Dec. 10, 1946. H. W. WASHBURN ET AL 2,412,237

MASS SPECTROMETRY

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Fig. 1.

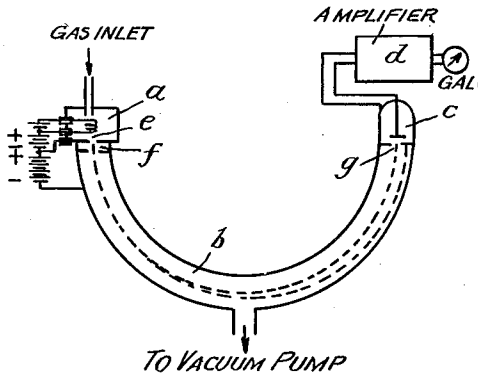


Fig. 3.

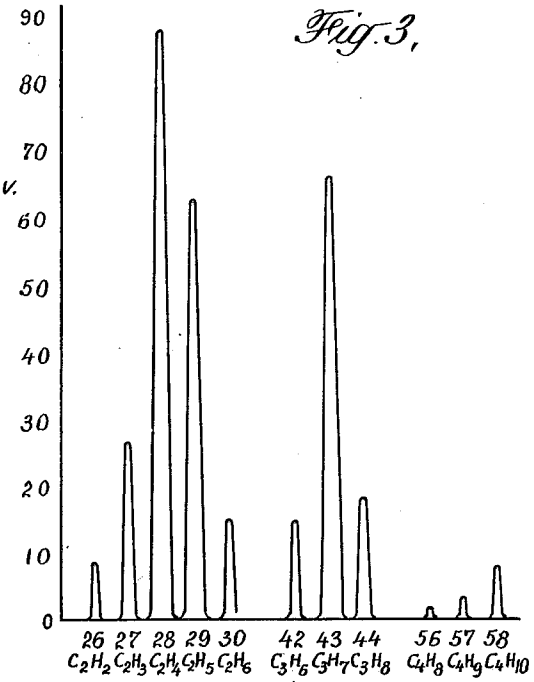
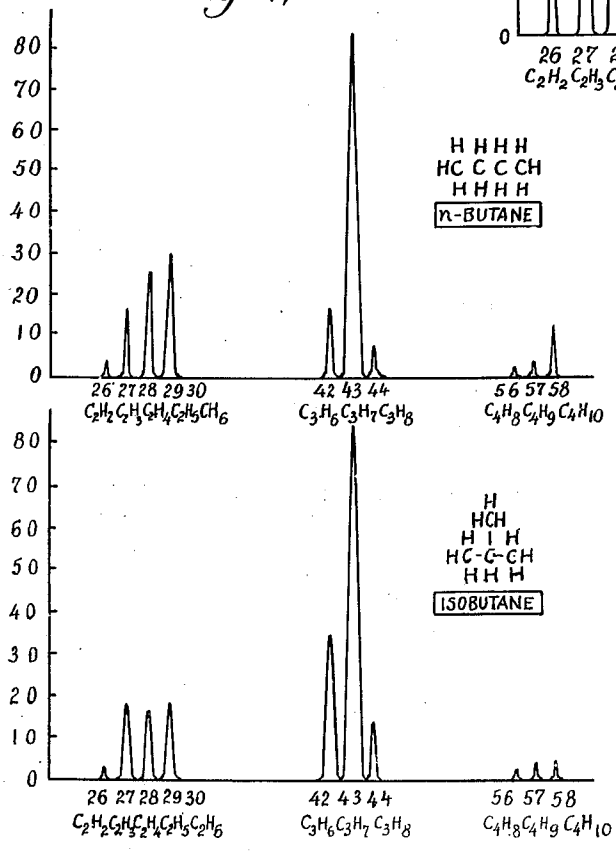


Fig. 2.



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MASS SPECTROMETRY

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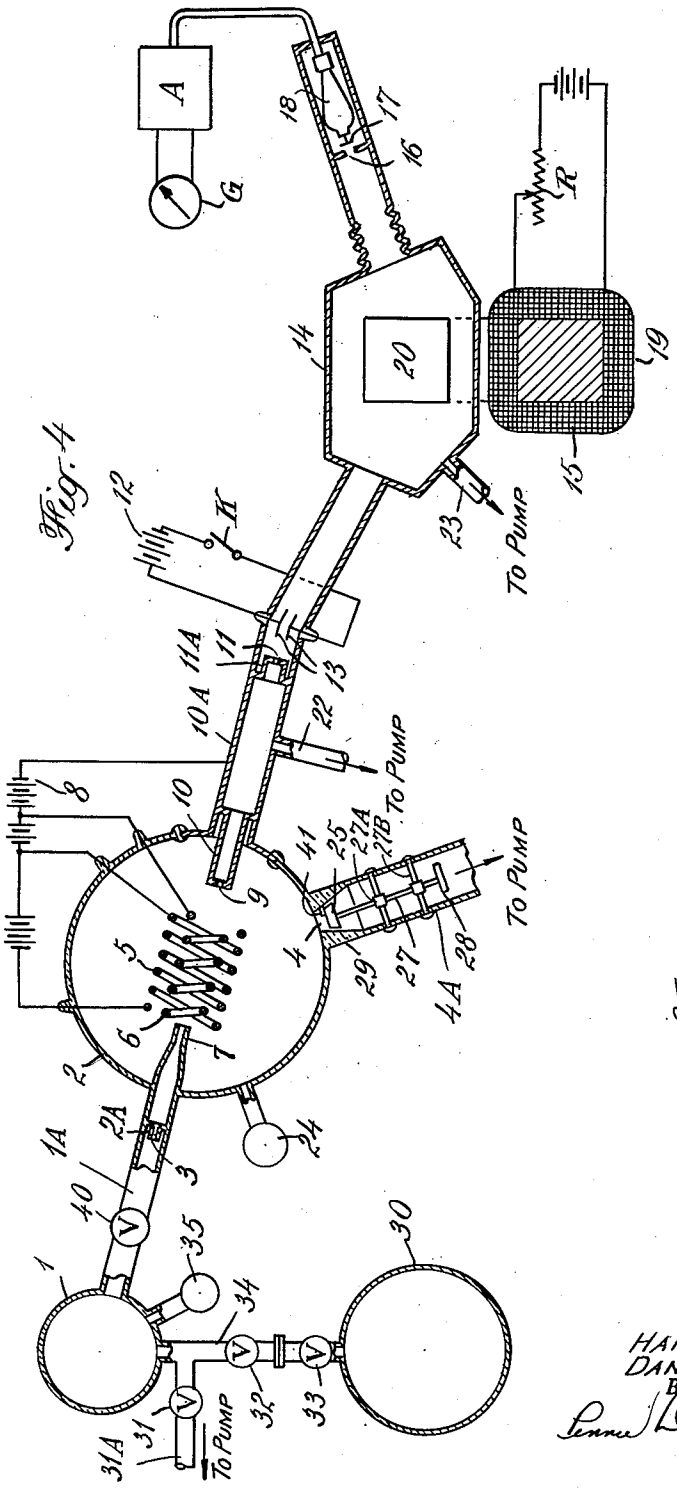


Fig. 4

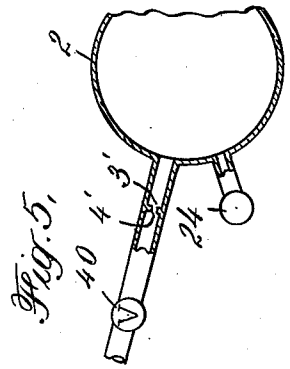


Fig. 5.

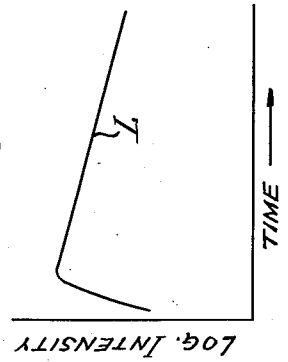


Fig. 6.

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MASS SPECTROMETRY

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Fig. 7.

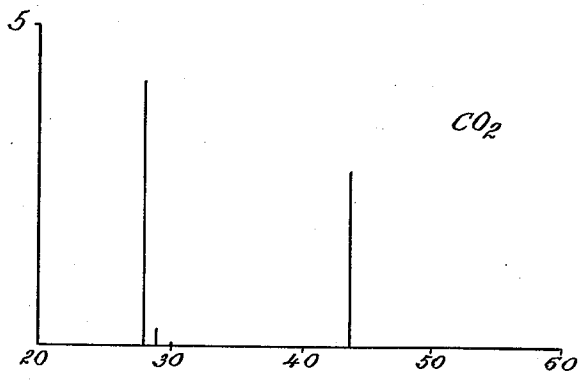


Fig. 8.

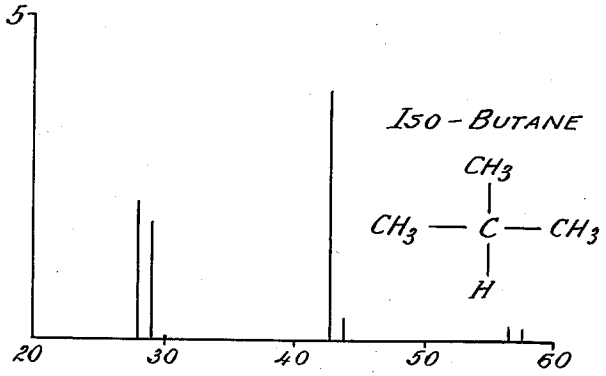
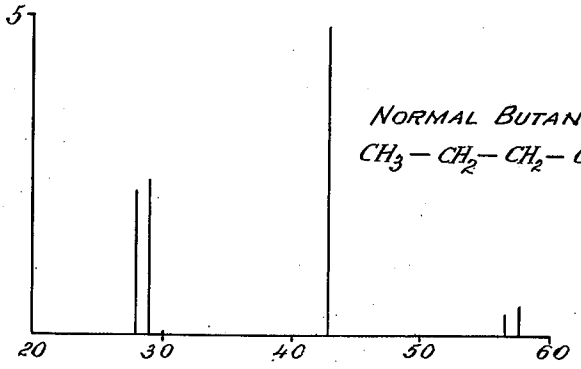


Fig. 9.



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Patented Dec. 10, 1946

2,412,237

UNITED STATES PATENT OFFICE

2,412,237

MASS SPECTROMETRY

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Application December 9, 1943, Serial No. 513,527

3 Claims. (Cl. 73—18)

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This invention is concerned with mass spectrometry and particularly with analysis by mass spectrometry of gaseous mixtures containing compounds, such as hydrocarbons, which can be cracked by bombardment with ionizing particles. The invention affords a means for identifying such compounds by means of typical cracking patterns and is particularly useful in distinguishing between isomers present in a gaseous mixture.

This application is a continuation-in-part of our co-pending application Serial No. 378,636, filed February 12, 1941.

A mass spectrometer is an apparatus for producing and sorting ions. Essentially it comprises a sample chamber, an ionization chamber, an analyzer tube and a collector. In the ionizing chamber a gas mixture to be investigated and admitted from the sample chamber is bombarded with ionizing particles, such as electrons, to produce ions. Due to the impression of an accelerating voltage, the ions pass as a heterogeneous beam out of the ionizing chamber into the analyzer tube where they are subjected to the action of a magnetic field and sorted in accordance with their specific mass, i. e. the ratio of mass of the ion to its charge. Thus, in the analyzer, the ions of different specific mass pursue different paths and form a plurality of diverging homogeneous ion beams each composed of ions of like specific mass. Ordinarily these paths are circular, ions of large mass having paths of greater radius than ions of small mass.

At the exit end of the analyzer tube there is a slit. 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 the beam of ions of that mass is directed at the slit. The ions pass through the slit and strike and discharge on a collector, where their quantity is measured, for example by a galvanometer connected to the collector through a suitable vacuum tube amplifier.

By varying the magnetic field or the accelerating voltage or both, the ion beams of different specific mass can be brought successively through the exit slit and discharged and measured, thus producing a mass spectrum.

In accordance with the instant invention, the sample admitted to the ionizing chamber should be representative of the mixture to be analyzed. At the same time, the space charge and interior surface effects should be kept low. Lastly, we have discovered that the ionizing chamber and the analyzer tube should be maintained at a

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pressure low enough to prevent collision between ions of different mass-to-charge ratio, i. e. low enough so that the mean free path of the ions is greater than the distance they have to travel from their point of formation in the ionization chamber to their point of discharge at the collector. Under such conditions, the mass spectrum of the mixture closely approximates the linear sum of the mass spectra of the separate components thereof obtained under similar conditions, even though cracking occurs.

It has been assumed heretofore [see for example "Rays of Positive Electricity and their Application to Chemical Analysis" by Sir J. J. Thompson (Longmans, Green & Co., 1921), p. 182] that compounds of equal molecular weight but different chemical formula (i. e. isomers) will produce the same mass spectrum, so that the mass spectrometer could not be used to distinguish between such compounds in a mixture unless means are employed to absorb or otherwise remove one of the isomers prior to analysis.

As a result of our investigations, we have discovered that in many instances it is entirely feasible and in fact advantageous to distinguish between isomers by mass spectrometry. Thus we have discovered that compounds which crack when they are bombarded by electrons or other ionizing particles, always crack in the same manner under a given set of operating conditions. Hence each such compound produces a typical mass spectrum or cracking pattern whereby it may be recognized and its proportions in the mixture determined.

It will be apparent, in the light of the foregoing discoveries, that the fact that certain compounds crack under the conditions prevailing in the ionization chamber of a mass spectrometer is no obtsacle to the use of the instrument for qualitative and quantitative analysis of mixtures containing such compounds. It will also be apparent that the ability of such compounds to crack under such circumstances can be usefully employed to distinguish between isomers present in a mixture. For example, one may determine both the n-butane and isobutane contents of a gaseous mixture despite the fact that both have the same mass, because these compounds under electron bombardment crack according to distinct patterns.

To summarize, our invention contemplates the improvement in the analysis of an original gaseous mixture by mass spectrometry which comprises bombarding the mixture with ionizing particles at a voltage so high that constituents in

the mixture are cracked and the resulting products are ionized, thus producing a mixture of ions that differs chemically from the original mixture. The mixture of ions thus formed is sorted in a magnetic field according to specific mass. The sorted ions are separately collected and discharged to produce a mass spectrum of the mixture of ions. The chemical analysis of the molecular mixture can then be determined by comparing the mass spectrum of the ion mixture obtained as described above with the mass spectra of other ion mixtures obtained by separately treating the constituents of the mixture under substantially the same conditions in the spectrometer. The sorting of the ions and preferably also the ionization should be conducted at pressures so low that the mass spectrum of the mixture is a linear summation of the mass spectra for the constituents of the mixture obtained under like conditions.

In accordance with my invention, we distinguish between isomers in mass spectrometry by bombarding the isomers with ionizing particles, the ionization voltage being so high that at least one isomer is cracked to produce ions of a plurality of different specific masses, the product of ionization of one isomer being different from the product of ionization of the other isomer.

As indicated above, the molecular mixtures preferably are ionized under such conditions that collision between ions of different specific charge is avoided both in the ionization region and in the analysis region, this being furthered by maintaining low pressures in these regions. Apparently the pressures should be so low that the mean free paths of the several kinds of ions present are greater than the distance travelled by the ions from their point of origin to the collector. Under proper conditions, the mass spectrum for a molecular mixture will be a simple linear summation of the mass spectra for the individual molecular constituents of the molecular mixture if the latter spectra are obtained under the same conditions. This being the case, the amounts of each kind of molecule present in the original molecular mixture can be calculated employing a series of linear (first power) simultaneous equations.

The bombardment of some gas mixtures, for example a mixture of paraffin hydrocarbons may, through cracking, result in the formation, from different components in the mixture, of ions having a common specific mass, i. e. a common mass-to-charge ratio. With such mixtures, as with others in cases in which a quantitative analysis is sought, it is desirable to flow a sample thereof into the ionization region while maintaining the sample region pressure and the ionization region pressure such that the respective components of the mixture flow into the ionization region at the rates which would prevail if they were present alone. At least a portion of the admitted sample is ionized and the amount of ionization products formed under standard or predetermined conditions can be measured to obtain a partial mass spectrum for the mixture.

The significance of this partial spectrum in terms of quantitative analysis of the gas mixture may be found by separately admitting to the ionization chamber of the spectrometer substances corresponding chemically to the respective components of the mixture at the same rates specified above. The admitted substances are ionized, the amounts of ionization products derived from the individual substances are measured

to obtain individual partial mass spectra for the substances.

The spectrum of the mixture and the spectrum of at least one of the components will include measurements for ion currents due to discharge of the ions having the same specific mass but derived from different substances, but this will not prevent quantitative analysis of the mixture by comparison of its partial spectrum with the partial spectra of the substances which are its components.

As disclosed in detail hereinafter and in copending application Serial No. 513,526, filed December 9, 1943, the desired linear relationship between the spectrum of a mixture and the spectra of its components is not obtained unless a representative sample of the mixture is admitted to the ionization zone, this being accomplished by introducing the mixture from a sample region maintained at a pressure so low that molecular collisions do not prevent each component from flowing at a rate in accordance with its partial pressure and independent of the partial pressure of other components. Ordinarily the ionization region will be at a still lower pressure, so that the mixture will be forced thereinto by pressure. The combination of this sampling procedure with the steps hereinbefore described for the analysis of a gas mixture, under conditions such that components thereof are cracked, is particularly advantageous.

These and other features of our 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 diagram of one form of mass spectrometer suitable for the practice of our invention;

Fig. 2 shows the separate cracking patterns for n-butane and isobutane;

Fig. 3 shows the pattern obtained from a mixture of equal parts of ethane, propane and n-butane;

Fig. 4 is a schematic diagram, partly in section, of another form of mass spectrometer which can be operated in accordance with our invention and which, in accordance with the invention described and claimed by one of us in application Serial No. 513,526, filed December 9, 1943, is provided with means for assuring that the gas admitted to the ionizing chamber is representative of the sample to be analyzed.

Fig. 5 illustrates a modified form of the inlet system of Fig. 4.

Fig. 6 represents graphically the time decay curve of ion currents produced by the ionization of a sample of pure gas in the spectrometer of Fig. 4; and

Figs. 7, 8 and 9 represent graphically the intensities of certain ion currents measured under standard conditions for CO_2, iso-butane and normal butane, respectively.

We have discovered that a compound which decomposes when subjected to ionization in a mass spectrometer nevertheless produces a typical mass spectrum which may be employed to identify the compound and the proportion thereof present in a mixture. Thus, we have discovered that, despite the fact that hydrocarbons are altered chemically (cracked) when subjected to the condition prevailing in a mass spectrometer, these hydrocarbons are altered in the same manner and produce the same proportions and amount of hydrocarbon ions that are produced when substantially pure samples of the hydrocarbons corresponding

to those of the mixture are subjected to treatment in the mass spectrometer under equivalent conditions, provided, among other factors, that prevailing pressures are sufficiently low, preferably so low that the ions undergoing measurement in the mass spectrometer enjoy substantially free paths, whereby collision between ions or ions and molecules is substantially avoided. In such case, the mass spectrum of the mixture will be a linear superposition of the individual spectra of the several components of the mixture.

It is possible to analyze the mixture quantitatively even when this linear relationship between spectra is not maintained, as when the mean free path of the molecules in a sample is relatively small with respect to the required ion travel path in the ionization chamber of the mass spectrometer, so that collisions occur. In this event, quantitative analysis is still possible by synthesizing a mixture with a view to duplicating that undergoing analysis, and varying the components in the synthetic mixture until it gives substantially the same mass spectrum as that of the mixture undergoing analysis. It will be recognized, however, that this method of analysis involves complexities not found in the low pressure methods.

The spectrometer shown diagrammatically in Fig. 1 consists of an ionization chamber *a*, an analyzer tube *b*, a collector *c*, and an amplifier *d*. The ionization chamber, analyzer tube and collector are enclosed in an air-tight container or envelope, which is kept under a high vacuum to avoid molecular and ionic collisions, as described in greater detail hereinafter. This container is placed in a uniform magnetic field, preferably supplied by a large electromagnet. The gas to be analyzed is introduced into the ionization chamber through a capillary leak or gas inlet.

In the ionization chamber, the gases are bombarded by electrons emitted by a filament. This bombardment ionizes the molecules and thereby they become positive ions. If the ionizing potential is sufficiently high the bombardment may also bring about cracking, in which case the ions will not correspond chemically to the molecules from which they were formed.

As a result of their positive charge the ions are accelerated toward a slit *e*, which is kept at a small negative potential with respect to the rest of the ionization chamber. After passing through *e*, the ions are further accelerated toward a slit *f*, which is kept at a large negative potential with respect to the slit *e*. This potential is usually of the order of a thousand or more volts. The ions thus pass through slit *f* at a high velocity. The path they take, however, is not straight, but curved, owing to the action of the magnetic field. The radius of curvature of the path for a given accelerating voltage depends upon its specific mass, i. e., the ratio of the charge on the ion to its mass or molecular weight. Hence the ions of a given specific mass will follow one curved path while those of a higher mass will follow another curved path of greater radius. By proper adjustment either of the magnetic field or of the accelerating voltage, or of both, ions of any desired mass can be made to follow a predetermined radius of curvature and thus to pass through an exit slit *g*. Only the ions passing through this slit can strike the collector *c*, where their quantity is measured by a suitable vacuum-tube amplifier and galvanometer or recorder.

Thus the quantity of ions present of any particular mass can be measured by properly adjusting the magnetic or electric fields of the spectrometer and measuring the deflection on the galvanometer. To complete the analysis it is then necessary to determine the relation between these spectrometer measurements and the amount of gases or vapors present in the mixture being analyzed.

As indicated hereinbefore, we have found that if the ionizing voltage is raised above a certain critical point, each gas or vapor can be made to produce ions of several different masses. The number of ions of each mass produced depends on the type and quantity of gas or vapor, and on the voltage of the ionizing electrons. In other words, each gas or vapor, has an ionization or cracking pattern, which is a function of the ionization voltage and the temperature of the ionization chamber. From a knowledge of these cracking patterns and their variation with ionization voltage, together with a knowledge of isotope ratios and packing fractions of the ions recorded, the quantities of the various gases and vapors present in the unknown sample can be determined. However, it is usually unnecessary to take all these factors into account in an analysis. Moreover, the method permits one to distinguish readily between isomers, for example normal and iso butanes.

In Fig. 2 are shown the separate cracking patterns for n-butane and isobutane. Equal quantities of the two gases were used in order to make the patterns comparable with each other, and the same ionizing potential was used in both instances. Pressure conditions on sample admissions, ionization and sorting were controlled to prevent collisions as described hereinbefore.

The carbon-hydrogen content of some of the components produced by cracking, together with the relative masses of such components, are shown on the horizontal scales of the partial spectra of Fig. 2. Vertical heights of the areas above the respective components represent the relative amounts of such components present in the respective mass spectra. The vertical scale is an abritrary one, depending upon the sensitivity of the apparatus, the amplification of amplifier *d*, the structural features of the particular mass spectrometer, and the operating conditions under which the mass spectra are obtained.

Fig. 2 reveals that the mass spectra of n-butane and isobutane are sufficiently different to make it possible to distinguish either of the gases from the other by inspection of the mass spectrum of the gas in question. When a mixture of these two gases is analyzed by a mass spectrometer the concentrations of each may be determined from the mass spectrum of the mixture.

The technique by which a quantitative analysis is made of a mixture of these two gases involves in this case the solution of two simultaneous equations based on the heights of the observed peaks and their ratios to each other. In actual practice the results may be obtained by direct methods, without having to go through the detailed calculations each time. A rapid qualitative and quantitative analysis of these or similar gases may be applied with considerable value in refinery operation and control.

An example of the analysis of a normal butane-isobutane mixture by means of linear simultaneous equations correlating cracking portions produced under the conditions of the invention is given below.

Referring to Fig. 2, it will be observed that the

heights of the 42 and 43 peaks for a standard measured quantity of isobutane are 33 and 86 respectively, while the corresponding heights for normal butane are 16 and 82. The heights of these peaks are here referred to as a unit quantity of each gas in the ionization chamber. Accordingly, it will be evident that for given quantities X_I and X_N of isobutane and normal butane respectively, which are present in the ionization chamber, the following equations give the heights P_{42} and P_{43} of the 42 and 43 peaks which will appear in the mass spectrum of a normal butane-isobutane mixture.

$$P_{42}=33X_I+16X_N \quad (1)$$

$$P_{43}=86X_I+82X_N \quad (2)$$

The coefficients X_I and X_N given in Equation 1 are the heights of the 42 peaks obtained from a unit quantity of each of the components. Similarly, the coefficients of X_I and X_N given in Equation 2 are the heights of the 43 peaks obtained from a unit quantity of each of the components. Solving Equations 1 and 2 simultaneously for the quantities of the components which are present in terms of the heights of the 42 and 43 peaks which occur in the mass spectrum of the normal butane-isobutane mixture we obtain:

$$X_I=0.0617P_{42}-0.0120P_{43} \quad (3)$$

$$X_N=0.0246P_{43}-0.0646P_{42} \quad (4)$$

Assuming for the moment that the heights of the 42 and 43 peaks found in the mass spectrum of a butane mixture are 325 and 1250 respectively, we find by substituting these values in Equations 3 and 4 that the relative quantities of isobutane and normal butane present in the ionization chamber are respectively, 5.0 and 10.0 measured in terms of the same volume units as were used in the calibration of the mass spectrometer in obtaining the spectra for the respective components shown in Fig. 2.

The above example represents only one of the various ways of applying our invention to the analysis of mixtures. In the particular illustration here given the relative intensities of the 42 and 43 peaks have been used for the determination of the composition of an isobutane-normal butane mixture. Both of these peaks represent the intensities of hydrocarbon ions containing the same number of carbon atoms.

In the foregoing computation, other pairs of peaks might have been used, i. e., the 28–42 pair or the 44–58 pair.

The Equations 1 and 2 illustrate the linear superposition which occurs in a simple practice of our invention in which the gas or vapor is admitted to the ionization chamber under such conditions that the ions produced during electron bombardment of the representative components present in the mixture, are directly proportional to the respective quantities of each such component present there. Such conditions may be maintained wherever the mean free path of the molecules in the ionization chamber is large compared to the length of the path which the ions must travel from the region of ionization to the inlet slit *f* of the mass spectrometer. Under such conditions as these we may obtain a linear superposition of the respective mass spectra of the components present in the ionization chamber.

It is not absolutely essential in our method that the relative intensities of different peaks be measured and compared. We might also take advantage of the fact that the relative amounts of a given type of ion produced from different components generally varies with the ionization potential and the temperature of the ionization chamber. Thus, for example, we may determine the composition of a normal butane-isobutane mixture by measuring the number of ions derived from such a mixture at two different ionization voltages. By comparing these results with measurements obtained from pure components under low pressure conditions such as those already described, we may compute the quantities of normal butane and isobutane from equations similar to Equations 1, 2, 3 and 4. In any case it will be clear that we may obtain an analysis of a mixture containing *n*-components by computations based on *n* independent measurements obtained in a mass spectrometer.

Accurate and detailed physical analyses such as those outlined above can be made with considerable rapidity. Instead of a galvanometer indicating the quantity of ions of any one type, an automatic recording device may be used, which will give a record of the intensity of the ion beams of all mass units from say, one to two hundred. Such a record may be produced in a few minutes. The actual recording can be done in approximately 5 minutes, while the pump-down time to clean up the apparatus requires an additional five to ten minutes before the next sample can be run.

The time necessary for analysis of a record depends on the number of constituents whose quantities are to be determined. When the quantities of three or four gases only are to be determined, only a few minutes is required for computation.

In Fig. 3 is shown the pattern obtained from a mixture of equal parts of ethane, propane and *n*-butane.

The analysis procedure in accordance with our invention is explained in detail in conjunction with Figs. 4, 5, 6, 7, 8 and 9.

Referring to Fig. 4, it will be observed that the apparatus comprises a sample chamber **1** connected to an ionization chamber **2** through a conduit **1A** containing a small concentrically disposed capillary tube **2A**. The end of the conduit terminates as a nozzle **7** which projects into the ionization chamber. A gas sample passing from the sample chamber to the ionization chamber must pass through the bore **3** of the capillary tube.

The ionization chamber may be evacuated through an outlet port **4** which is connected by a conduit **4A** to a vacuum pumping system (not shown). The outlet port may be closed by a poppet valve **25** mounted on a stem **27** which can be slid endwise in a pair of concentric supports **27A**, **27B**. A soft iron armature **28** is mounted on the valve stem opposite the valve. The position of the valve itself may be adjusted by the action of an externally disposed magnet (not shown). If desired, a detent **41** may be disposed in the valve seat or port to prevent the valve from being closed completely. In any case, the position of the member **25** in the port can be adjusted to control the pressure within the ionization chamber. This pressure may be measured by means of a Knudsen gauge **24** connected to the ionization chamber. A suitable Knudsen gauge is described in an article by Dumond and Pickles, Jr., in the Review of Scientific Instruments, volume VI, page 362 (1936).

A helical filament type cathode **5** is mounted within the ionization chamber co-axially with the nozzle **7** and a grid type anode **6**, which is disposed within the cathode. Gas which enters the ionization chamber from the nozzle is bom-

barded by electrons drawn from the cathode into the space within the anode, which is maintained at a positive potential with respect to the cathode. Positive ions are formed as the result of the bombardment and these are accelerated toward a grounded collimator tube 10 at the outlet of the ionization chamber by reason of a high negative potential maintained at the cathode and the anode by a high voltage battery or other power supply 8.

It will be observed that the collimator tube 10 is mounted in an outlet conduit 10A co-axially with the nozzle and the inlet conduit. The collimator tube projects slightly into the ionization chamber and has a slit 9 at its inside end through which ions may pass. The outlet tube is provided with a second collimator slit 11 in a collimator tube 11A. The two slits are in line with the axes of the anode, cathode and nozzle. Ions passing through both collimator slits pass between a pair of plates 13, between which an electrostatic field is maintained by a battery 12 when key K is closed. The ion stream issuing from the second collimator slit is deflected downward by the electrostatic field maintained between the plates and passes through a gap 20 in an analyzer chamber 14.

Both the outlet tube 10A and the analyzer chamber 14 are connected to the vacuum pumping system, respectively, by conduits 22, 23.

The ion stream passing through the gap 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, the heterogeneous ion beam which passes through the collimator slits into the analyzer tube is sorted into a plurality of homogeneous diverging ion beams. Any one of these beams may be brought to focus on a narrow exit slit 16 at the outlet of the analyzer tube. Ions which pass through this slit fall upon a collector 17, which is connected in a conventional manner to a grid of an electrometer tube 18. The electrometer tube is connected to a galvanometer G through a D. C. amplifier A. The intensity of the ion current due to discharge of the ions at the electrode 17 is measured by the galvanometer.

The electro-magnet is surrounded by a coil 19 which provides the magneto-motive force for establishing the magnetic flux in the gap 20 of the analyzer tube. By changing the magnetic field, the diverging homogeneous ion beams of different specific masses may be caused to sweep successively over the slit 16 and thus fall upon the collector 17. In this fashion, a measure of the charges borne by the several ion beams may be obtained and this measure represents the mass spectrum. Thus, a gaseous mixture admitted into the ionization chamber is there ionized; the resulting ions are propelled through the collimator where they are formed into a heterogeneous ion beam; the heterogeneous ion beam is sorted into a plurality of diverging homogeneous ion beams in the analyzer, and these homogeneous ion beams are successively collected to produce the mass spectrum.

The vacuum line connections 4A, 22, 23 maintain the interior of the apparatus at low pressure. The collimator and the interior of the analyzer are maintained at very low pressure by means of the vacuum lines 22, 23, the object being to maintain a pressure so low that the mean free path of molecules in that space exceeds the length of the paths which the ions must travel from the ionization chamber to the collector.

The pressure within the ionization chamber should be maintained at a level sufficiently high to provide ion currents of suitable intensity but low enough to prevent arcing within the chamber. Preferably, the pressure in the ionization chamber is such that the mean free path of molecules therein is of the order of the cross sectional dimensions of the chamber itself. For example, the ionization chamber may be maintained in a range of 10 to 40 $m\mu$ Hg, the pressure within the chamber being determined by the Knudsen gauge as described hereinbefore.

To consider the sample inlet system in somewhat greater detail, it will be noted that a sample of gas to be analyzed is contained initially in a detachable container 30, the outlet of which may be closed by the valve 33. Thus the outlet may be coupled by flanges to a tube 34 which is connected to the sample chamber proper. The tube 34 contains a valve 32. A pumping line 31A is connected in the line 34 between the sample chamber I and the valve 32. The pumping line is connected to the vacuum system (not shown) and contains a valve 31.

The pressure of the gas sample in the sample chamber may be determined by means of a pressure gauge 35, for example a Knudsen gauge. A valve 40 is connected in the inlet conduit 1A between the sample chamber and the ionization chamber.

The introduction of a gas sample into the ionization chamber is conducted as follows: The detachable container 30 is fastened to the inlet line 34 by the flanges. The stop cocks or valves 31, 32 are opened while the valve 33 is kept closed. The sample chamber and the tube 34 are then evacuated through the line 31A to the pump. When the pressure within the sample chamber has been reduced to a suitable value, say one micron, the valve 31 on the pumping line is closed. Then the valve 33 is open and some of the sample is admitted to the sample chamber. The valve 33 is manipulated so that only a limited amount of the gas sample enters the chamber, the pressure therein being kept relatively low and measured by means of the Knudsen gauge. Should excess gas be admitted to the sample chamber, the pressure may be reduced to a suitable value by opening the valve 31. When the pressure within the sample chamber is at a suitable value, i. e. such as to permit the molecules to flow through the bore 3 of the capillary tube, the stop cock 40 is opened to permit the flow of gas into the ionization chamber.

Of course prior to flowing the gas into the ionization chamber the pressure therein and in the analyzer have been reduced to suitable values as described hereinbefore.

The rate of flow of a pure gas through a capillary tube 2A 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.

The pressure in the sample chamber will in most cases be large compared to the pressure in the ionization chamber 2, so that if the radius of the bore 3 is small compared to the mean free path of the molecules in the sample chamber, the foregoing reduces to

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

When the radius of the inlet port 3 is small compared to the mean free path of the molecules, few molecular collisions occur within said tube 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 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 our invention illustrated in Fig. 5, the 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 molecular weight of said gas.

While the equations of flow (1) and (2) given hereinbefore are strictly applicable only to pure gases, we have found that in general, if we maintain the mean free path of the molecules at the inlet ports 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 2A is greater than the radius of the bore of the tube itself. For this reason the funnel-like end of the tube 2A 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.

By maintaining independent rates of flow for the separate components at both the intake and exhaust ports 3 or 3', and 4 of the ionization chamber 2, the ion currents detected at collector 17 represent the sums of the currents which would be observed for the individual components, and the measurements of various ion currents may be used to determine the constitution of the original gas mixture.

From the foregoing description it is clear that we are 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 this is not necessarily enough for our purpose, as it is also desirable to provide some method for maintaining the gas right at the entrance end of inlet ports 3 or 3' substantially typical of the entire mixture within said 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 analysis of the observations made correspondingly difficult. The process of obtaining uniform distributions of the various components is retarded by the collisions which occur between unlike molecules.

We maintain the mixture within sample chamber 1 substantially homogeneous in either of two ways; either by maintaining rapid interdiffusion rates within the sample chamber or by stirring the mixture mechanically.

We prefer to maintain the mixture substantially uniform throughout sample chamber 1 by maintaining the rates of interdiffusion within said sample chamber rapid compared to the rate at which gas is admitted to the ionization chamber. We achieve this result by maintaining within a source chamber 1 of proper shape a pressure low enough for the molecules to distribute themselves throughout said 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 remaining in chamber 1.

One way to maintain the mixture substantially uniform throughout the sample chamber 1, is to maintain the mean free path of molecules within the sample chamber 1 approximately equal to the length of said chamber 1. We 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.

Thus for a mixture of hydrogen and oxygen (having an inter-diffusion constant of 0.7 at S. T. P.) in a sample chamber 10 cm. in diameter at 0.10 mm. Hg, the mixing period is

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

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

We have found that we can provide a substantially uniform mixture in the sample chamber if the volume of gas admitted to the ionization chamber 2 during the mixing period is small compared with the volume of the sample chamber 1. Thus, for example, the quantities of hydrogen and oxygen flowing through a simple orifice such as 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 said sample chamber is substantially homogeneous at any instant during the transfer

of gas to the ionization chamber. In this way the portion of gas near the orifice is always maintained substantially typical of the gas remaining in the sample chamber.

By so maintaining the gas in the sample chamber 2 substantially homogeneous, complex corrections that might otherwise be required due to variations in sample concentration with time are precluded. Obviously the degree of homogeneity required and hence the sample chamber pressure permissible depends on the degree of accuracy required.

We 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 our purpose.

From the foregoing, it will be apparent that in order to carry out a quantitative analysis of a hydrocarbon mixture or the like with simplicity, in accordance with our invention, the following conditions should be met:

1. The flow of the components of the mixture into the ionization chamber should be dependent upon their respective partial pressures and independent of the partial pressures of other components. In other words, molecular flow into the ionization chamber should be established by reducing the pressure in the sample chamber, preferably to a point at which the radius of the orifice in the capillary tube is less than the mean free path of the molecules in the sample chamber;

2. The outlet from the ionization chamber should be small compared with the mean free path of the molecules therein; and

3. The rate of flow from the sample chamber to the ionization chamber should be small compared to the rate of diffusion within the sample chamber.

If the foregoing conditions prevail, each component of the gas mixture will flow through the ionization chamber independently of the presence of other components. Under these conditions, ions may be derived from each component within the ionization chamber substantially in direct proportion to the partial pressure of each component, and the mass spectrum for the mixture may be a linear superposition of the mass spectrum of the individual components of that mixture, especially if the mean free path of the molecules in the collimator and the analyzer is greater than the distance which the ions have to travel in these two parts of the apparatus.

Before considering the analysis of a gaseous mixture, it may be desirable to consider the conditions which exist during the analysis of a pure gas such as CO_2 in the apparatus of Fig. 4. To consider the analysis of such a pure gas, it should be noted that prior to admitting the CO_2 into the ionization chamber from the sample chamber, the indication of the galvanometer attached to the collector system is zero.

When the inlet system of ionization chamber 2 is opened by turning stop cock 40, the partial pressure of CO_2 within said 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 hereinabove described and ions of a predetermined mass-to-charge ratio are caused to fall on collector 17.

In Fig. 6, we have illustrated graphically the variation of ion current with time, measured after opening stop cock 40. This curve represents the collected ion current for a given ion such as CO^+ having a mass-to-charge ratio (specific mass) of 28 formed by bombardment of CO_2. Abscissae represent time, and ordinates represent the logarithm of the galvanometer G reading. After 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. 7. In this graph abscissae represent mass-to-charge ratios and ordinates represent galvanometer deflections per microlitre at standard temperature pressure of CO_2 originally present in the sample chamber.

Figs. 8 and 9, 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, iso-butane, normal butane, propane, and ethane. The tabulated values represent galvanometer deflections per microlitre at 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. 7, 8 and 9, 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 we 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 mix-

ture. For a mixture the intensity of a mass spectrum line formed by ions having a mass-to-charge ratio of R is

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

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

$$C_{30}=9.9=0.041X_1+0.56X_2+3.63X_3 \quad (5)$$

$$C_{44}=14.8=0.162X_1+3.30X_2 \quad (6)$$

$$C_{58}=4.1=0.405X_1 \quad (7)$$

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: $X_1=10\cdot\mu 1$ S. T. P.
Propane: $X_2=4\cdot\mu 1$ S. T. P.
Ethane: $X_3=2\cdot\mu 1$ 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 our method because of the control which we maintain on the rates of flow.

While we 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 said pure gases. Other modifications of our method may be made where pure gases are unavailable.

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

Our 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 our method of analysis is absolutely essential to mass spectrometry when one or more of the components yields only ions which are also produced by ionization of other components possibly present.

Not only can our method be used in the analysis of a mixture of several hydrocarbon gases having different molecular weights, but our method 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. 8 and 9 will show that other pairs of ions are also suitable.

From the foregoing illustrations it is clear that our method 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 our method is very suitable for soil gas analysis for petroleum prospecting purposes as our method leads to an accurate knowledge of the minute contents of soil gases where other methods fail to separately identify the various gases present, hence yielding only rough or approximate results. 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 our 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 are indicators of petroleum deposits, may be identified by our method even when non-indicators such as methane CH_4 and ethylene C_2H_4 are present. In adapting our method to soil gas analysis we 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 we make it easy to introduce relatively large amounts of petroleum indicators into the sample chamber while still maintaining the total pressure and the mean free path within a suitable range in accordance with the principles hereinabove set forth.

It is clear that 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 a 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 collector 17. We do not depend on the current measurement alone to bring the desired ions in focus at the exit slit but prefer to measure the magnetic field directly, such as by means of a magnetic balance (not shown). By properly setting the magnetic field at various values determined from previous tests the different ions to be measured are caused to fall successively on the collector 17.

To correctly determine any ion current independently of amplifier drift we read the galvanometer G. deflection with and without key K closed. When key K is open no ions are deflected into the magnetic field in gap 20, and the corresponding galvanometer deflection represents the zero of the apparatus. When key K is closed ions of predetermined mass-to-charge ratio fall on collector 17 causing an increment in the deflection of galvanometer G which is proportional to the concentration of such ions in ionization chamber 2.

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 we measure the background ion currents corresponding to those ions which we 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, in accordance with our invention, 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 gas as of different molecular weights which may contribute to a given ion currents, nevertheless such corrections are sufficiently accurate for the many commercial purposes, but 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. In case, however, 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.

With our invention we have provided a method and apparatus whereby the composition of a gas mixture may be determined from the mass spectrum of said mixture and the mass spectra of its components. Our invention provides a simple method for analyzing a gas mixture by assuring that a linear relation holds between the ion currents measured for a mixture and ion currents measured for the separate components thereof.

We claim:

1. In analyzing with a mass spectrometer having a sample region and an ionization region, a gas mixture having a plurality of components therein which upon ionization form ions of a common mass-to-charge ratio, the improvement which comprises pressure flowing a sample of said gas mixture into the ionization region while maintaining the sample region pressure and ionization region pressure such that the respective components of the mixture flow from the sample region into the ionization region at the same rates with which they would flow if present alone, ionizing at least a portion of the admitted sample, measuring the amount of ionization products formed under standard conditions to obtain a partial mass spectrum for said gas mixture, separately admitting substances corresponding chemically to the respective components of the mixture into the ionization chamber at such rates and ionizing said substances, measuring the amounts of ionization products derived from the individual substances, and thus obtaining individual partial mass spectra for said substances, said spectra for said mixture and said substances including measurements for ion currents due to said ions having said common mass-to-charge ratio, and determining the composition of said mixture by comparing said partial spectrum of said gas mixture with said partial spectra of said substances.

2. In a method of analyzing a gas mixture having a plurality of components therein which upon ionization form ions of a common mass-to-charge ratio, with a mass spectrometer having an ionization chamber and a sample chamber connected thereto, the improvement which comprises introducing each component of said gas mixture from a sample chamber at low pressure into the ionization chamber at still lower pressure while maintaining said pressures at values such that each component flows at a rate directly proportional to the partial pressure of each said component in said sample chamber and substantially independent of the partial pressures of other components present in said sample chamber, ionizing at least a portion of said admitted sample, determining from the ionization products formed

under standard conditions a partial mass spectrum for said gas mixture, and separately introducing substances corresponding chemically to components of the mixture into the ionization chamber under similar pressure conditions producing flow of each substance at the same rate with which the components flow in the mixture, separately ionizing the substances, determining from the ionization products of the substances individual partial mass spectra for said substances, said spectra for said mixture and said substances including measurements of ion currents due to said ions having a common mass-to-charge ratio, and determining the composition of said mixture by comparing said partial spectrum of said gas mixture with said partial spectra of said substances.

3. In a method of analyzing in a mass spectrometer a gaseous mixture of components which when ionized form some ion currents comprising ions of the same mass-to-charge ratios, the improvement which comprises pressure flowing the

mixture into an ionization chamber and controlling the pressure so that each component flows into the ionization chamber of said mass spectrometer at a rate independent of the concentrations of other components present, measuring ion currents corresponding to ions of different mass-to-charge ratios, including measurements of currents corresponding to ions of the same mass-to-charge ratio derived from different components, separately introducing into the ionization chamber a substance corresponding chemically to each component, similarly measuring for each of the substances ion currents comprising ions of the same mass-to-charge ratios as those measured for the mixture, and determining the relative quantities of said components in said mixture by comparing the ion currents measured for said mixture with the ion currents of the same respective mass-to-charge ratios measured for the individual substances.

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