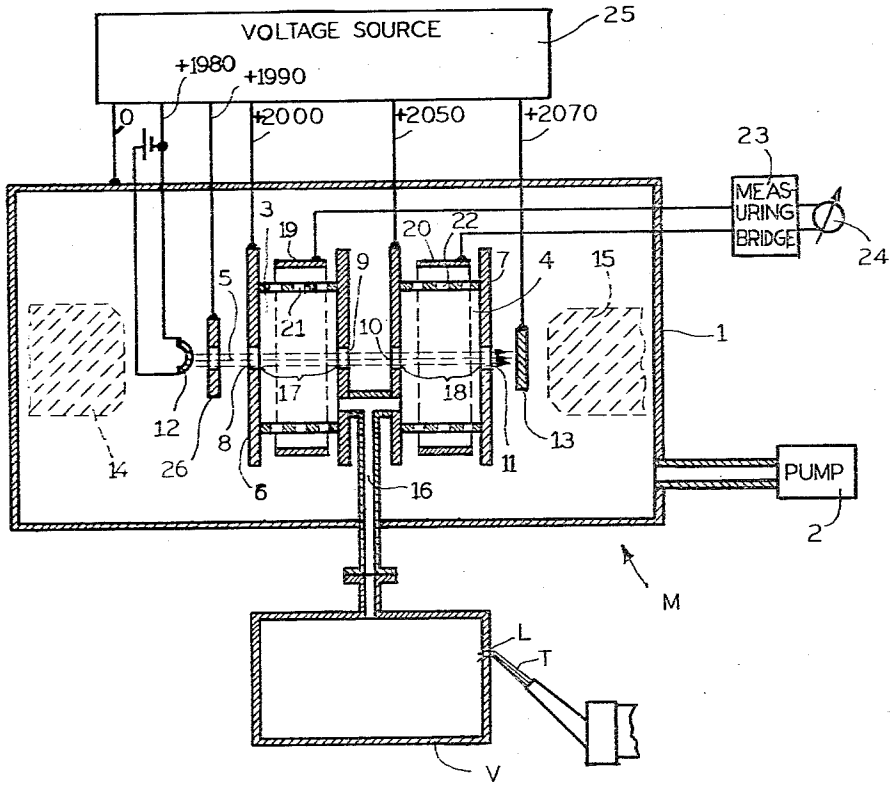
Nov. 28, 1967 L. JENCKEL 3,355,587

GAS ANALYSIS APPARATUS COMPRISING PLURAL IONIZATION CHAMBERS WITH DIFFERENT IONIZING ELECTRON BEAM ENERGY LEVELS IN THE CHAMBERS

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FIG. 1



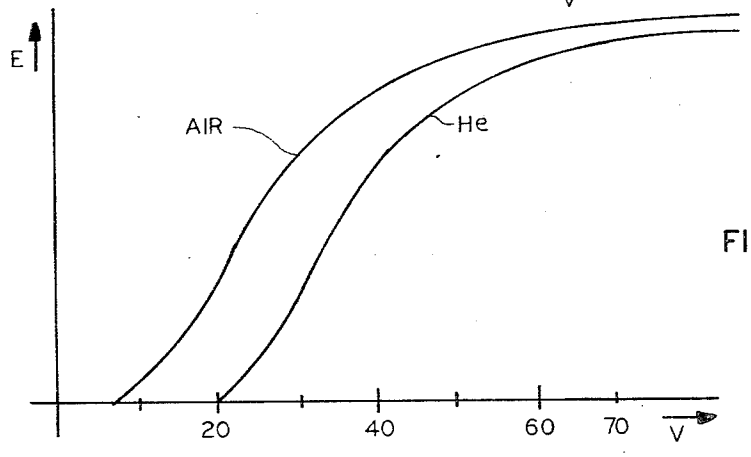




FIG. 3

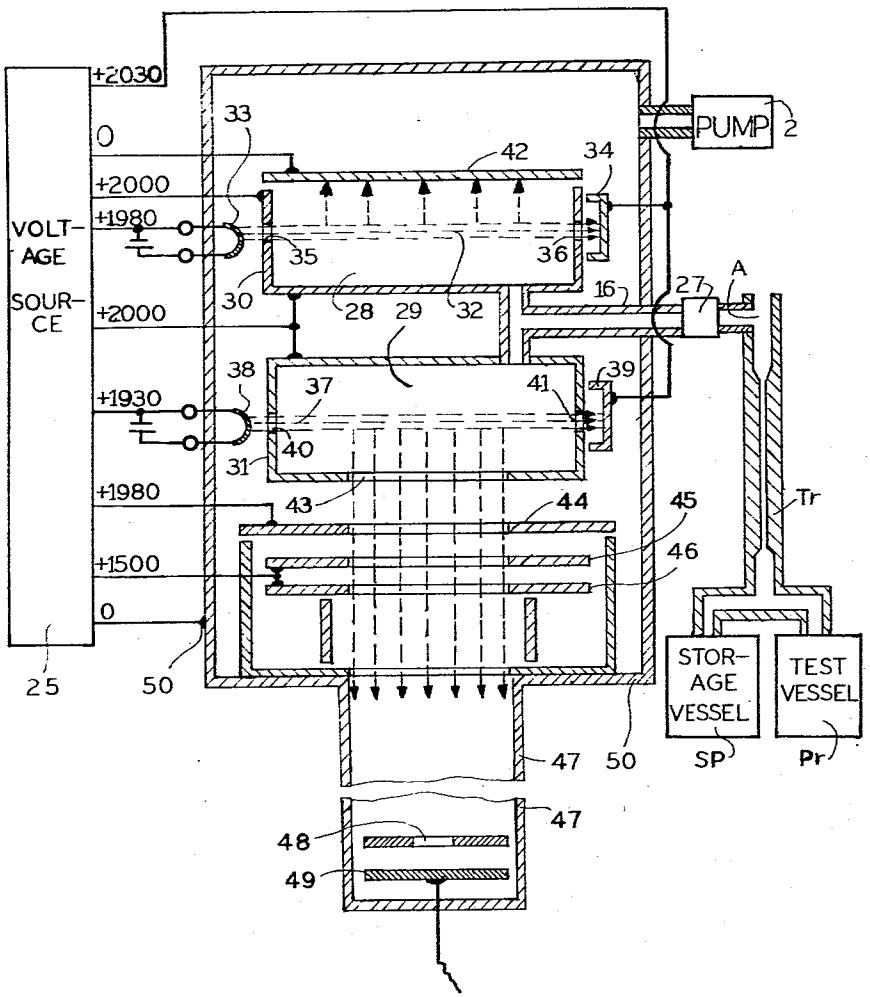
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FIG. 2




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3,355,587

# GAS ANALYSIS APPARATUS COMPRISING PLURAL IONIZATION CHAMBERS WITH DIFFERENT IONIZING ELECTRON BEAM ENERGY LEVELS IN THE CHAMBERS

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8 Claims. (Cl. 250—41.9)

This application is a continuation-in-part of application Ser. No. 265,579 filed Mar. 7, 1963, now abandoned.

The invention relates to a high vacuum gas ion source having a gas inlet system, a device for producing locally concentrated ionization energy in the high vacuum space of the ion source, a device for producing electric field forces which act in the ionization region, and a collector system for the ions extracted from the ionization region by the electric field forces.

In the case of known ion sources of this type the ionization can in each case be effected only with a determined energy. It is however also known that the probability of ionization is dependent both on the nature of a gas and on the energy utilized for ionization. In the examination of gas mixtures by ionization and measurement of ion current, the utilization of different degrees of ionization energy therefore leads to different percentile contributions by the individual gas components in the formation of the total ion current when different ionization probabilities exist for the different components.

The invention is based on the realization that the variation of the function of the probability of ionization as a function of ionization energy for different gas components could be utilized to improve the results of measurements. The difficulty then exists however that the percentile composition of the gas mixtures to be investigated is very frequently subject to fluctuations as a function of time, so that the ionization currents from measurements carried out at different times with different ionization energy will not be comparable to one another although the functions of the ionization probabilities are known.

The underlying aim of the invention is to provide a high vacuum gas ion source which permits practically simultaneous ionization with different ionization energies and separate measurement of the resulting different ion currents.

According to the invention this aim is achieved by constructing the ionization apparatus in such a manner that it produces ionization energies of different magnitudes in separate ionization zones of the same vacuum space, that the apparatus for producing the electric field forces extracting the ions from the ionization zones is so constructed that it produces separate electric fields acting in the different ionization zones, and that the collector system has a plurality of collectors associated with the different ionization zones and electric fields and for the separate collection of the ions coming from the individual ionization zones. Since the different ionization processes take place simultaneously in the same gas chamber, the ion currents produced differ from one another only in accordance with the different functions of the ionization probabilities.

The ionization apparatus may comprise an electron path along with ionization chambers each of which encloses an ionization zone and which are provided with passage apertures for the electrons disposed to define separate partial electron paths each with uniform electron velocity different from that of the other partial paths, said ionization chambers being at different acceleration potentials. The ionization therefore takes place in separate ionization chambers which are connected serially in such a manner that a single ionizing electron beam passes in succession through the ionization zones with different energy. This single beam arrangement has the advantage of producing output ion signal ratios independent of any fluctuations in the electron source.



The ionization apparatus may however also comprise a plurality of electron paths with which there are associated ionization chambers at different acceleration potentials, each of which encloses an ionization zone, and which are provided with passage apertures for the electrons. By this means good mutual screening of the different ionization zones in relation to one another can be achieved with relative ease.

Multi-ionization can be used with special advantage wherever it is required particularly to accentuate or suppress certain gas components of a gas mixture during measurement. Thus the method can be applied with advantage in leak detection, particularly when using helium as test gas, by twice ionizing and so selecting the ionization energies that the ionization probabilities are very much more sharply differentiated in the two ionization chambers for the test gas than for the other gas components. If then the currents derived from the two ionization processes have been equalized to zero in a measuring bridge before penetration of the test gas, the zero balance is sensitively upset by the incoming test gas. The sensitivity of the test gas detection can in such case be further enhanced by pumping off the penetrating gaseous substance by means of an ion getter pump which has a very much lower rate of evacuation for the test gas (helium) than for other gas components.

Further, the method using twofold ionization can be advantageously applied when it is desired to make use of a mass spectrometer as an ionization detector, with specific and continuous indication, for gas-chromatographic columns. With sufficiently low electron energy, inadequate for ionization of the helium used as carrier gas, an ion current is obtained in one of the ionization processes which affords a standard for measuring the partial pressure of a fraction of the sample leaving the end of the column. By the other ionization process carried out with higher electron energy the ions to be separated according to their mass in the mass spectrometer are obtained with optimum intensity. It is possible in this way to bring the ion current obtained at the outlet of the mass spectrometer into direct relation to the partial pressure prevailing in each of the respective components.

In order that the invention may be more readily understood, reference is made to the accompanying drawings which illustrate diagrammatically and by way of example two embodiments thereof, and in which:

FIG. 1 shows an apparatus for double ionization used in leak detection;

FIG. 2 shows an apparatus for gas analysis with double ionization used in combination with a gas chromatograph; and

FIG. 3 illustrates ionization probabilities as a function of the ionization energy for helium and air.

In the case of the example shown in FIG. 1, in respect of a double ionization process, this refers to an apparatus for leak detection.

It is known that a leak L in a vacuum apparatus V can be detected by an alteration in the pressure reading of an ionization manometer M connected to the apparatus, if the leakage point is sprayed from outside with a jet or test gas T. The alteration in the pressure reading occurs because the ionization probability for the test gas, for example helium, is a different one from that for the gas mixture composed of the residual gas in the vacuum container 1 and air penetrating from outside through the leak L. However, the sensitivity of detection in the conventional

method of leak detection is not very great, because the magnitude of the leak-indicative reading is a difference of two, much greater current values, the fluctuations of which are essentially determined by the fluctuations of the ionizing electron current and by fluctuations in the pressure in the vacuum system (fluctuations in the speed of pump 2, which serves to maintain the high vacuum in the vacuum container 1, outbursts of gas or variable leakage L).

In order to improve the sensitivity of detection, the ionization manometer M according to FIG. 1 is so constructed that two ionization chambers 3 and 4 are traversed in succession by the same electron beam 5.

The two ionization chambers 3 and 4 are enclosed by the boxes 6, 7 of current-conducting material which are disposed side by side and spaced apart and have apertures, 8, 9, 10, 11 for the passage of the electron beam 5.

The electron path is bounded by a cathode 12 on one side and by an anode 13 on the other side of the ionization chambers 3 and 4.

By means of a magnet disposed in the vacuum container 1, whose two poles 14 and 15 are indicated by broken lines in the drawing, the electron beam 5 can be concentrated and stabilized.

The vacuum apparatus V which is to be tested for leaks is connected directly to the two ionization chambers 3 and 4 through the gas inlet system of the manometer which in the present case consists of a simple pipe 16. A closure valve, not illustrated in the drawing, may be advantageously inserted in the inlet pipe 16 and held closed when removing or changing the vacuum apparatus to be examined, until the new measurement can begin.

The electrons are accelerated in stages, in a manner which will be described later on, on the electron path between cathode 12 and anode 13 so that they pass through the ionization chambers 3 and 4 at different speeds. Different ionization energies are thus obtained, to which the gas mixture entering both chambers 3 and 4 through the pipe 16 is subjected in the region of the partial paths 17 and 18 of the electron path.

For the purpose of extracting from the ionization chambers 3 and 4 the ions formed, an apparatus is provided for producing corresponding electric field forces, comprising annular electrodes 19 and 20 which concentrically surround the cylindrical walls 21, 22 of the ionization chambers 3 and 4, said walls being coaxial to the electron path 5, said electrodes being kept at a potential which is negative in relation to said walls. The cylindrical walls 21 and 22 of the ionization chambers 3 and 4 are apertured in grid form to form openings for the passage of the electrical ion-attracting fields into the ionization chambers and for the passage of the ions extracted from the ionization zones 17 and 18 by the field forces.

The collectors 19 and 20 are connected to an electrical measuring bridge 23 having a null indicator 24.

The voltages necessary for operation are supplied by a voltage source 25 and may, for example, have the magnitudes shown in FIG. 1 of the drawings.

An intermediate electrode 26 may in addition be inserted between the cathode and admission aperture 8 of the electrons in the ionization chamber 3.

The ionization energies in the chambers 3 and 4 are proportional to the speed at which the electrons pass through the portions 17 and 18 of their path. These speeds depend in turn on the magnitude of the voltage difference between the cathode 12 as starting point of the electrons and the potentials existing at the metal walls 6 and 7 enclosing the ionization chambers 3. In the example illustrated a voltage difference of 2000—1980=+20 v. exists between the cathode 12 and the chamber 6. The ionization energy in the ionization zone 17 is thus proportional to this voltage difference $V_1$.

If this energy is designated by $e \cdot V_1$, it can be said that the electrons enter the ionization space 3 with the energy $e \cdot V_1$ and pass through the space from the inlet aperture 8 to the outlet aperture 9 at uniform speed. After leaving chamber 3 the electrons are accelerated to a higher energy $e \cdot V_2$ through the potential difference of 2050—2000=+50 v. which exists between the chambers 6 and 7, $V_2$ being equal to 2050—1980=+70 v. With this new energy the electrons enter the second ionization chamber 4 and pass through the latter at correspondingly increased speeds from the inlet aperture 10 to the outlet aperture 11. From the latter they are accelerated to the anode 13 by the differential voltage 2070—2050=+20 v.

The electron energies $e \cdot V_1$ and $e \cdot V_2$ are selected so that the ionization probability for the test gas helium with which the vacuum apparatus V is sensed, is as different as possible in the two ionization chambers 3 and 4 but is less different for the remaining gas mixture.

In FIG. 3 the functions of the ionization probability E are illustrated diagrammatically as a function of the active ionization energy $e \cdot V$ for helium as test gas and for the gas mixture air. From the functional curve He for helium it can be seen that the ionization potential for helium is about 24 v. and consequently is not attained in the first ionization chamber 3, while in the second ionization chamber 4 practically maximum ionization probability exists at the voltage $V_2$=70 v. both for the helium molecules and for all molecules of air.

The electric fields for extracting from the chambers 3 and 4 the ions formed are produced by high negative differential voltages between the chambers 6 and 7 and the electrodes 19 and 20. These electrodes are at earth potential, so that the differential voltages for producing the fields amount to 2000 and 2050 v. respectively.

The ions extracted by the electric field forces from the region of the ionization zones 17 and 18 and accelerated through the apertures of the chamber walls 21 and 22 to the collectors 19 and 20 are deflected by the collectors 19 and 20 and after amplification in direct current amplifiers (not illustrated in the drawing) are fed to a measuring bridge 23 with null indicator 24. The measuring bridge preferably includes compensation means for nulling before the test gas helium is sprayed on the surface of the vacuum apparatus V to be tested for leaks. This null is independent of fluctuations in the current strength of the electron beam and of fluctuations in pressure because both ionization chambers 3 and 4 are traversed by the same electron beam 5 and the same pressure prevails in them both.

After the null is effected without test gas, the vacuum apparatus V is sensed with the test gas jet T. As soon as the test gas jet T encounters a leak L, the test gas helium enters the vacuum chamber V and immediately brings about a disturbance of the null, which can be observed through the deflection of the null indicator 24. This disturbance of the null is obtained because the test gas helium undergoes no ionization in the ionization chamber 3 but does undergo maximum ionization in the ionization chamber 4, so that there is an unequal increase of the ionization currents at the collectors 19 and 20.

The apparatus which has been described thus constitutes a very simple and sensitive method for the detection of helium ions and is particularly suitable for leak detection.

Moreover, this method is also useful for the quantitative analysis of binary mixtures for straightforward control measurements in operation, the only essential condition being that the relationship of the ionization probabilities be sufficiently different in both ionization chambers for both gas components A and B. If $E_{1A}$, $E_{2A}$, $E_{1B}$ and $E_{2B}$ are the ionization probabilities for the two gas components A and B in the two ionization chambers 1 and 2, then for the measurement the following condition must be satisfied:

$$\frac{E_{2A}}{E_{1A}} = \frac{E_{2B}}{E_{1B}}$$

In this case the two ion currents are measured:

$$I_1 = K(E_{1A} \cdot C_A + E_{1B} \cdot C_B)$$

$$I_2 = K(E_{2A} \cdot C_A + E_{2B} \cdot C_B)$$

where K is constant and is dependent on the geometry of the apparatus and the acceleration voltage for electrons (90 volts). Thus two independent equations are available for calculating the unknown concentrations $C_A$ and $C_B$. The ionization probabilities may be determined from standard measurements of the pure components. The described method of analysis is of particular interest in those cases in which a simple apparatus is desired, the accuracy of measurement demanded is not too high and a continuous measurement is required to be undertaken of mixtures which vary with time. It can be extended, with the arrangement of three and more ionization chambers one after another, to the analysis of mixtures with three and more components.

In the employment of double ionization for leak detection using helium as test gas it is especially advantageous for the double ion source to be pumped off with the aid of an ion getter pump, because the suction output of this type of pump for helium is very much less than for other gases to produce a higher partial pressure for helium in the ionization chambers than for the rest of the gas mixture.

The embodiment illustrated in FIG. 2 refers to a double ionization system combined with a mass spectrometer which serves for gas analysis in connection with a gas chromatographic separator column Tr. The gas chromatographic separator column Tr serves in known manner for allowing the components of the gas mixture to be examined, which is situated in a test vessel Pr, to pass out separately one after the other in respect of time at the outlet A. At the same time a carrier gas, for example helium, is passed over the separator column from a storage vessel Sp. The mixture of carrier gas and test gas components, which is variable in dependence on time, passes from the outlet A of the separator column through an admission system **27** simultaneously into two separate ionization chambers **28**, **29** which, as in the first example, are enclosed by metal boxes **30**, **31**. The first ionization chamber **28** is traversed by the electron beam **32** of an electron path with cathode **33** and anode **34** through apertures **35** and **36**, and the second ionization chamber **29** by an electron beam **37** of an electron path with cathode **38** and anode **39** through openings **40** and **41**.

From the ionization chamber **28** the ions formed are passed through an electric ion-attracting field to a collector **42**. Ions extracted from the ionization chamber **29** by an electric ion-attracting field pass through a slot **43** and by means of an ion optical system with accelerating and focussing electrodes **44**, **45** and **46** are fed in the form of a sharpely defined ion pencil beam to the separator tube **47** of a mass spectrometer of conventional construction, for example a sector field mass spectrometer, at the outlet of which the ions of the various components, classified in accordance with their mass numbers, pass through an outlet gap **48**, on passing through the mass scale, separately to a collector **49**. The separator tube **47** together with a casing **50** encloses the high vacuum chamber of the entire system.

The parts of the system which conduct voltage are fastened in the usual manner to insulating supports inside the high vacuum chamber. The pipes **16** and **27** supplying gas to the chambers under high voltage of the ionization spaces likewise consist partly or entirely of insulating material.

As in the first example, in the arrangement illustrated in FIG. 2, ionization with low ionization energy takes place in the first ionization chamber and in the second ionization camber **29** with greater energy. Through the arrangement of separate electron paths there is no direct spatial connection between the two ionization chambers by a common electron path.

The electron energies for the two ionization processes are once again selected so that the ionization probability for the carrier gas helium of the gas-chromatographic mixture is as different as possible in the two ionization chambers, but varies as little as possible for the remainder of the gas mixture. In this way it is possible to exclude to a great extent the carrier gas helium, which has a disturbing effect on measurement, from the total ion current.

In the first ionization chamber **28** the operation is carried out with a small ionization energy corresponding to a low ionization probability for the carrier gas helium. In the second ionization chamber **29**, on the other hand, the operation is carried out with so high an ionization energy that a maximum ion yield is achieved for the mass-spectrometric measurement. Since in this mass-spectrometric measurement separation into the individual components takes place in any case, the presence of ions of the carrier gas has no disturbing effect here.

There has been described novel apparatus for providing multiple ion signals especially useful in connection with discriminating between a carrier gas and other portions of a gas mixture and for use in connection with leak detection. It is evident that those skilled in the art may now make numerous modifications and uses of and departures from the specific embodiments described herein without departing from the inventive concepts. Consequently, the invention is to be construed as embracing each and every novel feature and novel combination of features present in or possessed by the apparatus and techniques disclosed herein and limited only by the spirit and scope of the appended claims.

What is claimed is:

**1.** Apparatus for detecting components of a gas mixture by ionization and measurement of the ion current comprising,

means for providing an electron beam of first energy level and an electron beam of second energy level different from said first energy level,

means for passing said gas mixture through said first energy level electron beam to ionize said mixture and produce a first ionization signal and through said second energy level electron beam to ionize said mixture and produce a second ionization signal.

first collector means responsive to ionization of said mixture by said first energy level electron beam for collecting ions to provide said first ionization signal,

second collector means responsive to ionization of said mixture by said second energy level electron beam for collecting ions to provide said second ionization signal,

first ionization chamber means including said first energy level electron beam,

second ionization chamber means including said second energy level electron beam,

means for establishing a first ion-transporting field for attracting ions from said first ionization chamber means to said first collector means,

means for establishing a second ion-transporting field for attracting ions from said second ionization chamber means to said second collector means,

each of said ionization chamber means being formed with apertures for allowing at least entry of the associated energy level electron beam,

and means defining a common container enclosing said means for providing an electron beam of first energy level and an electron beam of second energy level different from said first energy level, said first collector means, said second collector means, said first ionization chamber means, said second ionization chamber means, said means for establishing a first ion-transporting field and said means for establishing a second ion-tranporting field,

said first ionization chamber means and said second ionization chamber means being formed with said apertures along a common axis,

said means for providing an electron beam comprising a single electron source emitting a beam along said axis through both said ionization chamber means,

said apparatus including means to accelerate the electrons to the second energy level as the beam passes between said first and second ionization chambers.

2. Apparatus in accordance with claim 1 and further comprising balancing means for providing an output signal representation of the difference between said first and second ionization signals.

3. Apparatus in accordance with claim 1 and further comprising,

means for maintaining the velocity of the electrons in said first energy level electron beam substantially constant at a first velocity when passing through said first ionization chamber means,

and means for maintaining the velocity of the electrons in said second energy level electron beam substantially constant at a second velocity different from said first velocity when passing through said second ionization chamber means.

4. Apparatus in accordance with claim 3 and further comprising measuring bridge means for providing an indication of the relationship between said first and second ionization signals,

and means for coupling said first collector means and said second collector means to said measuring bridge means.

5. Apparatus in accordance with claim 4 and further comprising ion getter pump means for maintaining a high vacuum in said first and second ionization chamber means.

6. Apparatus for detecting components of a gas mixture by ionization and measurement of the ion current comprising,

means for providing an electron beam of first energy level and an electron beam of second energy level higher than said first energy level,

means including a common container for passing said gas mixture through said first energy level electron beam to ionize said mixture and produce a first ionization signal and through said second energy level electron beam to ionize said mixture and produce a second ionization signal,

first collector means responsive to ionization of said mixture by said first energy level electron beam for collecting ions to provide said first ionization signal,

second collector means responsive to ionization of said mixture by said second energy level electron beam for collecting ions to provide said second ionization signal,

first ionization chamber means including said first energy level electron beam,

second ionization chamber means including said second energy level electron beam,



means for establishing a first ion-transporting field for attracting ions from said first ionization chamber means to said first collector means,

means for establishing a second ion-transporting field for attracting ions from said second ionization chamber means to said second collector means,

each of said ionization chamber means being formed with apertures for allowing at least entry of the associated energy level electron beam and said mixture,

said mixture including a carrier gas characterized by an ionization potential that is above that of said first energy level and below that of said second energy level to establish a low ionization probability for said carrier gas in said first ionization chamber means while establishing a high ionization probability for all the components of said mixture in said second ionization chamber means,

focusing means interposed between said second ionization chamber means and said second collector means for focusing ions ionized in said second ionization chamber means into a pencil ion beam,

and mass spectrometry means for separating mass spectral components of said pencil ion beam whereby said first ionization chamber means may weakly ionize all of said mixture except said carrier gas so that ions attracted from said first ionization chamber means to said first collector means is representative of the partial pressure of said mixture excluding said carrier gas while said second ionization chamber means strongly ionizes said mixture including said carrier gas to provide a high concentration of ions for analysis by said mass spectrometry means.

7. Apparatus in accordance with claim 6 wherein said carrier gas is helium.

8. Apparatus in accordance with claim 6 and further comprising,

a gas chromatographic column means for providing said gas mixture,

and means for coupling said gas chromatographic column means to said first and second ionization chamber means.


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