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IONIC ANALYSIS

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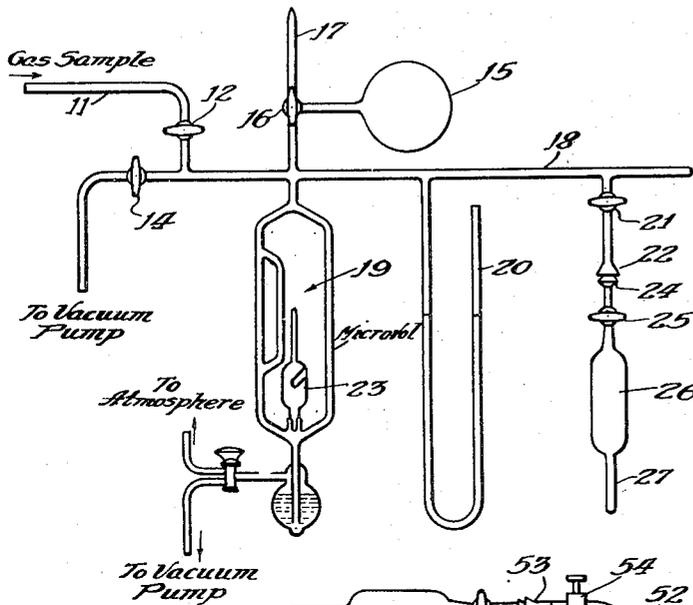


Fig. 1

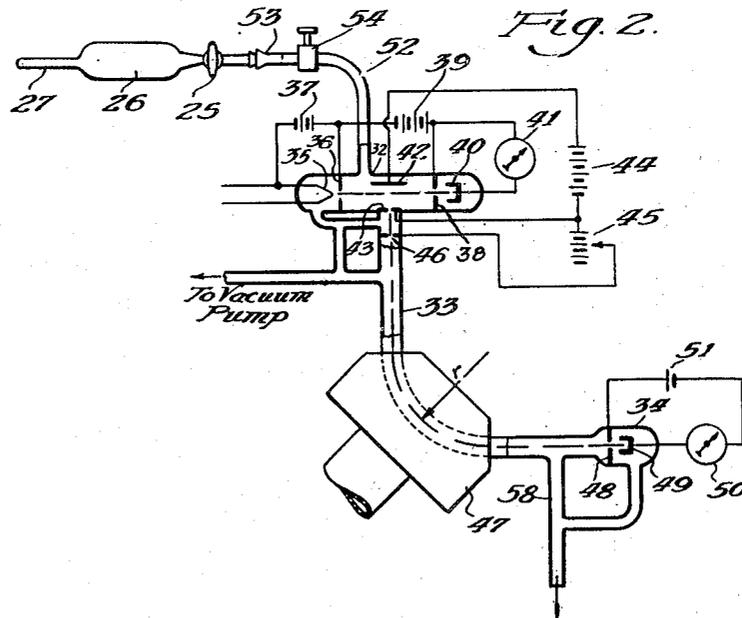


Fig. 2

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2,412,359

IONIC ANALYSIS

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3 Claims. (Cl. 73—18)

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This invention pertains to the art of gas analysis and has particular application to ionic analysis of gases, for example by mass spectrographic methods.

In the ordinary methods of investigating a gaseous mixture by the use of a mass spectrometer or similar ionic analysis devices, quantitative determination of the components of the mixture is normally not possible without recourse to some additional information. The intensities of the various positive ions produced, for example, in the mass spectrometer give a qualitative analysis of the relative abundances of the ions present, but do not relate these quantities to the concentration of the constituent gases present in the original mixture.

It is an object of this invention to provide a method and apparatus suitable for obtaining the additional information necessary to determine quantitatively by ionic methods the amount of at least one unknown constituent gas in a mixture of gases. Other objects of this invention will be revealed in this specification.

This invention relates more specifically to the use of an internal standard in quantitatively analyzing the constituents of a gas. By this invention a foreign gas which has particularly suitable properties is added in known proportions to dilute the gas sample undergoing analysis. This foreign gas, hereinafter referred to as the internal standard, is selected for each unknown sample on which an analysis is to be made. The gaseous mixture undergoing analysis, hereinafter referred to as the diluted gas, after admixing with the internal standard is subjected to examination in a mass spectrometer. As is well known in the art, the positive ion currents produced by a constituent of the sample having a certain mass number is indicative of the abundance of that constituent. Prior to this invention the complex procedure used in determining quantities from the analysis of an unknown gas sample by use of the mass spectrometer has prohibited its use except in a few of its possible applications. One of the chief limiting factors in the use of the mass spectrometer has been the difficulty in compensating for departures from a standard condition. By the inclusion of an internal standard in the sample from which the variables in the procedure can be standardized it becomes possible by this invention to adapt the mass spectrometer to a great variety of uses. Having first calibrated the mass spectrometer by running samples containing various known concentrations of the internal standard and each individual constituent

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which subsequently is to be quantitatively analyzed, the concentration of all or any one of the constituents in the original gaseous mixture may be readily determined.

The advantages of such a procedure are many. One of the chief advantages of this invention is that the partial pressure or concentration of any constituent of the diluted gas is directly related to positive ion currents. Thus, the corrections formerly required to bring the analysis to standard conditions are automatically made during the time that an analysis is being performed. In the methods taught by the prior art the partial pressure of any constituent in a sample of gas depended upon an analysis of all constituents in the sample. By this improved procedure a single constituent in the diluted gas may be secured independently of any other constituent in the sample and without any necessity for a complete analysis of all constituents. Obviously this is an advantage since the probability of introducing errors is materially reduced and since there is a material saving of time when the analysis is on only a few of the many constituents in a sample. The relative concentrations of the internal standard and the diluted gas undergoing analysis will remain constant regardless of total pressure in the ionization chamber of the mass spectrometer. Thus, a slow decrease in the ionization chamber pressure, due to the dissipation of the sample in the container will be of no import. Consequently a further advantage is that precise analytical results can be obtained irrespective of the pressure existing within the ionization chamber of the mass spectrometer. Similarly, slow changes in the total electron emission from the electron gun and in the electron velocity will not seriously affect the results since the magnitude of such changes will be reflected in the magnitude of the ion current due to the internal standard. This is certainly an advantage. In many cases a very minute sample is available for analysis. Another advantage of this invention, therefore, is that, being diluted, a larger sample of gas is available for analysis. Still another advantage is that the mass-number peaks of the internal standard provide known and prominent reference points on the graph of an analysis from which the mass-number-accelerating-voltage scale is standardized during the time that an analysis is being performed.

In the accompanying figures which illustrate possible embodiments of the apparatus used in this invention, the same reference number refers to the same or a corresponding part.

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Figure 1 illustrates in part the apparatus used in one method of preparing a sample of gases for ionic analysis in accordance with my invention;

Figure 2 shows in diagrammatic form the apparatus for analysis of the sample after it has been prepared.

Referring now to Figure 1, the sample to undergo analysis is admitted through tube 11 by opening stopcock 12 beyond which the system is completely evacuated. Stopcocks 14 and 16 are closed when the gas is introduced into this evacuated system. When a suitable pressure has been built up in the system, stopcock 12 is closed and the pressure in the system measured on the manometer 20. This pressure may be from a few microns to 500 millimeters of mercury.

A source of diluting gas 15 is attached to the system through three-way stopcock 16. The pressure of the diluting gas is appreciably greater than the ultimate total pressure of the system. The diluting gas may be introduced into the system through an ordinary two-way stopcock, but I prefer the use of a doser 17 as shown. As is well known in the art, the doser permits the addition of a high-pressure gas to a low-volume system with greater accuracy than is possible by connecting the high-pressure source directly to the system through a simple stopcock. In operation stopcock 16 is first turned to the position shown so that the low-volume doser 17 is filled with the diluting gas. Stopcock 16 is then turned counterclockwise one quarter turn so that the small volume of high-pressure diluting gas is added to the system. This step is repeated as many times as required to build up the desired partial pressure of diluting gas in the system. The partial pressure of diluting gas, which may be within the range of practically zero to 500 mm. of mercury, is the difference between total pressure and the partial pressure from the unknown which was formerly introduced through stopcock 12. This order of introducing the sample and the diluting gas is preferred in that the sample of unknown gas is usually at a lower pressure than the diluting gas. As an example, in an analysis of a gas sample containing hydrocarbons, a gas sample partial pressure of 50 microns of mercury and an internal standard partial pressure of 200 microns of mercury will be found suitable.

Since the normal process of gaseous diffusion is practically instantaneous, container 26 now contains a representative sample of the two gases in known relative partial pressures. Stopcocks 21 and 25 are now closed and container 26 disconnected from the system at ground joint 22. This container is now ready to be connected to the mass spectrometer gas-handling system.

The above-described procedure for preparing a sample which contains a known proportion of an internal standard gas has been found satisfactory where there is an appreciable quantity of the unknown gas. However, I prefer the following procedure where only very minute quantities of the unknown gas are available for analysis. The gas sample is introduced into the closed system via stopcock 12 as before. After stopcock 12 has been closed, all the gas sample is condensed on the re-entrant tube 23 of the Microvol gage 19 as described in U. S. Patent 2,286,384. The volume of this gas sample is there measured by the procedure described in said U. S. Patent 2,286,384. Thereafter it is all transferred to the small tubulation 27 on the container 26 by evaporation from the Microvol gage 19 and condensed in tubulation 27 by external refrigeration. The internal stand-

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ard gas is then admitted to the system via three-way stopcock 16 as before until a suitable pressure has been built up. This pressure is measured on manometer 20. Refrigeration is maintained on small tubulation 27 until a suitable partial pressure of internal standard gas has been added to the system. Obviously, a suitable correction may be applied to correct for the change in volume of internal standard gas which is at the temperature of the refrigerant. Stopcocks 21 and 25 are then closed and container 26 is disconnected from the system at joint 22. A sample having known proportions of an unknown gas and an internal standard gas is thus again prepared for attachment to the mass spectrometer system.

In applying such a refrigeration-condensation transfer method, the gases concerned must meet certain requirements. The gas sample should be completely condensable at the temperature of the selected refrigerant and the internal standard gas should not condense at this temperature. In practice, these requirements are rather easily fulfilled. Other methods of diluting a sample of unknown gas with an internal standard gas will occur to those skilled in the art.

The internal standard gas is chosen with the following requirements in view: First, the gas should be a relatively pure substance composed of simple stable atoms or molecules. Second, the ratio of the mass number to charge of positive ion upon ionization of such gas should not be the same as those of any of the gases in the unknown gas sample undergoing analysis, or at most the amount of such diluent gas initially present in the said gas sample should be negligible compared to the amount added to container 26 in the operations described above. The inert gases, particularly neon and argon, have proved quite satisfactory in most cases.

As mentioned above, before an analysis of an unknown gas sample can be made with a mass spectrometer under this improved procedure, it is necessary to make preliminary calibrations on the mass spectrometer, employing each constituent individually which subsequently is to be analyzed plus the same internal standard gas. In performing this calibration a mixture of the internal standard gas and one of the constituents of the unknown gas sample in pure form is made up according to the procedure described above for adding a diluent gas to a sample of unknown gas. The mixture is subjected to analysis in the mass spectrometer as described hereinafter. In the course of such analysis the positive ion currents of certain selected mass-number peaks are measured both for the internal standard gas and for the pure gas constituent. The instrument constant for any pure gas is obtained thus:

$$K_G = \frac{I_G P_S}{I_S P_G} \quad (1)$$

where:

S=internal standard gas
 G=pure gas
 K_G=instrument constant for pure gas G
 I_S=positive ion current due to S
 I_G=positive ion current due to G
 P_S=partial pressure of S in mixture
 P_G=partial pressure of G in mixture

In performing such a calibration, the total electron emission, the bombarding electron velocity, and the pressure in the ionization chamber are preferably kept constant. The use of this instru-

ment in analyzing an unknown gas sample will be described below.

To perform the quantitative analysis proper, the container 26 with the diluted gas therein is connected to the ionic analysis apparatus as shown in Figure 2. Figure 2 shows in diagrammatic form a mass spectrometer including an ionization chamber 32, a body portion 33 which contains a portion curved to a fixed radius r and an ion collector 34. The general operation of this apparatus is known and hence will be described only briefly. A heated filament 35 in a separately exhausted chamber inside the ionization chamber 32 produces electrons in the evacuated system. These electrons are accelerated towards a shield or perforated plate 36 by a source of voltage 37. Those electrons which pass through the perforation in plate 36 are accelerated towards a second perforated plate 38 by a source of potential 39. The electrons passing through the slit in the perforated plate 38 are collected by collector cup 40 and the abundance of such electrons can be determined by a sensitive electric meter 41 connected in the circuit as shown. The electrons in the region between the two perforated plates 36 and 38 are traveling at a relatively high velocity. Thus they produce ionization by collision with the gaseous atoms and molecules present in this region between plates 36 and 38.

There are a pair of parallel plates 42 and 43 forming the horizontal boundaries of this region of ionization. The lower plate 43, which contains a slit for the passage of ions, is charged negatively with respect to the upper plate 42 by a source of voltage 44. Hence positive ions within the ionization chamber 32 are accelerated toward lower plate 43 and some escape through the slit therein. Those ions striking this slit are further accelerated to a known or determinable velocity by applying an adjustable potential from source 45 between plate 43 and a second slotted plate 46 located below plate 43. The positive ions passing through the perforation in plate 46 form a beam of positive ions having different ratios of charge to mass depending upon the source of the particular ion. A magnetic field is applied between pole pieces 47 at right angles to the plane of curvature of these ions. This magnetic field encompasses the curved portion of body portion 33 of the mass spectrometer as shown. Pole pieces 47 form a part of an electromagnet which may be conventional in all respects. Consequently for convenience and clarity the electromagnet is shown only in part.

A perforated plate 48 is located in the ion collector 34. Depending upon the magnetic field strength surrounding the curved section of body portion 33 and upon the ionic velocity at plate 46, ions having a particular ratio of charge to mass are focused upon the opening in plate 48. Ions of a different beam ratio of charge to mass present in the ion beam leaving plate 46 do not strike the opening in plate 48. The determination of this ratio of charge to mass of the ions which will pass through the opening in plate 48 under any set of conditions has already been described many times in the art. A collector cup 49 insulated from the body of the instrument is located back of the opening in plate 48 and is connected to a very sensitive current measuring device 50. This current indicating device measures the relative abundances of ions passing through the perforation in plate 48. Preferably this collector cup is maintained at a slightly neg-

ative potential relative to the plate 48 by means of a source of potential 51.

By changing either the strength of the electric field due to source 45 or the strength of the magnetic field through which the ions pass, the various positive ions in the beam of differing ratio of charge to mass in the body 33 of the mass spectrometer are caused to focus one after another on the opening in plate 48 and into collector cup 49. Hence the relative abundances of these positive ions can be determined with a great deal of accuracy.

The container 26 containing the diluted gas sample is attached to the analyzer apparatus by inserting the male portion of ground joint 22 into the female portion of ground joint 53, the two ground joints being substantially identical. Needle valve 54 is then partially opened so that a portion of the gas containing the internal standard flows from container 26 through tube 52 into ionization chamber 32. Gas from this chamber may pass through the slits into the body portion 33 and thence to the vacuum pump or may be withdrawn directly from the ionization chamber and accelerating region of body portion 33 through suitable leads as shown to a vacuum pump. After a steady state has been reached, it is preferred that the gas pressure in chamber 32 be within the range between 0.001 mm. and 0.0001 mm. of mercury. The ionic analysis of the mixture is then performed in the manner described above. From this analysis, an ion current I_G of at least one positive ion of a constituent gas within the original mixture and an ion current I_S from at least one positive ion of the known diluent gas are determined.

The partial pressure of the constituent gas P_G undergoing analysis is calculated from the equation:

$$P_G = \frac{I_G P_S}{I_S K_G} \quad (2)$$

where:

P_S = partial pressure of internal standard gas S in mixture

K_G = instrument constant from Equation 1

The mole fraction N_G of a pure constituent gas G in the original mixture is given by the equation:

$$N_G = \frac{P_G}{P_T - P_S} = \frac{I_G P_S}{I_S K_G (P_T - P_S)} \quad (3)$$

where:

$P_T = P_o + P_S$ = total pressure of diluted gas

P_o = pressure of unknown gas sample in the dilution process

Where desired pressures may be converted to volumes by the proper application of well-known laws.

In the event that the unknown gas sample has no unique mass-number peak, or that it proves desirable to utilize deliberately a non-unique peak in the interests of precision, then quantitative determinations of all the constituent gases which contribute to the non-unique peak are preferably made. For example, where the unknown gas sample contains propane and ethane, and due to the higher precision obtainable, mass-number peak 29 ($C_2H_5^+$) is to be used for propane analysis, then since ethane also contributes to the peak at mass-number 29, another peak must be measured as, for example, mass number 28. In this instance, two simultaneous equations are

solved; the two unknowns being the mole fractions of ethane and of propane in the original gas sample. The known functions consist of the following: K_G for each constituent gas; positive ion currents for peak 28, peak 29, and the internal standard peak; and the two measured pressures P_s and P_o .

As a specific example, if a quantitative analysis of a gaseous mixture of hydrocarbons for propane in small concentration is required, a preliminary qualitative ionic analysis is run in the mass spectrometer on a portion of this gas and this will show the mass numbers of the constituents. It may be found, for example, that ethane, propane, and butane are present. For convenience a diluent gas having a positive ion of mass number/charge which is not that of any of the positive ions produced in the original mixture is provided. Neon has been found to meet this requirement. A measured pressure of propane is then diluted with a measured pressure of neon gas by use of the apparatus shown and described in connection with Figure 1. This diluted gas is now subjected to ionic analysis in the mass spectrometer and the positive ion currents of the mass-number peaks at 20 and at 44 are measured. From this and the dilution data the constant K_G of Equation 1 is found to be equal to 1.90. This completes the preliminary calibration.

For the analysis proper, a suitable gas sample is prepared by use of the apparatus shown and described in connection with Figure 1. An unknown gas sample pressure P_o of 50 microns of mercury is taken as an example and diluted to a total pressure P_T of 170 microns of mercury with neon gas. The partial pressure of the internal standard gas P_s is by difference 120 microns of mercury. This diluted gas is then subjected to analysis in the mass spectrometer as described above. Where the ionizing electrons are accelerated with a potential of 100 volts between plates 36 and 38, the ion current I_s is found to be 14×10^{-5} microamperes for neon peak mass number 20, and the ion current I_o is found to be 2×10^{-5} microamperes for propane peak mass number 44. From Equation 3, the mole fraction N_G of propane in the original sample submitted to analysis is found to be 0.18.

In certain examples, such as soil gas analysis, one or more of the constituent gases present in the original mixture may be of an extremely low concentration, for example only a few parts per million. In such cases there are advantages to be gained in employing as the internal standard for diluent gas a substance which has at least two isotopes, one of which is of relatively small but known concentration relative to the other. Both the isotopes should when ionized have ratios of mass number/charge which are not of the value of any of those of the constituents of the gas mixture to be analyzed. In the ultimate analysis the measurements are made of the positive ion current for the mass-number peak of the isotope of the internal standard or diluent gas occurring in relatively low concentration rather than those of the most abundant isotope. In such a case it is not particularly necessary that the internal standard gas be added to the unknown gas sample with the great precision specified in the above example since a relatively large concentration of the internal standard gas is added to produce a sufficient quantity of the rare isotope for ionic analysis. For example, if the rare isotope had approximately one hundredth the concentration

of the more abundant isotope, one hundred times as much of the diluent gas could be mixed with the unknown gases to be analyzed, compared to the amount that should be so mixed if the relative analysis were to be based on the ionic analysis of the more abundant isotope. Another advantage is that the intensity of the positive ion beam of the rare isotope would in this case be of the same order of magnitude as that of an unknown constituent in the sample under analysis.

If a diluent of the type possessing at least one abundant and one rare isotope is used in connection with the ionic analysis of gaseous mixtures containing very low concentrations of the constituent which are to be determined, the apparatus shown in Figure 1 can be employed advantageously.

It is, of course, apparent that other types of pressure gage may be substituted for either the Microvol gage or the manometer. Other changes of a similar nature will be apparent in the operation from the description which has been given. The scope of the invention is, of course, not limited by this description but is best set out in the appended claims.

I claim:

1. A method for the micro analysis of a gas forming a small constituent of a mixture of gases including the steps of introducing at least a portion of said gases into an evacuated zone until a known pressure is obtained in said zone, introducing into said zone a substantially pure diluent gas known to have a relatively stable, simple molecule until a second known pressure is obtained in said zone, said diluent gas being characterized in that it is substantially completely composed of molecules of simple and stable structure producing on ionization positive ions mostly of one known ratio of mass number to charge on the ion, said ratio being different than that of the positive ions of any constituent gas in said mixture, ionizing at least a portion of the contents of said zone at a low pressure, and measuring the relative amplitude of the positive ions of said diluent gas and those of said constituent gas.

2. A method for the micro analysis of a gas forming a small constituent of a mixture of gases including the steps of introducing at least a portion of said gases into an evacuated zone until a known pressure is obtained in said zone, introducing into said zone a substantially pure diluent gas known to have a relatively stable, simple molecule until a second known pressure is obtained in said zone, said diluent gas being characterized in that it is substantially completely composed of molecules of simple and stable structure producing on ionization positive ions mostly of one known ratio of mass number to charge on the ion and being further characterized in that the ratio of intensity of said positive ions to concentration of such diluent gas is known, the ratio of mass number to charge of said ions being different than that of the positive ions of any constituent gas in said mixture, ionizing at least a portion of the contents of said zone at a low pressure, and measuring the relative amplitude of the positive ions of said diluent gas and those of said constituent gas.

3. A method for the micro analysis of a gas forming a small constituent of a mixture of gases including the steps of introducing at least a portion of said gases into an evacuated zone until a known pressure is obtained in said zone, introducing into said zone a substantially pure

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diluent gas known to have a relatively stable, simple molecule until a second known pressure is obtained in said zone, said diluent gas being characterized in that it is substantially completely composed of molecules of simple and stable structure possessing at least one isotope occurring in relatively low concentration with respect to at least one other isotope of said molecules, said diluent gas producing on ionization positive ions of said isotope having a known ratio of mass number to charge on the ion and further characterized in that the ratio of intensity of said

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ions to concentration of such diluent gas is known, the ratio of mass number to charge of said ions being different than that of the positive ions of any constituent gas in said mixture, ionizing at least a portion of the contents of said zone at a low pressure and measuring the relative amplitude of a quantity directly proportional to the abundance of the positive ions of said one isotope of said diluent gas to the amplitude of a quantity directly proportional to the abundance of at least one positive ion of said constituent gas.

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