Aug. 15, 1944. R. C. LAWLOR **2,355,658**

METHOD AND APPARATUS FOR MASS SPECTROMETRY

Filed April 17, 1940 2 Sheets-Sheet 1

Fig-1-

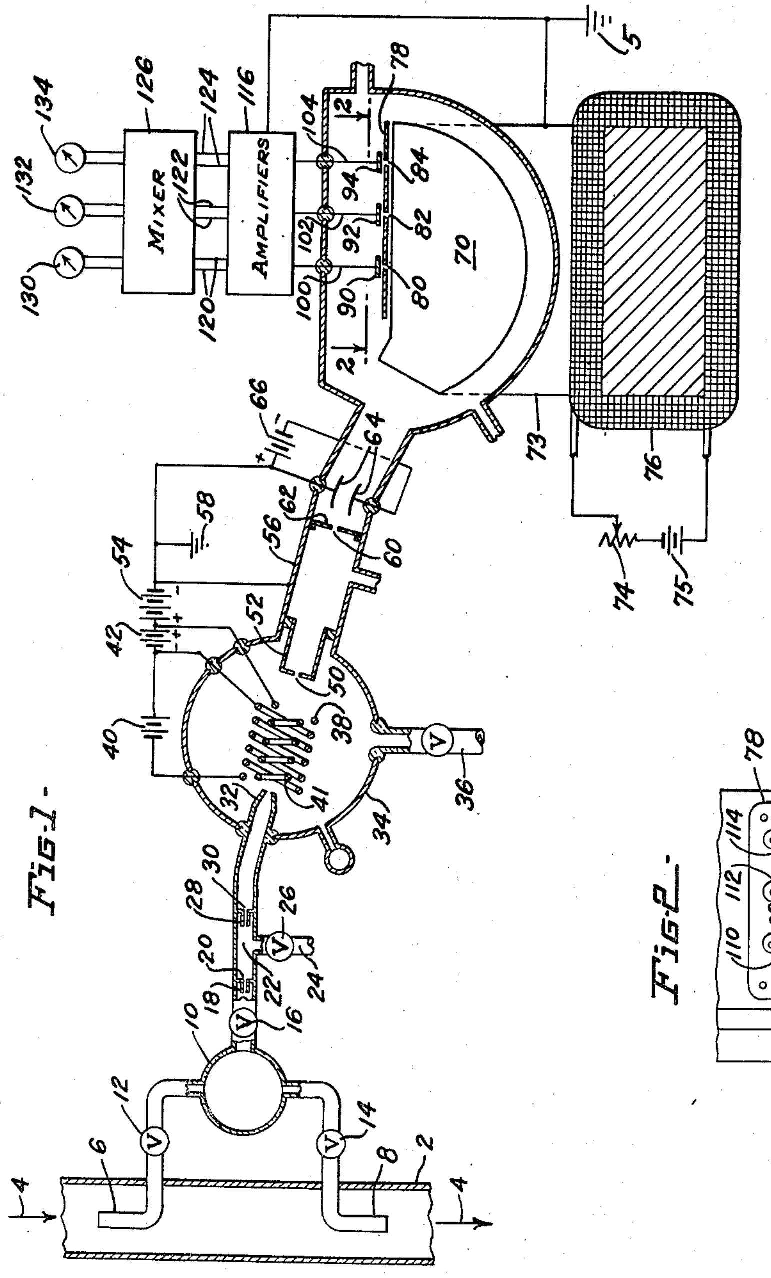
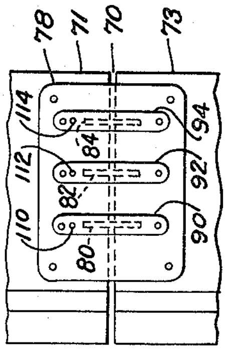


Fig-2-



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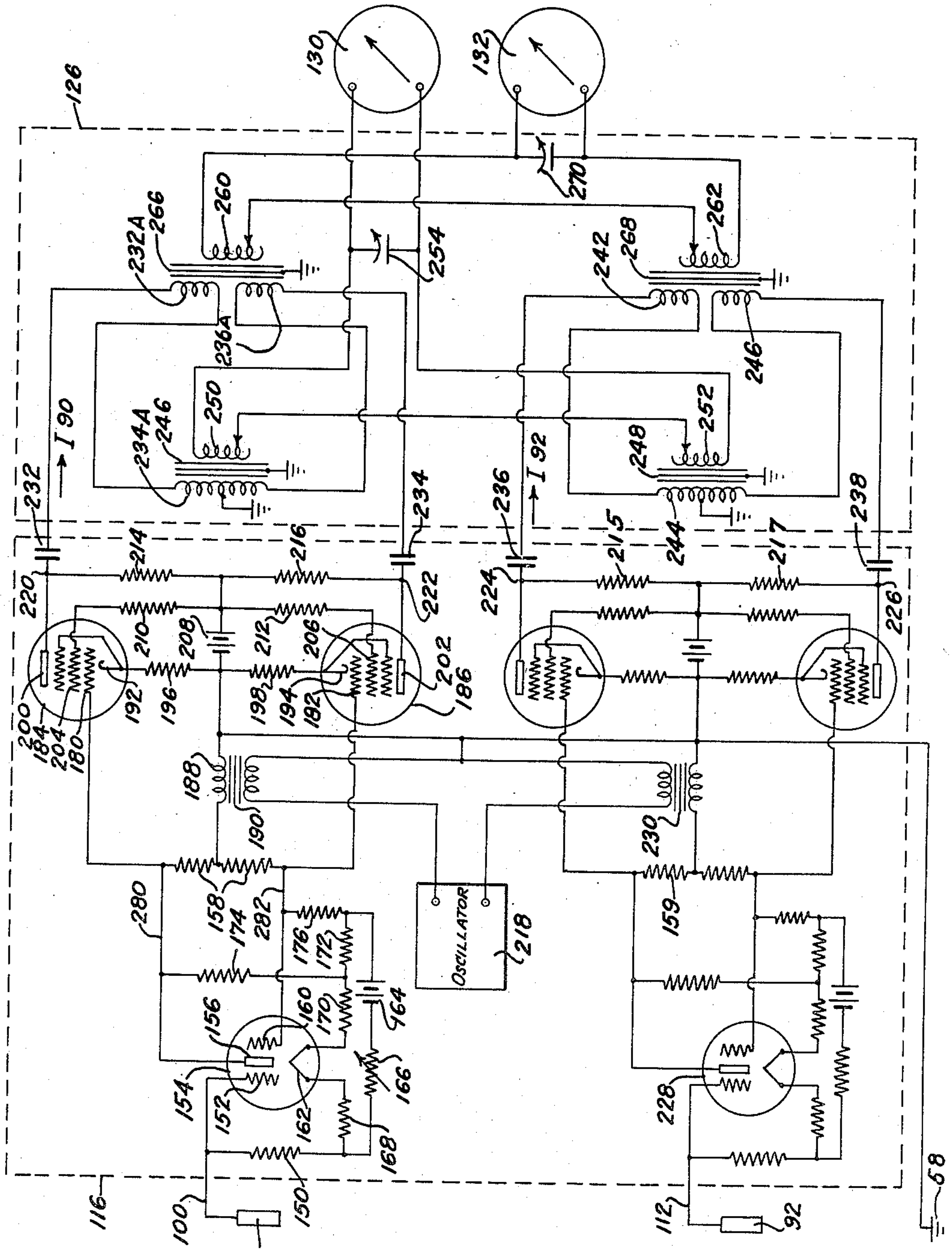

Fig-3

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UNITED STATES PATENT OFFICE

2,355,658

METHOD AND APPARATUS FOR MASS SPECTROMETRY

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Application April 17, 1940, Serial No. 330,127

13 Claims. (Cl. 73—51)

The present invention relates to improvements in mass spectrometry.

In general, a mass spectrometer is more satisfactory than any other instrument for determining the constitution of a gas, for the reason that a mass spectrometer is more sensitive, rapid, and accurate, than any other.

When a gas sample is introduced into a mass spectrometer, it is ionized and by the combined action of electric and magnetic forces the ions formed are segregated according to their mass-to-charge ratios.

The intensity of the segregated ion currents produced from a mass spectrum may be used to determine the constitution of the gas mixture under investigation. However, since any particular ion current collected often does not correspond to only a single component in the gas mixture, a complex set of calculations must ordinarily be made on the basis of the various measured ion currents in order to determine the concentrations of the respective individual components in the original gas mixture.

It is clear that the delay and complexity resulting from the need for such calculations is for some purposes undesirable. For example, if it is desired to use a mass spectrometer for continuously determining the composition of a gas mixture flowing through an output line at the termination of a refinery process, it is very important to be able to continuously indicate and/or record the instantaneous values of the concentrations of the various components yielded by the refinery process.

Accordingly, it is the principal object of my invention to provide for continuously indicating and/or recording the concentrations of the individual components of a gas mixture even though the various components upon ionization form ions of the same mass-to-charge ratios.

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 of specific apparatus embodying and utilizing my novel method. It is, therefore, to be understood that my method is applicable to other apparatus, and that I do not limit myself in any way to the apparatus of the present application, as I may adopt various other apparatus embodiments, utilizing the method, within the scope of the appended claims.

Referring to the drawings:

Fig. 1 shows a general organization of my apparatus, partly in cross-section and partly schematic.

Fig. 2 is a segmental view of the ion collecting apparatus taken on the line 2—2 of Fig. 1.

Fig. 3 is a wiring diagram of a preferred means for deriving separate indications of the concentrations of the two components of a binary gas mixture.

In the preferred embodiment of my invention a mass spectrometer is connected to a gas line for continuous analysis of the gases flowing therethrough and the output of the mass spectrometer is applied to a mixing circuit, which serves the purpose of producing a plurality of currents, each of which is a direct measure of a different gas component flowing through said gas line.

Referring to Fig. 1: A gas line **2**, in which gas is flowing downward as indicated by arrows **4—4**, contains therein a gas-collecting tube **6** pointing upstream and a gas discharge tube **8** pointing downstream. A portion of gas flowing through the gas line **2** passes into collecting tube **6** and thence into the sample chamber **10** and returns to the gas line through discharge tube **8**.

Valves **12** and **14** may be used to control the speed of flow through chamber **10** if desired.

As a result the gas within chamber **10** continuously and accurately reflects the composition of the gas flowing in gas line **2**. When valve **16** is open, gas is caused to flow through first capillary **18** in plate **20** into the intermediate chamber **22**. A large portion of the gas flowing into chamber **22** may be drawn off through vacuum line **24** at a rate determined by the setting of control valve **26**, thus serving to reduce the gas pressure that would otherwise exist within intermediate chamber **22**. A portion of the gas within chamber **22** passes through a second capillary **28** in plate **30** and is thereupon admitted through jet **32** into ionization chamber **34**.

The function of the pressure reducing system represented by the two capillaries **18** and **28** and pressure-control valve **26** is simply to limit the amount of gas admitted to ionization chamber **34** to a suitably low value required for the satisfactory operation of the mass spectrometer. The pressure within ionization chamber **34** is also determined in part by the rate at which gas is withdrawn through vacuum line **36**.

Within ionization chamber **34** is mounted a helical filament type cathode **38**, the electron emission from which is determined by a battery **40**, and a helical filament anode **41** mounted within cathode **38** and concentric therewith. By means of battery **42**, electrode **41** is maintained at a positive potential with respect to cathode **38**. Electrons emitted from cathode **38** are drawn towards the center of the electrode system **38—41**, where they bombard and ionize gas molecules contained therein. The positive ions formed are drawn toward collimator slit **50** at the entrance of grounded collimator tube **52** by means of the electric field supplied by battery **54** having its positive end connected to electrode **41** and its negative end connected to metallic chamber **56** and ground **58**.

A portion of the positive ions passing through collimator slit **50** also pass through collimator slit **60** in grounded collimator plate **62** thereby forming a heterogeneous ion beam corresponding in content and character to the gas mixture flowing in gas line **2**.

Said heterogeneous ion beam, after having been accelerated by the potential between electrode assembly **38—41** and collimator **52—62**, is deflected downward by means of the electric field maintained between plates **64** by battery **66**. Said ions pass into the gap **70** between the poles **71** and **72** (see also Fig. 2) of electromagnet **73**.

The strength of the magnetic flux in gap **70** may be set at a predetermined value by adjustment of rheostat **74** which supplies current from battery **75** to coil **76**.

Due to the combined action of the electric and magnetic fields, positive ions of various mass-to-charge ratios are brought to a focus at different predetermined positions in the plane of grounded shield **78**. Said grounded shield has slits **80**, **82**, and **84** cut therein at such positions that ions of predetermined mass-to-charge ratios are permitted to pass therethrough and fall upon the corresponding ion collectors **90**, **92**, and **94**, where said ions give up the respective positive charges and produce minute electric currents corresponding in magnitude to the concentration of the respective ions formed within ionization chamber **34**.

Referring more particularly to Fig. 2 for details of the ion collecting system, plate **78** is shown secured to the sides of magnetic poles **72** and **74** and metallically connected thereto in order to provide a ground connection for all ions falling on said plate. In front of the slots **80**, **82**, and **84** are positioned corresponding ion collectors **90**, **92**, and **94** mounted on plate **78** and insulated therefrom. Flexible leads **100**, **102**, and **104** are connected to said collectors at points **110**, **112**, and **114**.

Assume, for the moment, that a three component hydrocarbon gas mixture flowing through line **2** is being analyzed. Such a mixture, for example, might comprise ethane, propane, and normal butane. Also, assume that ions $C_2H_6^+$, $C_3H_8^+$, and $C_4H_{10}^+$ are being collected at collectors **90**, **92** and **94**. For such a mixture the intensity of the $C_4H_{10}^+$ ion current is a direct measure of the amount of butane present in said mixture. But, due to the fact that $C_3H_8^+$ is an ionization product of butane as well as propane, and that $C_2H_6^+$ is an ionization product of all three components, the intensity of the ion currents corresponding to these two ions $C_2H_6^+$ and $C_3H_8^+$ do not indicate directly the amounts of ethane and propane present in the mixture. I obtain separate indications of each of the gas components of the mixture by electrically subtracting a predetermined fraction of the $C_4H_{10}^+$ ion current from the $C_2H_6^+$ and the $C_3H_8^+$ ion currents and by electrically subtracting a predetermined fraction of the remaining $C_3H_8^+$ current from the $C_2H_6^+$ current. The values of said predetermined fractions may be determined from the relative intensities of the respective ion currents appearing in the mass spectra of pure samples of said components. One example of how such predetermined fractions are computed is illustrated hereinbelow in connection with the analysis of a mixture of normal butane and isobutane.

In order to achieve the above-described indications of individual components, ion currents produced at collectors **90**, **92**, and **94** are led into a bank **116** of amplifiers where they are amplified and preferably converted into corresponding A. C. voltages, and said corresponding A. C. voltages appearing across pairs of leads **120**, **122**, **124** are applied to the mixer **126** where said potentials are combined in such proportions and phase that separate indications of three components of the original gas mixture are produced in corresponding indicating meters **130**, **132**, **134**. An example of such a mixing system is hereinbelow described in detail in connection with the analysis of a binary mixture containing normal butane and isobutane. While it would be possible to obtain separate indications of the individual components of a mixture by properly combining direct current indications, I prefer to utilize alternating current indications, as alternating currents are easier to manipulate.

In the general organization of apparatus hereinabove described, the application of my invention to the analysis of a tertiary mixture of three hydrocarbon gases having differing molecular weights has been described. However, it is to be understood that my invention is applicable to the analysis of a gas mixture having a larger number of individual components, and that the number of ion collectors required for the analysis of any mixture should be at least equal to the number of components in said mixture to be separately measured.

In Fig. 3 I have shown a preferred embodiment of my invention which is applicable to binary mixtures for which two corresponding ion currents are measured and in which the intensity of each ion current is determined in part by each of the components present in said binary mixture.

Such a system as that shown in Fig. 3 is applicable, for instance, to the analysis of a mixture of two isomers as normal butane and iso-butane. While each of these gases on ionization forms ions of the same mass-to-charge ratio, the relative proportion of the ions formed is characteristic of each. In the table are shown the relative intensities of some of the collected ion currents obtained from these gases under certain conditions of analysis fixed with respect to rate of flow of each component through gas line **2**, rate of admission into ionization chamber **34**, voltages applied to electrode assembly **38—41**, etc.

Table

Mass-to-charge ratio	Principal ion	Normal butane current	Iso-butane current	Sensitivity ratio
28	$C_2H_4^+$	2.90	1.53	1.9
29	$C_2H_5^+$	3.58	1.44	2.5
30	$C_2H_6^+$	0.046	0.071	0.65
43	$C_3H_7^+$	8.25	5.78	1.43
44	$C_3H_8^+$	0.214	0.498	0.43
57	$C_4H_9^+$	0.327	0.191	1.7
58	$C_4H_{10}^+$	0.666	0.118	5.6

In the table the first column represents the mass-to-charge ratios of the corresponding ions given in the second column, and which are derived from both normal- and iso-butanes. The third and fourth columns indicate the relative intensities of the respective ion currents per unit of partial pressure of the corresponding gas in the flow line. The last column represents the relative sensitivity ratios of currents of similar ions derived from the two gases normal butane and iso butane.

In the analysis of such a binary mixture, ions of two different predetermined mass-to-charge ratios are caused to fall upon two separate ion collectors **90** and **92**. For a binary mixture the third ion collector **94** shown in Fig. 1 is not needed.

The two ions selected for this purpose should have as widely different sensitivity ratios as is consistent with the ultimate sensitivity of the system. Satisfactory operation may be obtained by collecting ions of mass-to-charge ratios of **29** and **43**; but where high ultimate sensitivity is not required, ions of mass-to-charge ratios **44** and **58** are most useful because of their wide differences in sensitivity ratios.

Referring to Fig. 3, the ion current discharged on collector **90** flows into the amplifier bank **116** where it passes through a grid resistor **150** and through other elements in the network to ground **58**. The potential difference appearing across resistor **150** is applied to control grid **152** of electrometer tube **154**. A corresponding change in anode **156** current causes a corresponding change in potential across the resistor **158** connected between said anode **156** and space-charge grid **160**.

Suitable operating potentials are applied to the electrodes **152**, **156**, **160** and filament **162** of electrometer tube **154** by battery **164** through resistors **166**, **168**, **170**, **172**, **174**, and **176**. The values of said resistors are so selected that: First, a suitable negative bias is applied to control grid **152**; second, the potential difference appearing across resistor **158** is normally zero when no ion current is being discharged at ion collector **90**; and third, the amplification factor of electrometer tube **154** is independent of minor fluctuations in temperature and the electromotive force of battery **164**.

The terminals of resistance **158** are connected to the control grids **180** and **182** of pentode vacuum tubes **184** and **186** of a balanced push-pull modulator. The midpoint of resistor **158** is connected to ground **58** through the secondary winding **188** of transformer **190** and also to the cathodes **192** and **194** of corresponding pentodes **184** and **186** through biasing resistors **196** and **198**. Voltage is supplied to anodes **200** and **202** and screens **204** and **206** by battery **208** through resistors **210**, **212**, **214**, and **216**.

In the preferred form of my invention alternating currents of fixed frequency are supplied from oscillator **218** through transformer **190**. When no ion current is falling upon ion collector **90** there is no potential difference across resistor **158** and accordingly there is no alternating current potential appearing at the output terminals **220** and **222** of the balanced modulator. However, when positive ions fall on ion collector **90** the potential of grid **180** swings negative and the potential of grid **182** swings positive with respect to ground **58** as a result of the potential appearing across resistor **158**. By means of the above described system I am able to produce an alternating current potential appearing across output terminals **220** and **222** in direct proportion to the number of ions per second falling on collector **90**.

In similar manner an alternating current potential is developed across the terminals **224** and **226** at the output of a second similar balanced modulator coupled in similar manner to ion collector **92** through electrometer tube **228**.

By virtue of the fact that oscillator **218** supplies potentials to both balanced modulators through two transformers **190** and **230** connected in series and because of the similarity in characteristics of said two balanced modulators, the alternating currents appearing at the output of said two balanced modulators are in phase.

The outputs of said two balanced modulators are applied through coupling condensers **232**, **234**, **236**, and **238** to mixing circuit **126**. An alternating current of amplitude I_{90} corresponding to the ion current falling on collector **90** flows from terminal **220** through primary winding **232A**, center grounded primary windings **234A**, and primary winding **236A** to output terminal **222**. Similarly an alternating current of amplitude I_{92} corresponding to the ion current falling on collector **92** flows from terminal **224** through primary **242**, center grounded primary winding **244**, and primary winding **246** to output terminal **226**.

The ratios of the windings of transformers **246** and **248** are so selected that the electromotive forces induced in the secondaries **250** and **252** when added together vectorally or algebraically combine to produce in meter **130** an indication of the concentration of normal butane. Condenser **254** shunted across the series-connected secondaries **250** and **252** is of such a value that the secondary circuits of transformers **246** and **248** are tuned to the frequency of oscillator **218**.

In similar manner the ratio of the windings **260** and **262** of transformers **266**, **268** are adjusted to such values that when the potentials induced in said secondaries are combined in mixer **126**, they produce an indication on meter **132** which is a measure of the concentration of isobutane. Condenser **270** serves to tune the series-connected secondaries **260** and **262** to the frequency of oscillator **218**.

If ions of masses **29** and **43** are collected by collectors **90** and **92**, respectively, then, as will be clear from the table, the two currents I_{90} and I_{92} are given by the equations

$$I_{90}=3.58X_n+1.44X_i \qquad (1)$$

$$I_{92}=8.25X_n+5.78X_i \qquad (2)$$

where X_n and X_i are respectively the rates of flow of normal butane and isobutane in the mixture flowing in the line **2**. Solving equations (1) and (2) for X_n and X_i, it is found that

$$X_n=0.680I_{90}-0.170I_{92} \qquad (3)$$

$$X_i=-0.970I_{90}+0.421I_{92} \qquad (4)$$

Thus, to obtain separate indications corresponding to the two constituents of the mixture under analysis, transformers **246**, **248**, **266**, and **268** having the relative transformer ratios 0.680, 0.170, 0.970, and 0.421, respectively, are used, and the potentials induced in the two secondary circuits combined in opposite phases (that is, in appropriate multiples of 180°). In short, the electrical potentials or currents are combined in phases displaced from each other by multiples of 180°. Angles which are multiples of 180° are (for the purposes of this invention) 0°, 180°, 360° etc.

In the preferred embodiment of my invention illustrated here, I use pentode vacuum tubes as amplifier elements in the balanced modulators because of the high internal resistance of said tubes. The plate resistances **214**, **216**, **215**, and **217** are also of such high values that the mutual coupling between the first pair of secondaries **250** and **252** and the second pair of secondaries **260** and **262** is so low that currents existing in either of the secondary circuits do not produce appreciable electromotive forces in the other of said secondary circuits. This decoupling system is especially useful when current meters are used for indicators **130** and **132**.

Usually the value of grid resistor **150** is so large that almost all of the potential between grid **152** from the ion collector **90** to ground **58** appears across said grid resistor and accordingly very little ion current potential drop appears across either half of resistor **158**. If, however, the potential drop through the two halves of resistor **158** should be of any substantial amount they may be equalized if desired by insertion of an appropriate balancing resistor in either the plate lead **280** or the screen lead **282** as required by the particular values of the other circuit elements. While this is not usually necessary it may be desired for symmetry.

In the above description of my invention it has been assumed that each of the two push-pull modulators described is balanced in such manner that the signals appearing in each output is zero when the corresponding ion currents are zero. However, it is to be understood that this is not absolutely essential to my invention and that many variations of the above-described embodiment of my invention will readily occur to those skilled in the art.

I claim:

1. In a mass spectrometer the combination which comprises a plurality of ion collectors each disposed in said mass spectrometer at such positions as to respectively collect charges carried by ions of different mass-to-charge ratio, at least one electric signal indicator, and electric means connecting each of said collectors to at least one of said indicators, said electric means including signal combining means connecting at least one of said indicators to a plurality of said collectors.

2. In a mass spectrometer the combination which comprises a plurality of ion collectors each disposed in the ion image field of said mass spectrometer in such positions as to respectively collect ions of a different mass-to-charge ratios, a plurality of amplifiers, a common source of alternating current signals connected to the input of said amplifiers, a connection from each of said collectors to one of said amplifiers adapted to vary the amplitude of the alternating current signal appearing at the output of said amplifier in accordance with the amplitude of the respective ion currents collected, alternating current signal combining means connected to the output of said amplifiers, and at least one indicator connected to the output of said combining means.

3. In a method of analyzing a mixture containing a plurality of chemically different components, involving the transformation of a portion of the mixture into a plurality of separate ion beams, each beam comprising ions of a different mass-to-charge ratio and the intensity of each beam depending on the amount of more than one of said components present in the mixture, the improvement which comprises converting the respective ion beams into a plurality of electrical currents, electrically combining said electrical currents in such proportions and in such a sign relationship depending on the effect of different components on the intensities of said beams so as to produce a plurality of signals each indicating respectively the amount of a different component of the mixture.

4. In a method of analyzing a mixture containing a plurality of chemicaly different components, involving the transformation of a portion of the mixture into a plurality of separate ion beams, each beam comprising ions of a different mass-to-charge ratio and the intensity of at least one of said ion beams depending on the amount of more than one of said components present in the mixture, the improvement which comprises converting the respective ion beams into a corresponding plurality of electrical currents, electrically combining the current corresponding to said one ion beam with at least one other of said electrical currents in such proportions and in such a sign relationship depending on the effects of different components on the intensity of said one ion beam so as to produce a signal which indicates the amount of one of the components affecting the intensity of said one ion beam.

5. In a method of analyzing a mixture containing a plurality of chemically different components, involving the transformation of a portion of the mixture into a plurality of separate ion beams, each beam comprising ions of a different mass-to-charge ratio and the intensity of each beam depending on the amount of more than one of said components present in the mixture, the improvement which comprises converting the respective ion beams into a plurality of alternating electrical currents of the same frequency, electrically combining said alternating electrical currents in such proportions and in such phase relationships depending on the effect of different components on the intensities of said beams so as to produce a plurality of signals each indicating respectively the amount of a different component of the mixture.

6. A method according to claim 5, in which the electrical currents are combined with relative phases which are integral multiples of 180°.

7. In a method of analyzing a mixture containing a plurality of chemically different components, involving the transformation of a portion of the mixture into a plurality of separate ion beams, each beam comprising ions of a different mass-to-charge ratio, and the intensity of at least one of said ion beams depending on the amount of more than one of said components present in the mixture, the improvement which comprises converting the respective ion beams into a corresponding plurality of alternating electrical currents of the same frequency, electrically combining the current corresponding to said one ion beam with at least one other of said electrical currents in such proportions and in such phase relationships depending on the effect of different components on the intensity of said one ion beam so as to produce a signal which indicates the amount of one of the components affecting the intensity of said one ion beam.

8. A method according to claim 7 in which the electrical currents are combined with relative phases which are integral multiples of 180°.

9. In a mass spectrometer having a source of ions and ion segregating means for separating and focussing ions of different mass-to-charge ratios to produce a plurality of corresponding ion currents, the improvement which comprises a plurality of circuits operatively associated with the ion segregating means and responsive to different ion currents for producing a corresponding plurality of electric currents, the amount of each

electric current corresponding to the amount of ions of a different mass-to-charge ratio formed at the ion source, at least one electric signal indicator, an electric signal combining means so connecting the plurality of circuits to the indicator and so arranged as to apply to the indicator an electric signal which corresponds to a combination of said electric currents.

10. In a mass spectrometer having a source of ions, ion segregating means for separating and focussing ions of different mass-to-charge ratios and a plurality of means for collecting charges carried by corresponding ions of different mass-to-charge ratios, the improvement which comprises a plurality of circuits connected to corresponding collecting means for producing a corresponding plurality of electric currents, the amounts of said currents corresponding to the amounts of the respective corresponding ions formed at the ion source, at least one electric signal indicator, an electric signal combining means so connecting the plurality of circuits to the indicator and so arranged as to apply to the indicator an electric signal which represents a combination of said electric currents.

11. In a mass spectrometer, the combination which comprises an ion current collector responsive to a selected beam of ions produced in the spectrometer, a source of alternating current, and a circuit interconnecting said collector and said source arranged to convert said alternating current into another alternating current modulated in accordance with the intensity of the collected ion current.

12. In a method of analyzing a mixture containing a plurality of different components involving the transformation of a portion of the mixture into a plurality of separate ion beams, each of which comprises ions of a different mass-to-charge ratio, the improvement which comprises introducing a single frequency signal into a plurality of different channels, modulating the signals in the respective channels in accordance with the number of ions in the respective ion beams to produce a plurality of modulated currents, and combining the modulated currents in a mixing circuit to produce mixed signals.

13. In a mass spectrometer the combination which comprises an ion current collector, means connected to the collector and arranged to produce an alternating current, and means for modulating the alternating current in accordance with the intensity of the collected ion current.

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