April 10, 1945. D. D. TAYLOR 2,373,151

ANALYTICAL SYSTEM

Filed July 29, 1942 2 Sheets-Sheet 1

Fig. 1.

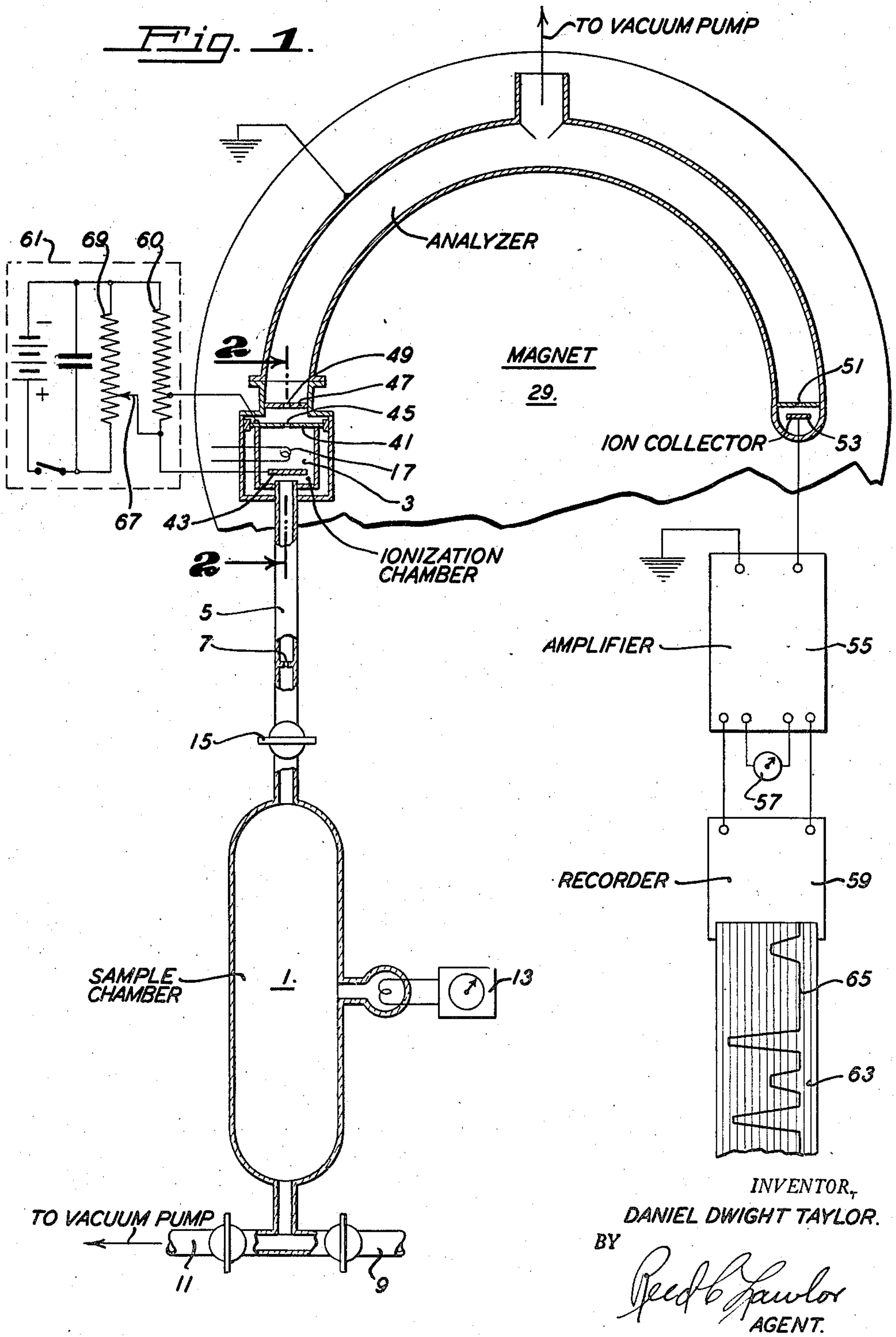

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Fig. 2.

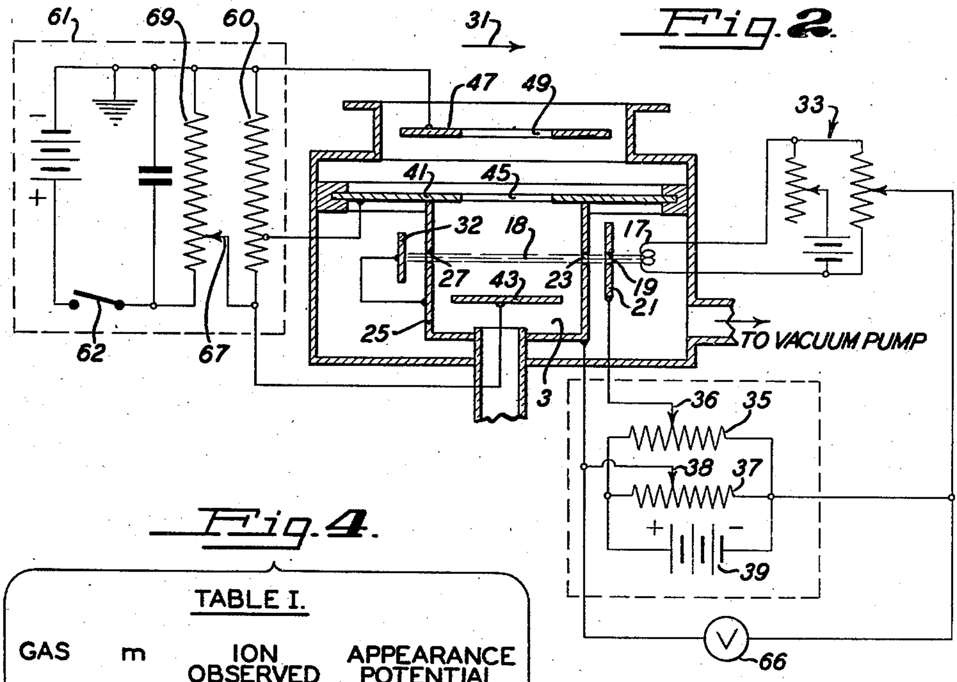
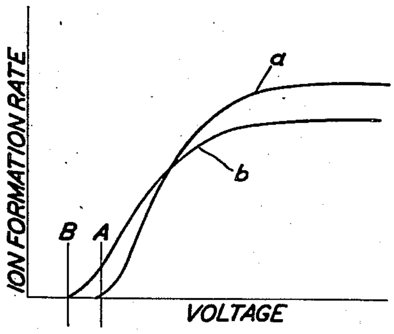


Fig. 4.

TABLE I.

GAS	m	ION OBSERVED	APPEARANCE POTENTIAL
N_2	28	N_2+	16.5
	14	N+	24.0
O_2	32	O_2+	13.
	16	O+	20.5
CO	28	CO+	14.1
	12	C+	23.
	16	O+	24.
CO_2	44	CO_2+	14.4
	16	O+	19.6
	28	CO+	20.4
	12	C+	28.3
	32	O_2+	20.0

Fig. 3.



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UNITED STATES PATENT OFFICE

2,373,151

ANALYTICAL SYSTEM

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Application July 29, 1942, Serial No. 452,809

4 Claims. (Cl. 73—18)

My invention relates to mass spectrometry, and more particularly to the analysis of a chemical mixture containing a plurality of components which upon ionization may form ions having the same mass-to-charge ratio. More specifically, my method makes possible the analysis of such a mixture with respect to an individual component therein, by forming such ions under conditions such that they are produced from only the individual component, even though under other conditions said ions may be formed from more than one component.

When analyzing a mixture with a mass spectrometer, the mixture is generally introduced from a sample region into an ionization region in gaseous or vapor form. In the ionization region, molecules of the mixture are ionized by subjecting them to the ionizing action of particles such as electrons. Such electrons are commonly directed by the action of an electric field into the ionization region where they encounter and ionize molecules of the mixture. The ions formed are then withdrawn into an analysis region where ions of different mass-to-charge ratios are segregated into beams which may be detected by successive focusing thereof upon an ion collector. As the beams are successively detected at the collector, the beam intensities may either be measured directly with a suitable indicator or else automatically and permanently recorded prior to indication. The peak intensities of the ion beams are representative of either the amounts of the withdrawn ions or the rates of formation of the respective ions. Such a record or set of measured peak intensities forms a mass spectrum.

Either before or after a mass spectrum of a mixture has been obtained, reference samples containing different proportions of the components that may be present in the mixture are similarly subjected to analysis in a mass spectrometer under substantially the same ionizing conditions to which the mixture was subjected, and corresponding mass spectra obtained for the reference samples. Usually, though not necessarily, the reference samples are relatively pure samples of the respective components that may occur in the mixture.

The composition of the mixture is then determined by comparing the mass spectrum of the mixture with the mass spectra of the reference samples. Such a comparison is most simply carried out by a mathematical procedure involving the comparison of the peak intensities of the beams forming the spectra.

In practice, the analysis of such a mixture is greatly facilitated if the intensity of each peak occurring in the mixture spectrum represents the sum of the intensities of corresponding peaks that would be obtained in mass spectra of the separate components if present alone. A method for producing this effect, which is known as linear superposition, is disclosed and claimed in copending patent application, Serial No. 513,526, filed December 9, 1943, by Harold W. Washburn. Briefly, this method involves maintaining the sample in a sample chamber homogeneous at all times during analysis, flowing the components from the sample chamber into an ionization chamber through a gas inlet at mutually independent rates, ionizing each component in proportion to its partial pressure in the ionization chamber and independently of the amounts of the other components there, and providing such pressure conditions in the mass spectrometer that collisions between ions withdrawn from the ionization chamber with any molecules either in the ionization chamber or in the analyzing chamber are relatively infrequent.

When conditions suitable for achieving linear superposition during the analysis of a mixture are obtained, the intensity of any peak occurring in the mass spectrum of the mixture due to ions of mass-to-charge ratio m may be represented by the following equation:

$$I=\sum_i {}^{V}P_i^m X_i \qquad (1)$$

where

X_i=the partial pressure of component i in the mixture, and

${}^{V}P_i^m$=a sensitivity coefficient representing the efficiency of he mass spectrometer in producing ions of mass-to-charge ratio m obtained from component i by particles having an ionization energy of V electron volts.

The sensitivity coefficient may be expressed as the ratio of the number of divisions of measured peak height or the number of units of beam intensity per micron (μ) of partial pressure of component i present in the chamber. Values of the sensitivity coefficients may be most readily determined from the intensities of the beams occurring in the mass spectra obtained from pure components.

In the event that linear superposition is not achieved, the analysis of the mixture may be made by obtaining mass spectra of known mixtures approximating the unknown in composition and comparing the spectrum of the unknown mixture with the spectra of the known mixture by the method which is more fully explained in my copending patent application, Serial No. 324,950, filed March 20, 1940.

The amount of ions of mass-to-charge ratio m originating from a given component i is found to vary over a wide range with changes in the energies of the ionizing particles. For simplicity, hereinafter, the ionization of a sample by particles having a given amount of energy corresponding to the kinetic energy of electrons which have been accelerated by some predetermined voltage will be referred to simply as ionization of the sample or component at such a voltage.

The ionization curves of ions of a given mass-to-charge ratio formed from different components which may be present in a mixture are not generally of the same shape. Generally, such ions have different appearance potentials when formed from the different components. I utilize this fact in the analysis of a mixture of two such components by ionizing the mixture at a voltage intermediate the appearance potentials of such ions for the two components, measure the amount of ions of such mass-to-charge ratio formed from only one of the components, and determine the amount of that component present in the mixture from the amount of such ions formed and the sensitivity coefficient of that component at the intermediate voltage.

In one form of my method all the ions measured are formed at a sufficiently low ionization voltage so as to produce ions of a different mass-to-charge ratio for each component present.

In another form of my invention, the ionizing potential is changed during analysis, a low potential being used to produce ions of one mass-to-charge ratio from one component, and a high ionization potential being used to produce ions of a different mass-to-charge ratio from another component.

My method may also be applied to the analysis of a multi-component mixture when the production of ions of a given mass-to-charge ratio from a large number of components may occur at a high voltage, but from a fewer number of components at a low ionization voltage. In this case the use of an ionization voltage intermediate the highest and the lowest appearance potentials of such ions from those components, greatly simplifies the computation of the mixture computation by making the values of some of the sensitivity coefficients ${}^{V}P_i^m$ equal to zero.

My method is particularly applicable to the analysis of a mixture containing a plurality of homologous components, that is components of different molecular weights, which contain some atoms or radicals common to their molecules.

Accordingly, the principal object of my invention is to provide an improved method for analyzing chemical mixtures with a mass spectrometer.

Another object is to provide a method of mass spectrometry in which the contribution of one component to the production of certain ions may be made practically negligible compared to the contribution of some other component.

Another object of my invention is to provide a method for obtaining independent indications of individual components of a mixture, even though the components may under some conditions, produce ions of the same mass-to-charge ratio.

Still another object of my invention is to provide a method for the analysis of a mixture containing homologous components.

My invention possesses numerous other objects and features of advantage, some of which, together with the foregoing, will be set forth in the following description embodying and utilizing my novel method. It is therefore to be understood that my invention is applicable to analyses of a variety of mixtures and may be employed with several types of mass spectrometers which may utilize other kinds of ionizing particles, and that I dot not limit myself, in any way, to the analyses, to the apparatus, or to the ionizing particles, of the present application, as I may adopt various other modifications of my invention utilizing the method, within the scope of the appended claims.

My invention may be more readily understood by direct reference to the drawings in which:

Fig. 1 shows a general organization of a mass spectrometer to which my method may be applied.

Fig. 2 is a schematic drawing partly showing a section taken on a line 2—2 of Fig. 1 of part of the mass spectrometer including the ionization chamber and the ionization energy controls.

Fig. 3 is a graph including two curves showing typical variation of the intensity of an ion beam with accelerating voltage of electrons used as particles for ionizing two different components.

Fig. 4 is a table showing the appearance potentials of various ions formed from nitrogen, oxygen, carbon monoxide, and carbon dioxide.

Referring to the drawings:

In Fig. 1, I have shown a sample chamber **1** connected to an ionization chamber **3** through a tube **5** containing a restricted orifice **7**.

A sample to be analyzed is introduced through the sample inlet line **9** into the sample chamber **1**, which has been previously evacuated through the vacuum pumping line **11**. When the pressure of the sample is at a suitable value as determined by a pressure gauge **13** and the mass spectrometer is otherwise in condition for operation, a valve **15** is opened to admit the sample into the ionization chamber.

As illustrated in Figs. 1 and 2, electrons emitted from a heated filaments **17** are directed in a beam **18** through aperture **19** in the electron beam intensity control electrode **21**, through aperture **23** in electron accelerating electrode **25** which is formed by part of the wall of said ionization chamber **3**, and through aperture **27**, in the opposite part of the wall of said ionization chamber, said beam being directed along the line perpendicular to the face of a magnetic pole **29** by the combined action of the magnetic field indicated by arrow **31** in Fig. 2, which field is directed downward perpendicular to the plane of the drawing in Fig. 1, and electric fields parallel to the magnetic field. The electrons passing through said apertures impinge on electron catcher **32** electrically connected to electrode **25**. The electric fields are provided by potentials applied from voltage supply circuit **33** to filament **17**, and electrodes **21** and **25**. Said voltage supply circuit includes means for varying the relative potentials between said filament **17** and said electrodes.

One way of accomplishing this variation is to connect the filament to the negative end of a pair of parallel connected rheostats **35** and **37** through which a current is flowing from a battery **39**, and to connect said electrodes **21** and **25** to rhesotats 35 and 37 respectively through sliding contacts 36 and 38 for picking off suitable positive potentials.

When electrons in said electron beam 18 encounter molecules of the sample in the ionization chamber, positively charged ions are formed in amounts characteristic of the structure of the molecules and in amounts proportional to the electron beam intensity. The amounts of ions produced are dependent on the energy of the electrons in beam 18. The positive ions formed are accelerated toward first slit electrode 41 by action of a small electric potential which maintains said first collimating slit electrode negative with respect to a pusher electrode 43 on the opposite side of said electron beam. Some of the accelerated ions pass through a narrow slit 45 in said first collimating electrode 41 and are thereupon accelerated by a large negative potential between said first collimating slit electrode 41 and second collimating slit electrode 47. Some of the accelerated ions then pass through a second slit 49 in said second collimating slit electrode.

Owing to the combined action of said ion accelerating fields and the magnetic field, positive ions passing through said collimating slits follow circular paths, and ions of a predetermined mass-to-charge ratio are focused at exit slit 51 positioned in front of an ion collector 53. When an ion beam impinges ion collector 53 a corresponding ion current is produced, which current is amplified by amplifier 55 and indicated by galvanometer 57.

In order to provide for automatically recording a mass spectrum of a sample, an automatic recorder 59 is connected to the amplifier so as to record the intensities of ion beams of different mass-to-charge ratios which are successively moved past said collector slit 51 by automatically changing voltages supplied to said pusher electrode 43, and said collimating slit electrodes 41 and 47, by electrical connection to suitable points of a potential divider 60 in ion beam deflection control circuit 61, which circuit may be prepared for operation by closing key 62 and set into operation by opening said key.

As beams comprising ions of different corresponding mass-to-charge ratios are swept past said exit slit 51, ions in the different beams are successively discharged at the ion collector 53, and corresponding ion currents actuate recorder 59 thereby producing a mass spectrogram 63 of the sample, said mass spectrogram being in the form of a trace 65 in which successive trace displacements represent corresponding intensities.

In order to determine how the intensity of any particular ion beam varies with the energy of the electrons in the electron beam, I adopt one of two procedures. In the first, the total accelerating voltage to which ions are subjected may be set at a predetermined value by adjustment of the total potential between pusher electrode 43 and collimating slit electrodes 41 and 47 by suitable positioning of the slide contact 67 on potentiometer 69 in the deflection control circuit 61, thereby focusing ions of any predetermined mass-to-charge ratio desired at the exit slit 51. With the mass spectrometer adjusted to detect ions of predetermined mass-to-charge ratio, the energy of the electrons in the ion beam may be adjusted to successively different values indicated by voltmeter 66 and the corresponding intensities of the ion beam measured by means of galvanometer 57. This procedure is repeated for each peak of interest in each component of interest. In the second procedure I set contact 38 successively at different points of rheostat 37 to establish different values of electron accelerating voltages as indicated by a voltmeter 66, and make a mass spectrogram of the sample under investigation at each of these voltages for each component in which I am interested, by the recording method hereinabove described. If desired, the beam deflection control circuit 61 may be operated to sweep over only a single peak of interest at each of the voltages by suitable adjustment of contact 67 and proper manipulation of key 62.

In both of these methods the voltage between the filament 17 and the electron beam intensity control electrode 21 is maintained constant and preferably at a value such that the total electrical current borne by electron beam 18 is constant.

In Fig. 3 I have plotted a typical ionization curve *a* representing a plot of the intensity of the beam of ions comprising ions of predetermined mass-to-charge ratio obtained from a pure component as a function of electron accelerating voltage. As indicated by this curve, practically no ions are formed when this voltage is at a value less than that indicated by the point A, which represents the appearance potential of the ions in question. Curve *b* represents the ionization curve of another component having a lower appearance potential B. By reference to these curves, it is seen that, if the ions to which the curves refer are of the same mass-to-charge ratio, the component corresponding to curve *b* may be determined by measuring the amount of ions being formed when the ionization voltage is between the values corresponding to the appearance potentials of the two components.

In the table shown in Fig. 4, I have shown the appearance potentials of various ions formed from nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), and carbon dioxide (CO_2). Examples of the use of my invention in the analysis of various mixtures of these components are discussed hereinbelow.

Example I—Mixture of CO and CO_2

A mixture of carbon dioxide and carbon monoxide may be analyzed by obtaining a mass spectrum of the mixture at an ionization voltage between 14.4 and 20.4 volts, thus producing ions CO^+ and CO_2^+ respectively from CO and CO_2 without introducing any CO^+ ions from CO_2. The amounts of said components present may then be determined readily from the observed beam intensities by dividing the respective beam intensities by the corresponding sensitivity coefficients of the respective components at the ionization voltage used on the mixture.

If desired, the sensitivity of the analysis with respect to CO_2 may be increased by using a higher voltage when measuring the intensity of the CO_2^+ ion beam.

Example II—Mixture of O_2 and CO_2

To analyze a mixture of oxygen and carbon dioxide, the same methods hereinabove described in connection with Example I, are adopted except that when O_2^+ ions are being detected for the determination of the amount of molecular oxygen present in the mixture, an ionization voltage between 13 and 20 volts is used.

Example III—Mixture of CO, O_2, and CO_2

The amounts of carbon monoxide, oxygen, and carbon dioxide present in a mixture of these components may be determined by measuring the intensities of corresponding molecular ion beams comprising ions O_2^+, CO^+, and CO_2^+ respectively formed at a voltage between 14.1 and 20.0 volts, which are respectively the appearance potentials of CO^+ from CO and CO_2^+ from CO_2.

Example IV—Mixture of CO and N_2

The amount of carbon monoxide may be determined in a carbon monoxide-nitrogen mixture by measuring the intensity of the beam comprising ions of mass-to-charge ratio 28, if the ions are being formed at a potential between 14.1 and 16.5 volts which are respectively the appearance potentials of CO^+ and N_2^+. The amount of nitrogen in such a mixture may then be determined by increasing the ionization potential to a value greater than 24.0 volts, the appearance potential of N^+ and measuring the intensity of the N^+ beam formed.

Example V—Mixture of N_2 and CO_2

By ionizing a mixture of nitrogen and carbon dioxide at a voltage between 16.5 volts, the appearance potential of N_2^+ and 20.4 volts, the appearance potential of CO^+, individual beams corresponding to the two components may be produced.

Example VI—Mixture of N_2, O_2, CO, and CO_2

Individual indications of the amounts of the three components, oxygen, carbon monoxide, and carbon dioxide present in a mixture containing these gases and nitrogen, may be obtained by measuring intensities of the corresponding beams comprising ions O_2^+, CO^+, and CO_2^+, respectively, produced at a voltage between 14 and 16.5 volts. The amount of nitrogen present in such a mixture can then be determined by measuring the intensity of a beam of atomic nitrogen ions N^+ produced at a voltage greater than 24 volts.

From the foregoing discussion it is apparent that I have provided a new method of mass spectrometry which under many conditions simplifies computations, and in many cases makes it possible to analyze a mixture with respect to some components without the necessity of determining the quantities of other components also present.

While my invention has been illustrated in connection with the analysis of mixtures from which it is possible to obtain beams which correspond individually to the mixture components, it is clear that my method may also be utilized when the ionization voltage is such that other components affect the intensities of the beams as well as those hereinbefore considered. When more than one component affects the intensity of a beam, simultaneous equations of the type given in Equation 1 may be used to compute the composition of the mixture under invenstigation, the advantage of my improvement in this case being that there are fewer terms in such equations, thereby increasing the speed of the computation a corresponding amount.

I claim:

1. In analyzing a mixture containing a plurality of components with respect to one component, the method which comprises ionizing a sample of said mixture at such a predetermined ionization voltage that ions of a selected mass-to-charge ratio which may be formed from each of said components at some ionization voltage are actually formed from only said one component, ionizing at the same voltage a reference sample containing a known amount of said one component, measuring the amounts of said ions formed from both said samples, and determining from said measurements the quantity of said one component present in the mixture.

2. In the analysis of a mixture containing two components both of which are capable of forming ions of the same mass-to-charge ratio at different ionizing potentials involving the determination of the amounts of said components in the mixture by comparison of measurements of the quantities of ions of different mass-to-chrage ratios formed in a mass spectrometer from said mixture and from reference samples including different proportions of the components, the improvement which comprises ionizing said mixture at one ionization voltage to form ions of a given mass-to-charge ratio from only one of said components, ionizing said mixture at another ionization voltage to form ions of the same mass-to-charge ratio from only the other component, measuring the quantities of such ions formed at the respective voltages, and utilizing measurements of the quantities of ions formed at the respective voltages to determine the quantities of the corresponding components present in the mixture.

3. In the analysis of a mixture containing a plurality of components involving the comparison of measurements of the quantities of ions of predetermined mass-to-charge ratios formed in a mass spectrometer from said mixture and from reference samples including different proportions of the components, the improvement which comprises ionizing said mixture at such an ionization voltage that ions of a given mass-to-charge ratio which may be formed from each of said components at some ionization voltage are formed at said ionization voltage from less than all of said components to provide a basis for determining the quantities of said latter components present in the mixture.

4. In the analysis of a mixture containing a plurality of components such that ions of the same mass-to-charge ratio can be formed from more than one of the components, involving the determination of the amount of said components in the mixture by comparison of measurements of the quantities of such ions of different predetermined mass-to-charge ratios formed in a mass spectrometer from said mixture and from reference samples including different proportions of the components, the improvement which comprises ionizing said mixture during the measurement of the respective amounts of such ions at such an ionization voltage that such ions of each mass-to-charge ratio are formed from only one of said components.

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