respectively.

Referring to Fig. 1, an unknown gas mixture held in a sample chamber 1 is admitted to an ionization chamber 2 through an inlet capillary tube 2' and a jet 7, and withdrawn from the ionization chamber by evacuation through an outlet port 4. Thus, the bore of the capillary tube acts as an inlet port or orifice 3.

Gas within the ionization chamber 2 is bombarded by electrons drawn from a helical fila-

ment type cathode 5 into the space within a grid type anode 6 which is maintained at a positive potential with respect to the cathode. Positive ions are formed from molecules thus bombarded and these ions are accelerated toward a grounded collimator tube 10 by virtue of a high positive potential maintained at the cathode 5 and the anode 6 by a high voltage battery 8.

Some of the accelerated ions pass through a collimator slit 9 and proceed through a second collimator slit 11, thereby forming a limited heterogeneous positive ion beam which, when a key K is closed, is deflected downwardly by an electrostatic field maintained between a pair of plates 13 by a battery 12. The stream of ions proceeds through a gap 20 in a chamber 14 where said stream is bent upward by a magnetic field provided by an electromagnet 15.

Due to the combined effects of the electric and magnetic fields and the geometry of the mass spectrometer, positive ions of a predetermined mass-to-charge ratio are caused to pass through a narrow exit slit 16 and fall upon a collector 17 connected in conventional manner to a grid of an electrometer tube 18. The intensity of the ion current falling upon the collector 17 is measured by a galvanometer G in the output of a D.-C. amplifier A connected in conventional manner to the electrometer tube.

The particular mass-to-charge ratio of the ions which fall upon the collector 17 may be changed by varying the current through a coil 19 which provides the magneto-motive force for establishing the magnetic flux in the gap 20 through which the ions are caused to flow. By changing the magnetic field, ions of different charge-to-mass ratios are caused to fall successively upon the collector. This produces a series of ion currents which can be measured and employed for determining the constituents of an unknown gas mixture admitted into the ionization chamber from the sample chamber.

The space from the collimator tube 10 to the electrometer tube 18 is maintained at a very low pressure by means of vacuum pumps connected at exhaust ports 22, 23, so that the mean free path of molecules in said space exceeds the length of the paths traversed by the ions in their travel from the anode 9 to the collector 17.

In the foregoing gas analysis procedure, the pressure within the ionization chamber 2 is maintained large enough to provide ion currents of suitable intensity. Preferably the pressure is low enough for the mean free path to be large compared to the dimensions of the ionization chamber. A pressure suitable for this purpose lies within a range of about 10 to 40 mμ Hg.

The pressure within the ionization chamber may be measured by means of a Knudsen gauge 24 and controlled by adjustment of a poppet valve 25 at the mouth of an exhaust tube 26 enclosing the outlet port 4. A suitable Knudsen gauge is described in articles by J. W. N. Dumond, and W. M. Pickles, Jr., in the Review of Scientific Instruments, volume VI, page 362 (1936).

At the end of a poppet valve shaft 27 opposite the poppet valve is a soft iron armature 28 by means of which the position of the poppet valve may be adjusted by the action of an externally operated magnet (not shown). Although it is shown in a vertical plane, the valve shaft 27 preferably is horizontal. A detent 41 determines the position of maximum closure. The outlet system is described in more detail and claimed in a co-pending patent application of Harold W. Washburn, Serial No. 513,527, filed December 9, 1943, and entitled Mass spectrometry.

Gas to be analyzed is gathered in a detachable container 30 and the latter is attached to the sample chamber through a conduit 34.

Prior to introduction of a gas mixture from the detachable container 30 to the sample chamber, stop cocks 31, 32 are opened while a stop cock 33 is kept closed, in order to evacuate sample chamber 1 and the connecting conduit 34. When the pressure within the sample chamber has been reduced to a suitable value, say one micron, the valve 31 is closed and some of the unknown gas mixture is admitted into the sample chamber by opening the valve 33 for a time. The pressure of the unknown gas mixture within the sample chamber 1 is measured by means of a pressure gauge 35, such as a McLeod gauge. In case too much gas is admitted to chamber 1 a portion of said gas may be withdrawn by opening the cock 31 for a short time interval.

A stop cock 40 is opened to cause gas to flow into the ionization chamber. The rate of flow of a pure gas through the capillary tube 2' is given by the equation

$$Q=3.34\frac{R^3}{L\sqrt{d_1}}\left[\frac{R}{4.22l}+\frac{1+0.81\frac{5R}{l}}{1+\frac{5R}{l}}\right](p_1-p_2) \quad (1)$$

where:

Q=rate of flow in c. c./sec., referred to a unit pressure of one dyne/cm.^{2},

R=radius of tube,

L=length of tube,

d_1=density of said pure gas at a pressure of one dyne/cm.^{2},

l=mean free path of molecules within chamber 1,

p_1=pressure in chamber 1,

p_2=pressure in ionization chamber 2.

In most practical cases to be considered here, the pressure in the sample chamber 1 will be large compared to the pressure in the ionization chamber 2 so that, if the radius of the inlet port 3 is small compared to the mean free path of the molecules in chamber 1, Equation 1, reduces to

$$Q=3.34\frac{R^3}{L\sqrt{d_1}}p_1 \quad (2)$$

When the radius of the inlet port 3 is small compared to the mean free path of the molecules, few molecular collisions occur at that point and hence the rate of flow through the tube becomes independent of the internal viscosity of the gas. Thus, when a gas mixture is being admitted to the ionization chamber through the inlet port 3, the flow of molecules of one type will be substantially unaffected by the flow of molecules of any other type present. The rate of flow of each component is governed by Equation 2 where d_1 and p_1 are respectively the densities and partial pressures corresponding to the individual components.

In another form of my invention illustrated in Fig. 2 an inlet port 3' consists of a small orifice in a plate 4'. In this case also each component of a gas mixture will flow through the inlet port 3' at an independent rate if the mean free path of the molecules is large compared with the radius of the orifice.

The rate of flow of pure gas through either inlet port 3 or inlet port 3' varies inversely as

the square root of the molecular weight of said gas.

While the equations of flow (1) and (2) given hereinbefore are strictly applicable only to pure gases, I have found that in general, if I maintain the mean free path of the molecules at the inlet port 3 or 3' large compared to the radius R, collisions between molecules of different kinds of gas near or within the inlet port are made so infrequent that molecules of different kinds flow through said orifice substantially unimpeded by the presence of other molecules.

It is clear that the effective radius of the funnel-shaped flanged end of capillary tube 2' is greater than the radius of the bore of the tube itself. For this reason the funnel-like end of the tube 2' is preferably mounted, as shown, on the low pressure side of the orifice where the mean free path is largest.

At a suitable working pressure the mean free path in ionization chamber 2 will be very large compared with the radial thickness of the annular space between valve 25 and cone-shaped valve seat 29. At 10 mu Hg and 0° C., for instance, the mean free path of nitrogen molecules is 650 cm. At such pressures each component of a mixture will flow out of the exhaust port 4 at an independent rate inversely proportional to the molecular weight of said component.

Under the conditions prescribed above, the ion currents detected at the collector 17 will represent the sums of the currents which would be observed for the individual components if these were present alone, and the measurements of the several ion currents may be used to determine the constitution of the original gas mixture.

From the foregoing description it is clear that I am able to maintain the rate of flow of each component gas through the ionization chamber 2 substantially independent of the presence of other components. However, when extreme accuracy is required, it is also desirable to provide some method for maintaining the gas right at the entrance end of the inlet port (3 or 3') substantially typical of the entire mixture within the sample chamber. Otherwise, the mixture flowing into the ionization chamber 2 will be seriously affected by the rates of interdiffusion of the components within the sample chamber 1 and the anlysis of observations made correspondingly difficult. The process of obtaining uniform distributions of the various components is retarded by the collisions which occur between unlike molecules.

I maintain the mixture within sample chamber 1 substantially homogeneous in either of two ways; (1) by maintaining rapid interdiffusion rates within the sample chamber or (2) by stirring the mixture mechanically. I prefer to maintain the mixture substantially uniform throughout the sample chamber by maintaining the rates of interdiffusion within said sample chamber rapid compared to the rate at which gas is admitted to the ionization chamber. I achieve this result by employing a sample chamber of proper shape and by maintaining the pressure within the sample chamber low enough for the molecules to distribute themselves throughout that chamber so rapidly that the mixture is maintained substantially uniform and the mixture adjacent the mouth of the orifice is always substantially typical of the mixture present in the chamber.

One way to maintain the mixture substantially uniform throughout the sample chamber 1, is

to maintain the mean free path of molecules within the chamber approximately equal to the length of the chamber. I have found, however, that the pressures required to maintain the mean free path sufficiently large for this purpose, are unnecessarily low and that we can maintain mixtures sufficiently uniform at still higher pressures.

The time constant which measures the period during which a given degree of mixing occurs in a binary mixture is given by

$$T \sim \frac{X^2}{D^2} \qquad (3)$$

where D=diffusion coefficient; X=length of sample chamber.

For a mixture of hydrogen and oxygen (having an interdiffusion constant of 0.7 at S. T. P.) in a sample chamber 10 cm. in diameter at a pressure of 0.10 mm. Hg, the mixing period is

$$T \sim \frac{10^2}{0.7^2} \frac{0.10}{760}$$

$$\sim \frac{1}{37.24} \text{ sec.}$$

I have found that I can provide a substantially uniform mixture in the sample chamber if the volume of gas admitted to the ionization chamber during the mixing period is sufficiently small compared with the volume of the sample chamber. Thus, for example, the quantities of hydrogen and oxygen flowing through a simple orifice such as the inlet port 3' having a diameter of 1 mm. during the above calculated mixing period T are 0.67 cc. and 0.16 cc. respectively. Since each of these quantities of gas is very small compared to the volume of the sample chamber, it is clear that the mixture in the sample chamber is substantially homogeneous at any instant during the transfer of gas to the ionization chamber. Thus the portion of gas near the orifice is substantially typical of the gas remaining in the sample chamber.

By so maintaining the gas in the sample chamber substantially homogeneous, complex corrections that might otherwise be required due to variations in sample concentration with time are avoided. However, the degree of homogeneity required and hence the sample chamber pressure permissible depends on the degree of accuracy required.

I prefer to resort to stirring the mixture mechanically to maintain the mixture homogeneous when the gas in sample chamber 1 is at too high a pressure for interdiffusion to occur rapidly enough for my purpose.

By controlling the operating conditions of a mass spectrometer in accordance with the principles hereinbefore explained each component of a gas mixture is caused to flow through the ionization chamber 2 independently of the presence of other components; ions are derived from each component within the ionization chamber 2 substantially in direct proportion to the partial pressure of each component; and as a result the mass spectrum for a mixture is a linear superposition of the mass spectra of the individual components of said mixture.

Consider the conditions which exist during the analysis of a known pure gas such as CO_2 contained in sample chamber 1. Prior to admitting the CO_2 into the ionization chamber 2, the indication of the galvanometer G is zero. When the inlet system of the ionization chamber 2 is opened by turning the stop cock 40, the partial pressure

of CO_2 within the ionization chamber **2** begins to rise. Ions produced by electronic bombardment of CO_2 are formed in proportion to the partial pressure of CO_2. After a short time interval, of the order of one or two minutes, dynamic pressure equilibrium is established between the sample chamber **1**, the ionization chamber **2**, and the exhaust pumps. Thereafter the sample chamber pressure decreases substantially exponentially and the ion density in the ionization chamber **2** decreases in a corresponding manner. Part of the ions formed traverse the collimators **10—11** and ions of a predetermined mass-to-charge ratio are caused to fall on the collector **17**.

In Fig. 3, I have illustrated graphically the variation of ion current with time, measured after opening the stop cock **40**. The curve represents the collected ion current for a given ion such as CO^+ having a mass-to-charge ratio of 28 formed by bombardment of CO_2. Abscissae represent time, and ordinates represent the logarithm of the reading of the galvanometer G. After the stop cock **40** is opened, the ion current increases rapidly, shortly reaching a maximum and thereafter decreasing substantially exponentially as indicated by the straight line portion L of the curve.

The time constant of the decaying ion current depends on many factors, including the volume of the sample chamber **1**, the dimensions of the inlet ports (**3** or **3'**), and the molecular weight of the gas being analyzed.

For the analysis of some mixtures containing CO_2, only the CO_2 ions having a mass-to-charge ratio of 28 ($C^{12}O^{16+}$), 29 ($C^{13}O^{16+}$ and $C^{12}O^{17}$), 30 ($C^{13}O^{17+}$), and 44 ($C^{12}O_2^{16+}$) are of interest. The corresponding galvanometer deflections may be measured at convenient predetermined standard times of 2, 4, 6, and 12 minutes to obtain a standard mass spectrum. A spectrum for CO_2 obtained in this manner is shown in Fig. 4. In this graph abscissae represent mass-to-charge ratios and ordinates represent galvanometer deflections per microlitre at standard temperature and pressure of CO_2 originally present in the sample chamber.

Figs. 5 and 6, respectively, represent similar standard spectra for iso-butane and normal butane for mass-to-charge ratios of 28, 29, 30, 43, 44, 57 and 58.

The intensities of the ion currents measured at standard times are given more exactly in the table for CO_2, isobutane, normal butane, propane, and ethane. The tabulated values represent galvanometer deflections per μl standard temperature pressure of the respective gases for mass-to-charge ratios of 28, 29, 30, 43, 44, 57 and 58, obtained at the standard times given in column 1.

Table

Standard time	$\frac{m}{e}$	Ethane	Propane	Normal butane	Iso-butane	CO_2
2	28	24.0	17.5	2.90	1.53	5.97
4	29	4.52	19.3	3.38	1.36	.044
6	30	3.63	.56	.041	.063	.009
10	43	.00	3.85	6.62	4.63	.00
12	44	.00	3.30	.162	.378	2.60
17	57	.00	.00	.216	.126	.00
20	58	.00	.00	.405	.072	.00

An examination of the partial spectra represented in the table and Figs. 4, 5 and 6, shows that the spectra differ widely and may be utilized in identifying the respective gases.

It is clear that if a mixture of any of the aforementioned gases is admitted to the mass spectrometer under the operating conditions which I have prescribed hereinbefore, each component of the mixture will act independently of each of the other components. Accordingly, the spectrum observed for the mixture will be a superposition of the separate spectra of the gas components combined in proportion to the amounts of the respective components present in the mixture. For a mixture the intensity of a mass spectrum line formed by ions having a mass-to-charge ratio of R is

$$C_R=\Sigma_j K_{Rj} X_j \qquad (4)$$

where K_{Rj} is the sensitivity of the mass spectrum for ions of mass-to-charge ratio R and derived from a unit amount of gas component j, and X_j is the quantity of component j present in the mixture.

Now assume that a mixture of ethane, propane, and normal butane is being analyzed, and that the partial spectrum for this mixture consists of standard time galvanometer deflections $C_{30}=9.9$, $C_{44}=14.8$, $C_{58}=4.1$, corresponding, respectively, to ions having mass-to-charge ratios of 30, 44, and 58. From Equation 4 and the table it is clear that for this case

$$C_{30}=9.9=0.041X_1+0.56X_2+3.63X_3 \qquad (5)$$
$$C_{44}=14.8=0.162X_1+3.30X_2 \qquad (6)$$
$$C_{58}=4.1=0.405X_1 \qquad (7)$$

where X_1, X_2 and X_3 are the quantities of normal butane, propane and ethane, respectively, in the sample. Solving Equations 5, 6 and 7 simultaneously, it is found that the contents of the sample are, respectively:

N-butane: $X_1=10\cdot\mu$l S. T. P.
Propane: $X_2=4\cdot\mu$l S. T. P.
Ethane: $X_3=2\cdot\mu$l S. T. P.

The example just given shows that where the number and nature of the components of a gas mixture is known, the composition of the gas may be determined by reading the galvanometer deflections corresponding to a limited number of different ions produced by electronic bombardment of the mixture. In general, the number of different ion currents measured should be at least equal in number to the number of components contributing to the production of said ions. Obviously, if the number of observations exceeds the number of components present the extra observations may be used to check the results.

In case it is not known in advance of the analysis what components are present, the nature of the components may be determined by a study of the complete mass spectrum of the mixture or by supplementary methods.

In any case, standard spectra are determined for gas components contributing to the presence of particular ion currents measured for a mixture, and the composition of the mixture determined by comparing the mass spectrum for the mixture with the mass spectra of the components. The calculations of the composition of the mixture are simplified by the method because of the control maintained on the rates of flow.

While I prefer to obtain the standard spectra for pure gas from samples of the pure gas, it is clear that standard spectra for n pure gases may be obtained if desired from the spectra for n different mixtures of these pure gases. Other

modifications of the method may be made where pure gases are unavailable.

The numerical example given above illustrates how my method of mass spectrometry may be utilized to determine the composition of a gas mixture. It has particular advantages when the two or more gas components present in the gas sample produce ions of the same mass-to-charge ratio.

My method of mass spectrometry is particularly useful in the analysis of a gas mixture the components of which yield some ions of the same mass-to-charge ratio. And the method of analysis is essential to mass spectrometry when one or more of the components yield only ions which are also produced by ionization of other components possibly present.

Not only can the method be used in the analysis of a mixture of several hydrocarbon gases having different molecular weights. It may also be used to measure the concentrations of hydrocarbon mixtures made up of a plurality of structurally different hydrocarbons having the same molecular weight. For example, to measure the concentrations of iso-butane and normal butane in a mixture known to contain only these two gases, it is only necessary to measure ion currents corresponding to two of the common ions formed. The pair of ions having mass-to-charge ratios of 57 and 58 may be used for this purpose. An examination of the table and Figs. 5 and 6 will show that other pairs of ions are also suitable.

From the foregoing illustrations it is clear that the method of the invention may be utilized to obtain rapid and accurate analysis of gas mixtures where conventional gas analysis methods are slow, tedious and inaccurate.

The procedure described above is also particularly useful where the gas sample to be analyzed is very small. For this reason the method is applicable to soil gas analysis for petroleum prospecting purposes and leads to an accurate knowledge of the minute contents of soil gases where other methods fail to separately identify the various gases present.

In the usual method of soil gas analysis, groups of hydrocarbons are only roughly identified and measured. Individual hydrocarbon constituents of soil gases cannot be completely separated and identified by conventional gas analysis procedures. By analyzing soil samples in accordance with my method, however, it is possible to identify individual hydrocarbons present in said samples.

When soil gases are extracted from soil samples collected in the vicinity of a petroleum deposit, minute quantities of hydrocarbons such as ethane, propane and butane are normally found. Such hydrocarbons, or other substances, which may be indicators of petroleum deposits, may be identified by my method even when non-indicators such as methane CH_4 and ethylene C_2H_4 are present.

In adapting my method to soil gas analysis I prefer to concentrate significant hydrocarbons by any conventional method, such as temperature separation, prior to introducing the sample into the mass spectrometer sample chamber 1. While it is not possible to completely separate minute quantities of hydrocarbons from each other, yet by concentrating them the introduction of relatively large amounts of petroleum indicators into the sample chamber is facilitated while still maintaining the total pressure and the mean free path within a suitable range in accordance with the principles herein set forth.

The relative amplitudes of the standard mass-spectral lines of any gas as illustrated in Figs. 4, 5 and 6 are dependent on the decay rates of the ion currents as well as upon the conditions of ionization. For any given set of conditions, however, the composition of the mixture may be determined by obtaining standard spectra of the components of a gas mixture together with a standard spectrum for the mixture.

In the actual analysis of a gas mixture certain steps in addition to those already described above are desirable.

By means of the rheostat R the current in the coil 19 is adjusted to a value which produces a magnetic field which causes ions of a predetermined mass-to-charge ratio to fall on the collector 17.

To obtain accurate readings it is desirable to measure the background spectrum due to residual gases in the ionization chamber prior to opening the inlet system. To do this I measure the background ion currents corresponding to those ions which I also measure from the sample. This background spectrum is preferably measured just before or just after a gas sample is run. The background spectrum is subtracted from the spectrum observed for the mixture, prior to computing the composition of the mixture according to Equation 4. It is to be understood, of course, that the measurement of the background is not necessary where the background is of negligible magnitude.

When analyzing small samples of gas, such as soil gases containing hydrocarbons or other petroleum indicators, observations of the intensities of the ion beams may be made successively at different times and corrections applied to the observations to compensate for the loss of gas from the sample during the observation times.

In case ionization currents are measured for a mixture at times other than standard times, the readings may be corrected to standard times by applying to the mixture readings, correction factors corresponding to the decay rates of the gas components contributing to said ionization currents. In the apparatus used such corrections are of the order of 1 to 5% per minute. While this correction procedure neglects differences in decay rates for gases of different molecular weights (which may contribute to a given ion current), nevertheless such corrections are sufficiently accurate for many commercial purposes. Where extreme accuracy is desired, the spectra of the separate components are corrected to the times corresponding to the times at which the ionization currents are determined for the mixture.

When the gas sample to be analyzed is small, its composition may be determined by the method outlined above. If the sample is large, certain simplifications may be made in the computation procedure. A large sample chamber may be used to hold a large sample, the inlet port 3 may be made smaller in diameter, and the analysis carried out without exhausting the sample during the run. With large samples contained in large sample chambers and admitted slowly to the ionization chamber the composition of the sample does not change appreciably during the course of the readings and the time decay of the various ion currents is not appreciable. Under these conditions the standard times at which the readings are made need not be determined accurately, if

at all. Under some conditions it is clear that the decay of ion currents will not be appreciable in the time interval during which readings are made and that for all practical purposes the readings may be considered as having been made simultaneously.

I claim:

1. In a method of analyzing a gas mixture with a mass spectrometer having an ionization chamber and a sample chamber connected thereto, the improvement which comprises flowing the mixture from the sample chamber into the ionization chamber while maintaining the sample chamber pressure and the ionization chamber pressure so low that each component of the mixture flows from the sample chamber into the ionization chamber at a rate dependent on the partial pressure of that component in the mixture and independent of the partial pressure of any other component of the mixture.

2. In a method of analyzing a gas mixture with a mass spectrometer having an ionization chamber and a sample chamber connected thereto, the improvement which comprises flowing the mixture from the sample chamber into the ionization chamber while maintaining the sample chamber pressure and the ionization chamber pressure so low that each component of the mixture flows from the sample chamber into the ionization chamber at a rate dependent on the partial pressure of that component in the mixture and independent of the partial pressure of any other component of the mixture, and ionizing components of the mixture in the ionization chamber while maintaining the pressure therein such that the number of ions derived from an individual component varies in accordance with the partial pressure of that component and independently of the partial pressures of other components.

3. In a method of analyzing a gas mixture with a mass spectrometer having an ionization chamber and a sample chamber connected thereto, the improvement which comprises flowing the mixture from the sample chamber into the ionization chamber and simultaneously ionizing components of the mixture in the ionization chamber while maintaining the sample chamber pressure and the ionization chamber pressure so low that each component of the mixture flows from the sample chamber into the ionization chamber at a rate dependent on the partial pressure of that component in the mixture and independent of the partial pressure of any other component of the mixture, the pressure in the ionization chamber also being such that the number of ions derived from an individual component varies in accordance with the partial pressure of that component and independently of the partial pressure of the other components.

4. In a method of analyzing a gaseous mixture involving admitting the mixture into an ionization zone from a sample chamber, ionizing components of the mixture in the zone, withdrawing resulting ions from the zone, and determining the amount of withdrawn ions of a selected mass-to-charge ratio, the improvement which comprises flowing the components of the mixture into the ionization zone simultaneously and at rates dependent upon the partial pressure of the respective component and independent of the partial pressures of the other components by maintaining the pressure in the sample chamber below a specific level, and ionizing the components in the ionization zone while maintaining the pressure therein at level such that the number of ions derived from a component varies in accordance with the partial pressure of that component and independently of the partial pressures of the other components.

5. In a method of analyzing a gaseous mixture involving admitting the mixture from a sample chamber into an ionization zone through a passage, ionizing components of the mixture in the zone, withdrawing the resulting ions from the zone, and determining the amounts of withdrawn ions of a selected mass-to-charge ratio, the improvement which comprises flowing the components of the mixture simultaneously into the ionization zone but at mutually independent rates by maintaining in the sample chamber a pressure that is higher than in the ionization zone but so low that the mean free path of molecules of the components of the mixture in the sample chamber is at least as long as about half of the least cross-sectional dimension of the passage, and maintaining the pressure in the ionization zone such that the number of ions derived from each component varies in accordance with the partial pressures of that component and independently of the partial pressures of the other components.

6. In the analysis of a gas mixture containing a plurality of components with a mass spectrometer having an ionization chamber and a sample chamber connected thereto through an orifice, the improvement which comprises pressure flowing the mixture through the orifice from the sample chamber into the ionization chamber while maintaining the pressures in the chambers at such values as to flow each component at the same rate with which it would flow if it alone were present, simultaneously ionizing each component in the ionization chamber while maintaining the pressure in the ionization chamber at a value such that each component is ionized to the same extent that it would be ionized if it alone were present, and measuring the rate of formation of resulting ions of a selected mass-to-charge ratio.

7. In analyzing a gas mixture with a mass spectrometer involving passing the mixture from a simple region through an orifice into an ionization region, the improvement which comprises flowing each component from the sample region into the ionization region at a rate which varies directly with the partial pressure of said each component and inversely as the square root of the molecular weight thereof by maintaining the pressure in the sample region greater than the pressure in the ionization region and at a value at which the mean free path of molecules is sufficiently large for the molecules of each component to pass through said orifice without substantial collision with other molecules.

8. In a method of analyzing a gas mixture with a mass spectrometer, the improvement which comprises diffusing each component of a gas mixture into and out of an ionization region at an independent rate, and maintaining the pressures of the gas in the mass spectrometer at a value such that the diffusion rates of the respective components are inversely proportional to the square root of the molecular weights of the respective components, and measuring the relative rates of formation of ions of different mass-to-charge ratios produced in said region.

9. In a method of analyzing a limited quantity of a gas mixture originally contained in a limited sample region of a mass spectrometer in which only a single ion current corresponding to a single

predetermined mass-to-charge ratio may be measured at any one time while the pressure of a component in said mixture is diminishing at a substantial rate, the improvement which comprises the steps of continuously admitting said mixture into the ionization chamber of said mass spectrometer while maintaining the sample region pressure and ionization region pressure at levels such that the respective components of the mixture flow from the sample region into the ionization region at mutually independent rates, successively measuring ion currents corresponding to ions of different mass-to-charge ratios, said measurements being made at predetermined times after initiating the flow of said mixture into said ionization chamber, separately admitting into said ionization chamber known quantities of substances corresponding chemically to the respective components of said gas mixture, and measuring ion currents of said mass-to-charge ratios at times corresponding to said predetermined times after initiating the flow of each of said substances into said ionization chamber, and determining the composition of said mixture by comparing the ion currents measured for said mixture at such times with the ion currents measured for said substances at corresponding times.

10. In a method of mass spectrometry involving the flow of different components of a mixture from a limited sample region into an ionization region at such different rates that the composition of the mixture is changing during the analysis, the improvement which comprises flowing the mixture into the ionization region, ionizing the mixture in the ionization region, successively measuring at predetermined times the rates of formation of ions of different mass-to-charge ratios formed while the amount of the mixture in the sample region is decreasing so as to obtain a mass spectrum of the mixture, similarly obtaining mass spectra of substances corresponding chemically to individual components, and determining the composition of the mixture by comparing the measured rates of formation of the respective ions in the mass spectrum of the mixture with those in the mass spectra of the substances and in this determination compensating for changes in the composition of said mixture during analysis by reducing the measurements of the ion formation rates of given mass-to-change ratio in the mixture and in the individual substances to a common time basis by correcting the measurements in accordance with the rates of flow of the individual components.

11. In a method of analyzing a gaseous mixture involving admission of the mixture into an ionization zone, the ionization of components of the mixture in said zone, the withdrawal of the resulting ions from the zone, and the determination of the amounts of withdrawn ions of different mass-to-charge ratios, the improvement which comprises admitting the components of the mixture simultaneously to the ionization zone but at mutually independent rates, and maintaining the pressure in the ionization zone at such a low value that ions being withdrawn from the zone do not collide substantially with molecules of the gaseous mixture, whereby the amounts of ions of each mass-to-charge ratio formed in the ionization of the mixture are equal respectively to the linear sum of the quantities of such ions which would be formed if each of the components were present alone.

12. In a method of analyzing a gaseous mixture involving admission of the mixture into an ionization zone, the ionization of components of the mixture in said zone, the withdrawal of the resulting ions from the zone, and the determination of the amounts of withdrawn ions of different mass-to-charge ratios, the improvement which comprises admitting the components of the mixture simultaneously to the ionization zone but at mutually independent rates, and maintaining the pressure in the ionization zone at such a low value that the distance travelled in the zone by ions being withdrawn from the zone is relatively short as compared with the mean free path of molecules of the gaseous components of said zone, whereby the amounts of ions of each mass-to-charge ratio formed in the ionization of the mixture are equal respectively to the linear sum of the quantities of such ions which would be formed if each of the components were present alone.

13. In a method of analyzing a gas mixture, the improvement which comprises the steps of pressure flowing the gas mixture from a high pressure sample region into a low pressure analysis region while maintaining the pressures in said regions at values such that each component in the mixture flows at a rate which is independent of the presence of other components present in the mixture, ionizing molecules of each component in the low pressure region while maintaining the pressure in said region so low that ions are produced from the components in amounts corresponding to the partial pressures of the respective components in said low pressure region, and measuring the respective rates of formation of ions of different mass-to-charge ratio so formed.

14. In a method of analyzing a gas mixture with a mass spectrometer having an ionization region, and a sample region connected thereto through a restricted orifice, the steps which comprise pressure flowing different components of the gas mixture from the sample region into the ionization region through the orifice at different rates whereby the relative amounts of the components remaining in the sample chamber are changed during the flow process, while maintaining the pressure in the sample region at such a value that the molecules of the respective components enter the orifice from a relatively small part of the sample region adjacent the mouth of the orifice without any substantial proportion of collisions with other molecules and mixing the components remaining in the sample region rapidly enough in relation to the differences in said flow rates and the dimensions of the sample region to maintain the mixture of the gas sample substantially homogeneous throughout the entire sample region, thereby maintaining a typical sample in the small part of the sample region adjacent the mouth of the orifice representative of the entire sample in the sample region.

15. In the analysis of a gas mixture containing a plurality of components with a mass spectrometer having an ionization chamber, a sample chamber connected thereto through a first aperture, and a low pressure zone connected thereto through a second aperture, the improvement which comprises pressure flowing the mixture through the first aperture while maintaining the pressures in the two chambers at such low values that each component flows into the ionization chamber at the same rate with which it would flow if it were present alone, ionizing each component in the ionization chamber while the

pressure in the ionization chamber is of such a low value that each component is ionized in the same manner that it would be ionized if it were present alone, withdrawing the resulting ions of each component simultaneously from the ionization chamber at the same rate that the ions of each component would be withdrawn if that component were present alone and were being ionized, pressure flowing all of the non-ionized molecules from the ionization chamber into the low pressure zone by maintaining the relationship between the pressures in the ionization chamber and such zone at such values that the non-ionized molecules of each component flow into the zone at the same rate at which they would flow if that component were present alone, and measuring the rate of withdrawal of the resulting ions of a selected mass-to-charge ratio, whereby the contribution of each component to the total number of such ions withdrawn is the same as it would be if the component were present alone.

16. In a mass spectrometer, the combination which comprises an ionization chamber, a sample chamber, a conduit connecting the sample chamber to the ionization chamber, and a tube sealed within said conduit with at least part of the tube spaced from the conduit wall and extending from the sealed portion thereof in the direction of the sample chamber and opening toward the sample chamber.

17. In a mass spectrometer, the combination which comprises an ionization chamber, a sample chamber, an intermediate chamber of fixed volume, a first conduit containing a restricted orifice connecting the intermediate chamber to the sample chamber, a stopcock in said conduit, means for exhausting the intermediate chamber independently of the sample chamber and connected to the intermediate chamber through a second conduit, and a stopcock in said second conduit.

18. In a mass spectrometer, the combination which comprises an ionization chamber, a sample chamber, an intermediate chamber, a first conduit having a restricted orifice therein connecting the intermediate chamber to the sample chamber, a valve in said conduit between said orifice and said intermediate chamber, means for exhausting the intermediate chamber independently of the sample chamber and connected to the intermediate chamber through a second conduit, and a valve in said second conduit.

19. In a mass spectrometer, the combination which comprises an ionization chamber, a sample chamber, an intermediate chamber of fixed volume, means for admitting a portion of a sample from the sample chamber into the intermediate chamber in gaseous form, a conduit connecting said intermediate chamber and said ionization chamber, a valve in said conduit, means for indicating the pressure of gas present in said intermediate chamber, a second conduit connected to the intermediate chamber, and means connected to the intermediate chamber through the second conduit withdrawing a portion of any gas contained therein.

20. In a mass spectrometer, the combination which comprises an ionization chamber, a sample chamber, an intermediate chamber, a first conduit having a restricted orifice therein connecting the intermediate chamber to the ionization chamber, a valve in said conduit between said orifice and said intermediate chamber, evacuating means, a second conduit connecting the intermediate chamber and the evacuating means, and a valve in said second conduit.

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