

[54] **APPARATUS AND METHODS FOR SEPARATING, CONCENTRATING, DETECTING, AND MEASURING TRACE GASES**

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[58] Field of Search: **250/41.9 I, 41.9 SB, 41.9 G**

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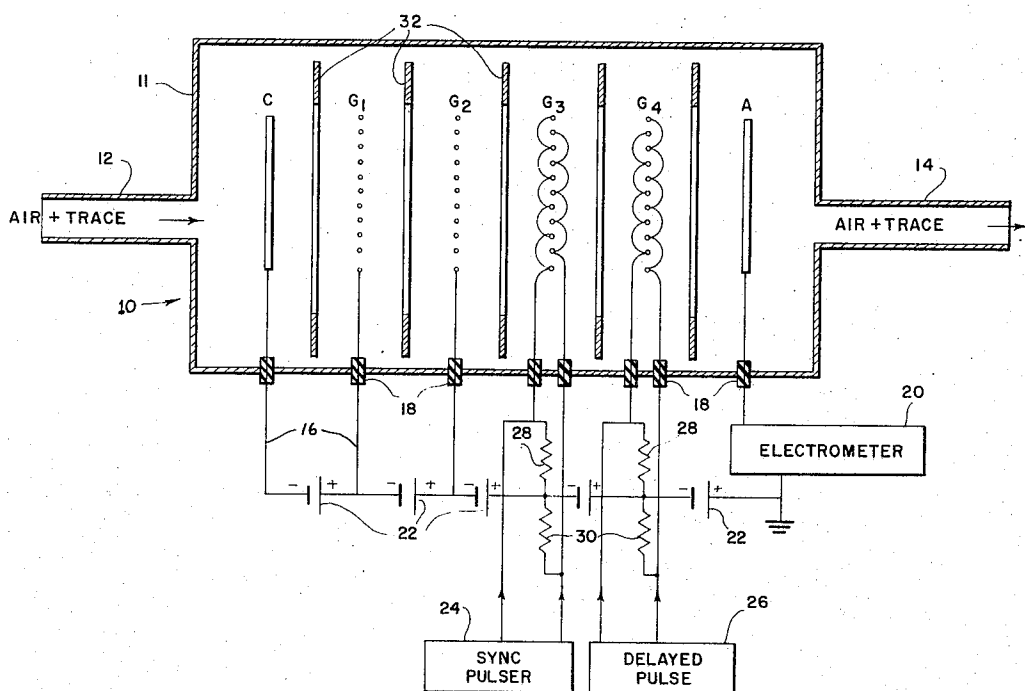
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[57] **ABSTRACT**

Apparatus and methods for sorting and detecting trace gases which undergo ion-molecule reactions. Positive or negative ions of the trace gas are formed by ion-molecule reactions between the molecules of the trace gas and primary ions from another source. Ions are classified by selective ion gating according to their velocity in an electric drift field.

43 Claims, 10 Drawing Figures



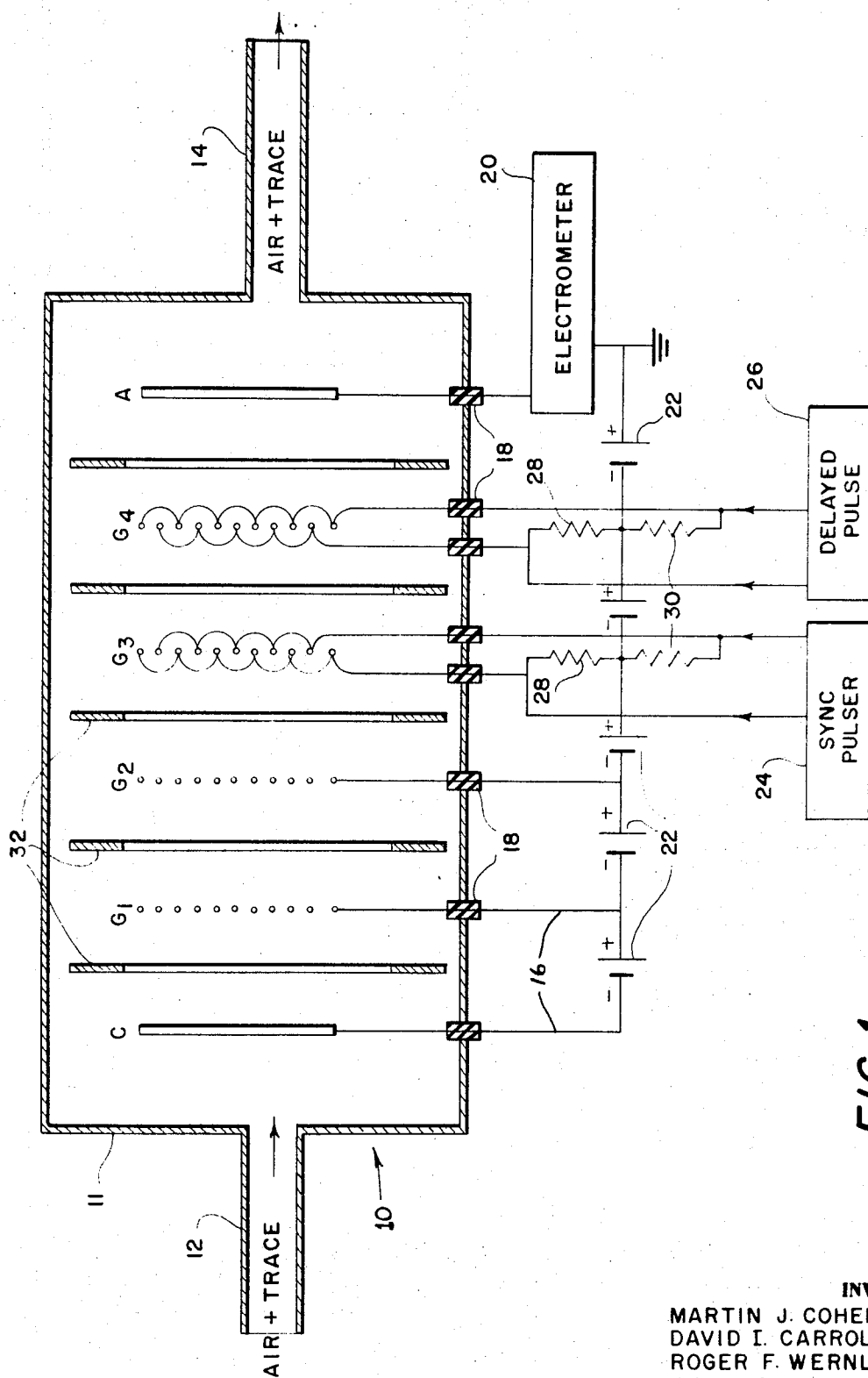


FIG. 1

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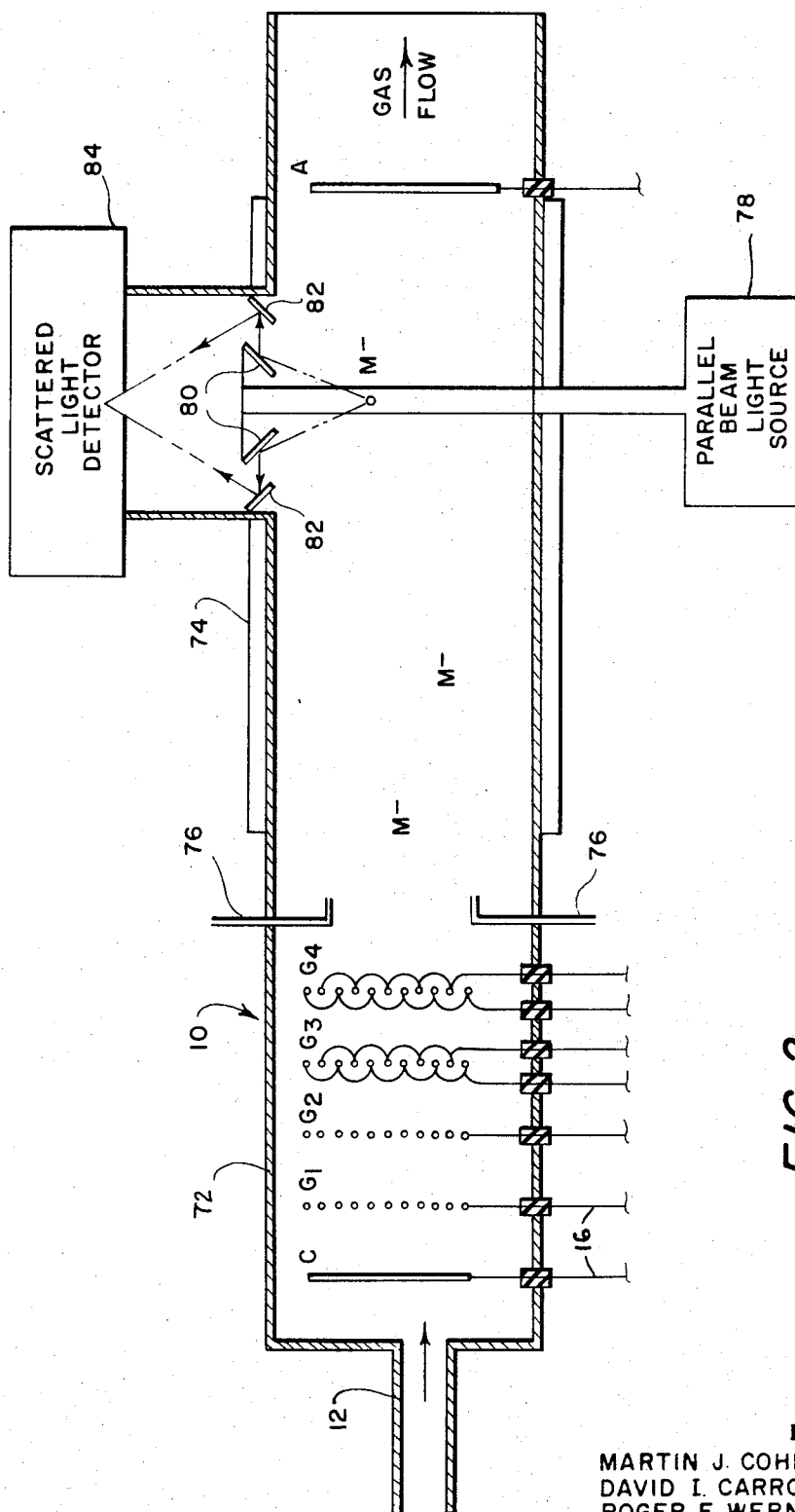


FIG. 2

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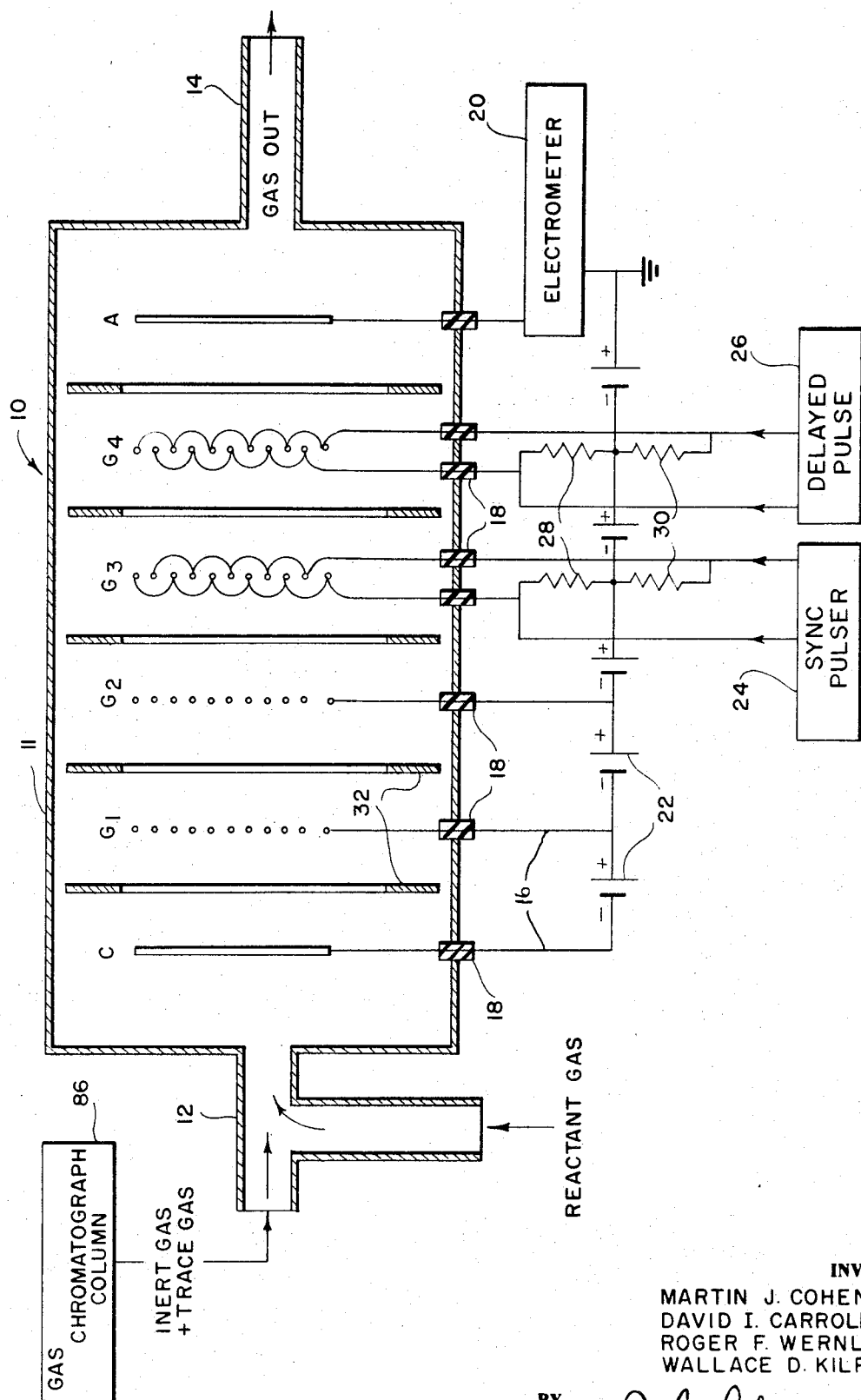


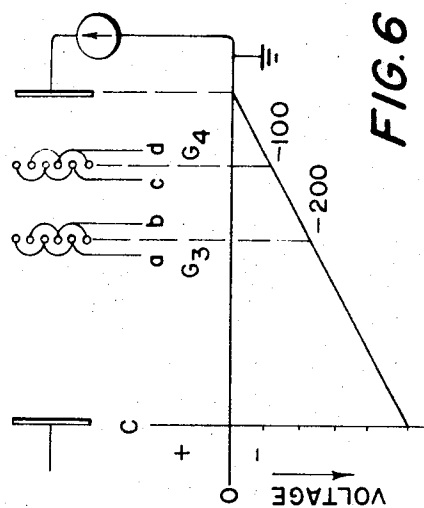
FIG. 3

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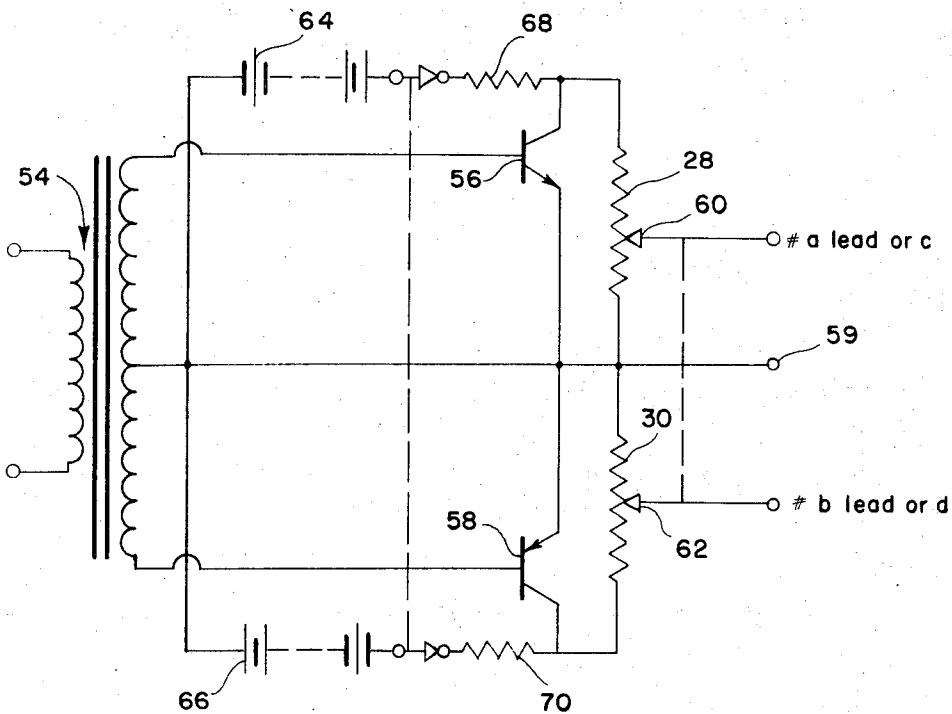
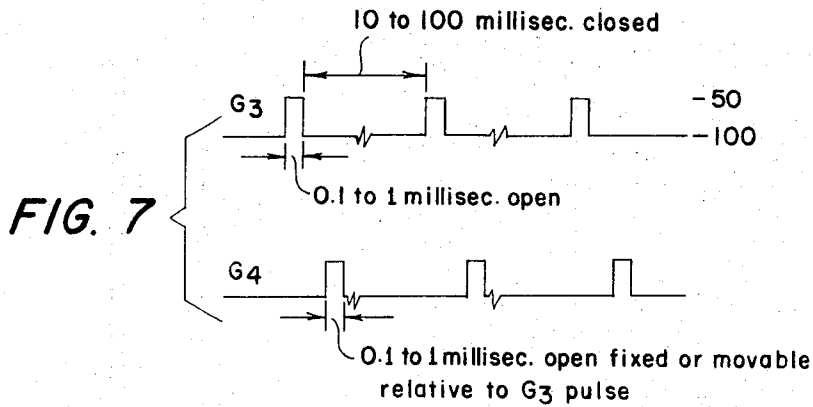


FIG. 9

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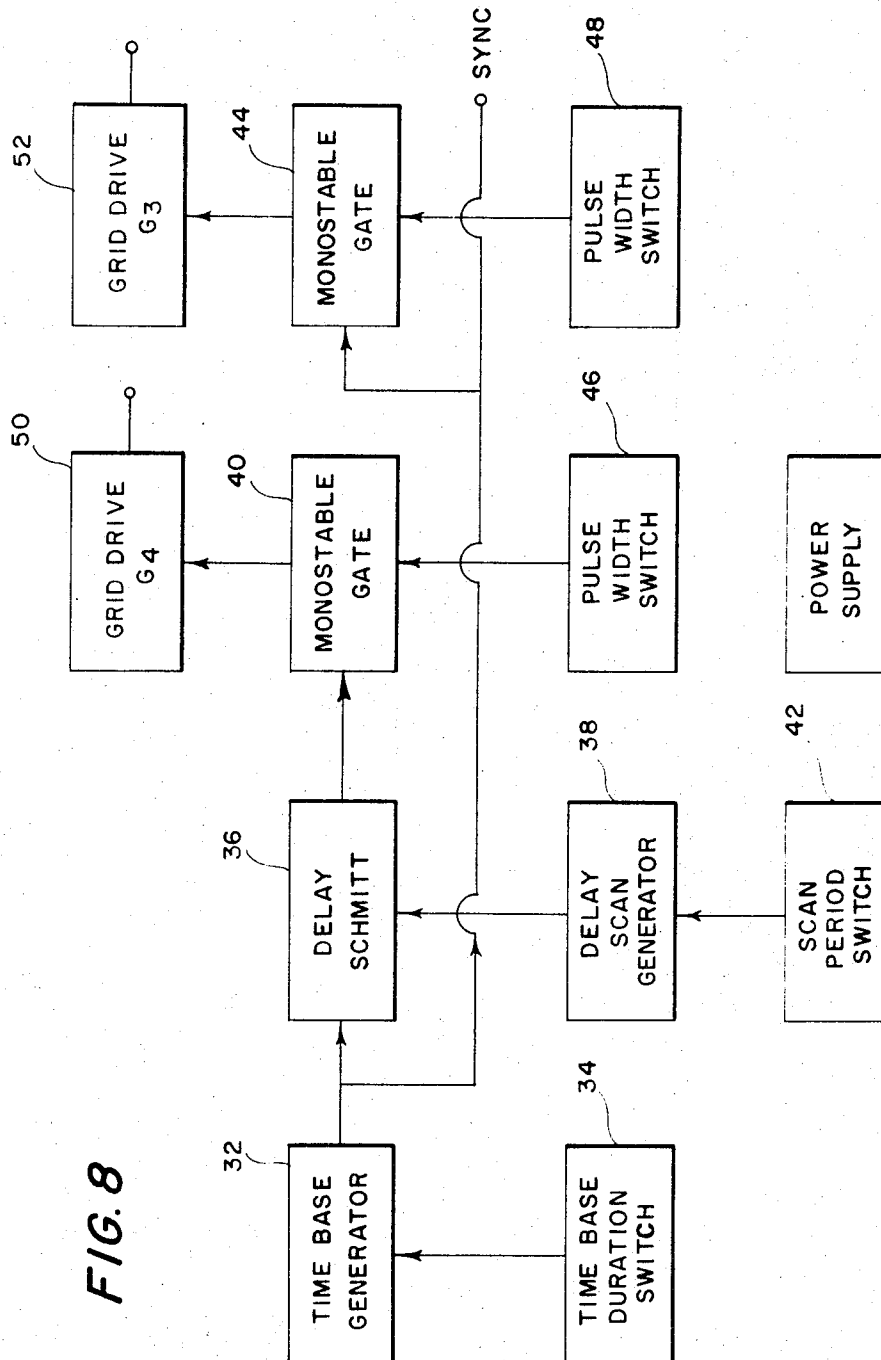


FIG. 8

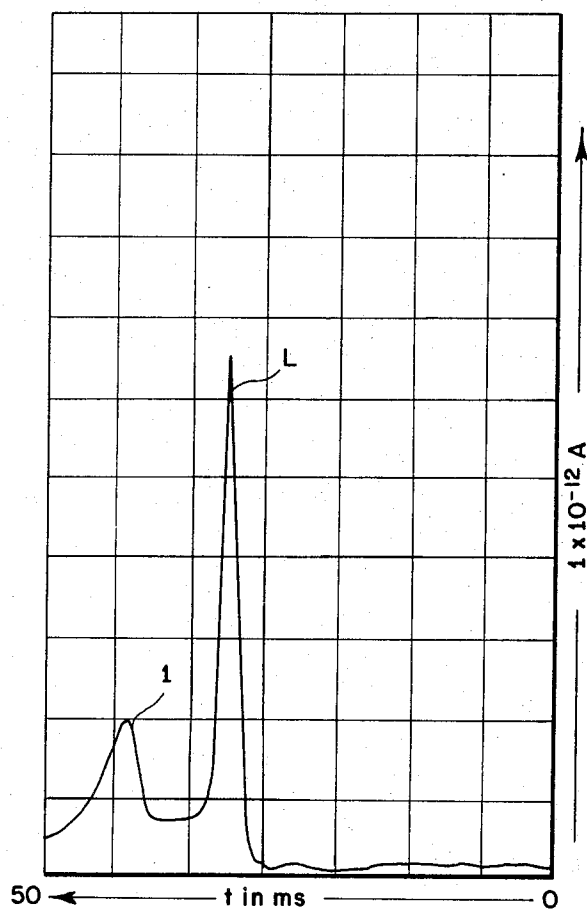
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ION DRIFT TIME SPECTRUM FOR COMPRESSED AIR WITH
CONTINUOUS ULTRAVIOLET LIGHT; PRESSURE 775 mm Hg AND
ELECTRIC FIELD OF 293 V/cm; DRIFT TIME IS FROM FIRST
TO SECOND ELECTRICAL SHUTTER.

FIG. 10

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APPARATUS AND METHODS FOR SEPARATING, CONCENTRATING, DETECTING, AND MEASURING TRACE GASES

BACKGROUND OF THE INVENTION

This invention relates to apparatus and methods utilizing ions formed by ion-molecule reactions. More particularly, the invention is concerned with the detection of trace vapors which undergo ion-molecule reactions and with the separating, concentrating, and measuring of molecular quantities of trace substances in gaseous samples.

Heretofore, gas chromatography has been the best available solution to the problems of discriminating between organic gases and detection of trace vapors. While gas chromatography will resolve many trace gases with high sensitivity, the apparatus is limited to small samples per unit time. Moreover, the apparatus is complex, expensive, bulky, slow, and requires skilled operators. A need has existed for greatly improved instrumentation.

BRIEF DESCRIPTION OF THE INVENTION

It is accordingly a principal object of the invention to provide such improved instrumentation and more particularly to provide improved systems, apparatus, components, and methods for the separation, concentration, analysis, detection, and measurement of molecular quantities of trace substances, such as impurities in large gaseous samples.

Briefly stated, the apparatus and methods of the invention are concerned with what will be termed "Plasma Chromatography," or merely "PC," involving the formation of either positive or negative ions by reactions between the molecules of the trace substances and primary ions. The secondary ions may then be concentrated, separated, detected, and measured. This separation is accomplished by utilizing the difference in velocity or drift time of ions of different mass in an electric field applied to a gas. In a preferred form of the invention, primary ions or reactant are formed by electron attachment, for example, to the molecules of a reactant gas. A drift field causes the primary ions to migrate toward an ion gate or shutter grid, during which the primary ions react with molecules of a gas to be detected, converting the molecules to secondary or product ions. At a predetermined time the ion gate is opened to permit a group of ions of predetermined mobility to pass toward a second ion gate. Thereafter the second ion gate is opened to pass a portion of such ions to detection means. The invention has rapid response, very high sensitivity and mass resolution, and high signal-to-noise ratio. It is simple and compact, analyzes large or small quantities of gas continuously, without requiring the collection of isolated samples, and performs its functions without substantial fragmentation or decomposition of the test material.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be further described in conjunction with the accompanying drawings, which illustrate preferred and exemplary embodiments, and wherein:

FIG. 1 is a longitudinal sectional view, somewhat diagrammatic, illustrating one form of Plasma Chromatography (PC) apparatus in accordance with the invention;

FIG. 2 is a similar view, illustrating an alternative detection arrangement;

FIG. 3 is a similar view illustrating the use of PC apparatus of the invention in a gas chromatography system;

FIG. 4 is a similar view illustrating separation and concentration of gaseous components in accordance with the invention;

FIG. 5 is a potential gradient diagram for one form of the invention;

FIG. 6 is a similar diagram for another form of the invention;

FIG. 7 is a waveform diagram illustrating the application of pulses to shutter grids of the invention;

FIG. 8 is a block diagram of a suitable shutter grid drive system;

FIG. 9 is a schematic diagram of a shutter grid drive circuit; and

FIG. 10 is a waveform diagram showing a representative PC output curve.

DESCRIPTION OF THE INVENTION

Referring to the drawings, as shown in FIG. 1 one form of PC apparatus in accordance with the invention employs a gas-enclosing cell 10 comprising an envelope 11, of metal, for example, having an inlet 12 and an outlet 14, which may constitute portions of a duct into which the envelope may be integrated. The envelope contains a series of electrodes, which may have parallel plane geometry, for example, and which may include a principal electrode of one polarity, e.g., cathode C, a first passive grid G1, a second passive grid G2, a first shutter grid or ion gate G3, a second shutter grid or ion gate G4, and a principal electrode of opposite polarity, e.g., and anode A. The electrodes may be spaced apart distances of the order of a few centimeters or less (e.g., cathode to anode spacing of about 10cm.) and may have lead wires 16 which pass through the envelope by means of insulators 18. The cathode or the region of the envelope near the cathode is provided with an ionizing source, such as a photoemission source upon the cathode, a radioactive source such as tritium located at or near the cathode, a multiple point or wire array (corona) source operating near the cathode, or an RF ionization source near the cathode. The grids may be of the parallel wire type. Alternate wires of each of the shutter grids are connected together to form two separate groups, so that each shutter grid comprises two interdigitated sub-grids of parallel wires, each group of wires being provided with its own lead 16. The anode may be a collector plate connected to an output device, such as the electrometer 20, which may be Carry Instruments Model 401 (vibrating reed) type with current sensitivity of 10^{-15} amperes at a time constant of 300 milliseconds.

An electric drift field is provided between the cathode, at a first region of the envelope 11, and the anode, at a second region of the envelope. In the form shown the source of the drift field is a series battery chain 22 with suitable taps being connected to the electrodes. Alternative sources of drift field, such as a resistive voltage divider with its ends connected to a DC supply, may be employed instead of the batteries. The anode A is connected to ground through the input circuit of the electrometer. The apparatus is illustrated as it is employed for detecting negative ions, and hence

the cathode is shown negative with respect to the anode. If the polarity were reversed, the apparatus could be employed with positive ions.

Adjacent elements of each shutter grid are normally maintained at equal and opposite potentials relative to a grid average potential established by the battery chain 22, and under these conditions the shutter or gate is closed to the passage of electrically charged particles. The potential sources which provide the equal and opposite potentials just referred to may be considered to be part of grid drive circuits within blocks 24 and 26 entitled "Sync Pulser" and "Delayed Pulse." The components of these blocks are effective to drive the adjacent elements of each shutter grid to the same potential, the grid average potential, at predetermined instants, alternate grid wires being shown connected to the battery chain by resistors 28 and 30. The grid drive system will be described more fully hereinafter.

A series of guard rings 32 is provided along the perimeter of the envelope to maintain the uniformity of the electric field between the electrodes. The guard rings are also connected to successive points on the battery chain. Suitable supports and spacers, such as quartz rods and tubes, may be employed to support the various electrodes within the envelope.

The apparatus shown in FIG. 1 may be employed for detecting and measuring trace vapors which undergo ion-molecule reactions. The concentration of the trace vapors within a carrier gas, such as air, may be as little as one part in from 10^{12} to 10^{16} . The apparatus can operate at pressures from as low as 5 torr to atmospheric and above as long as the gas collision mean free path is very much smaller than the cell dimensions. Although the basic principle of ion-molecule reactions is well documented in the literature, the utilization of this principle in accordance with the invention is novel.

In an illustrative use of the invention, air carrying a suitable gaseous trace substance, such as pyruvic acid, for example, flows through the envelope by means of the inlet 12 and the outlet 14. Any suitable source of flow pressure, such as a fan, may be employed to move the carrier gas and the trace substance. In the region between the cathode C and the first grid G1 primary ions of the carrier gas, or of one or more of the main constituents thereof, such as oxygen, are formed under the influence of the source of electric charge in this region. For example, low energy electrons may be provided at the cathode by a source of ultraviolet light (not shown) directed upon a reflective porous surface thereof, and negative oxygen ions may be formed at the cathode, as by direct attachment of the electrons to the oxygen molecules. The ions drift toward the anode A under the influence of the drift field.

The region from G1 to G2 is the ion-molecule reaction region. Within this region (and of course to a certain extent elsewhere within the envelope) the primary ions formed at the cathode react with molecules of the trace vapor to convert these molecules to secondary ions. In the region from C to G1 the electrons attach preferentially to the plentiful oxygen molecules, but in the region from G1 to G2 the oxygen ion reaction cross-section is sufficient to ensure a substantial and efficient conversion of trace vapor molecules to secondary ions.

The region from G2 to G3 is a potential isolation region for isolating the shutter grid G3 from the preceding regions of the envelope. During operation of the apparatus, shutter grid G3 is periodically opened to sample the products of the reaction and other ion species present. The opening of grid G3 at a predetermined time and for a predetermined duration constitutes a timed reference pulse during which a group of ions is passed into the ion mobility analysis region between G3 and G4. As the ions drift from G3 to G4 they become grouped or classified in accordance with their velocity (a function of mass) in the drift field. At a predetermined time delayed relative to the opening of grid G3, grid G4 is opened for a predetermined duration to select a portion of the ion mobility spectrum within the region G3 to G4 for passage to the anode. The ions which reach the anode produce a current in the electrometer 20, which may integrate the ion current over multiple cycles of PC cell operation.

FIG. 10 illustrates an ion drift time spectrum for compressed air with a continuous ultraviolet light source of electric charge. The operating pressure was 775 mm Hg and the electric drift field was 293 volts per centimeter. The drift time in milliseconds is illustrated from the first (G3) to the second (G4) shutter grid. The peak at L represents a significant trace ion species in the group of ions passed through gate G4, while the smaller peak 1 represents a less significant ion species and constitutes a tail of the main peak L.

It is desirable, in general, to have the potential between C and G1 as high as convenient in order to reduce primary ion loss by processes of ion recombination and diffusion. In the ion-molecule reaction region from G1 to G2, however, it is desirable to have as long a time as possible to permit the desirable ion-molecule reaction to proceed to or toward completion, in order to give a definitive product mobility. Thus, the difference of potential between G1 and G2 is preferably low (e.g., 1 volt/cm), while the voltage gradient in the regions between C and G1 and between G2 and A is preferably substantially greater. This is illustrated in the voltage gradient diagram of FIG. 5. FIG. 6 illustrates the voltage gradient for a modified PC cell construction in which the passive grids G1 and G2 are eliminated. The voltage gradient is then constant from C to A as shown.

FIG. 7 illustrates representative waveforms for driving the shutter grids. The top line shows the pulse waveform for driving one group of grid wires of grid G3, which may be termed *a*. The waveform for driving the remaining group, *b*, of grid G3 would be identical to the waveform for group *a*, except that the polarity of the pulses would be reversed relative to the base line. For example, the pulses applied to *a* may have a peak value of -50 volts assuming a grid average potential of -100 volts, while the pulses applied to *b* may have a peak value of -150 volts assuming the same grid average potential.

The bottom line of the waveform diagram illustrates the pulses applied to one group, *c*, of the grid wires of grid G4. The pulses applied to the remaining group, *d*, would be equal and opposite in polarity relative to those applied to *c*. It will be noted that the pulses applied to grid G4 are delayed in time relative to those applied to grid G3. The delay time may be fixed, so as to

select a species of ions with predetermined mobility, or may be variable to permit the selection of a variety of ion species. If the delay period is varied slowly enough to permit the electrometer to respond, the output signal can be recorded directly to give ion current versus transit time in the drift field.

FIG. 8 illustrates a suitable system for driving the shutter grids and permitting the selection of time base duration, grid opening delay, grid pulse width, and automatic scan of the delay period. Time base generator 32 generates a synchronization pulse and a linear voltage ramp over a selected recurrent time base, which may be varied, from 0.1 to 100 ms, depending upon the setting of time base duration switch 34. Any of the many adjustable ramp and sync pulse generator circuits of the prior art may be employed for this purpose. The time base ramp voltage at the input of the Schmitt trigger delay circuit 36 is compared with an external voltage, which may be set by a manual potentiometer or by the delay scan generator 38. When the time base ramp crosses the reference voltage, as set by the delay scan generator 38, for example, the Schmitt circuit is triggered on, triggering a monostable pulse former or gate 40, such as a one-shot multivibrator. The delay scan generator 38 produces a linear voltage ramp (by means of any suitable ramp generator circuit of the prior art) over a selectable time period of from 1 to 100 minutes selected by the scan period switch 42. The delay in opening of monostable gate 40 thus increases with the scan ramp from the minimum to the maximum value set by the time base selected. This feature permits a chart recorder automatically to scan ion current as a function of transit time.

A second monostable gate circuit 44 is triggered directly from the sync pulse output of the time base generator 32 to operate grid G3. The gate width of both direct and delayed monostables is selectable over a range of from 10^{-5} to 10^{-3} seconds by means of the pulse width switches 46 and 48. The outputs of the two gates are transformer coupled to two identical grid drive circuits 50 and 52. Suitable grid drive circuitry is shown in FIG. 9.

Timing or gate signals from a monostable gate (40 or 44) are applied through transformer 54 to transistors 56 and 58 of complementary type, the emitters of which are connected to the grid reference potential terminal 59, and the collectors of which are connected to one end of resistors 28 and 30, the opposite ends of which are connected to the grid reference terminal 59. Resistors 28 and 30 are the resistances of potentiometers having variable taps 60 and 62 connected to the respective groups of wires *a*, *b*, or *c*, *d* of one of the shutter grids. Batteries 64 and 66 are connected in series with current-limiting resistors 68 and 70 across the resistors 28 and 30, respectively, and the polarities are chosen so that when the transistors 56 and 58 are turned off, the taps 60 and 62 are provided with equal and opposite potentials relative to the grid reference potential at terminal 59. Periodically both transistors are turned on simultaneously by the timing signals applied through transformer 54, short circuiting the resistors 28 and 30, so that the potential at the taps 60 and 62 is clamped to the grid reference potential at terminal 59.

Typically the grid drive circuits are operated at up to 5 kv above ground and have an insulation resistance of 5000 megohms or better to prevent loading of a resistive divider providing the drift voltage. The grid bias voltages may be variable over wide ranges. Very high insulation resistance is maintained in the grid drive circuits by fabricating specially insulated toroidal coupling transformers. A primary winding is first wound on the toroid and the assembly potted in epoxy resin. The secondary is then wound over the first epoxy and the entire assembly repotted. This procedure permits the coupling of pulse signals from 10 microseconds to 10 milliseconds with voltage insulation of 50 kv. In order to maintain high insulation resistance, the grid bias voltages are derived from an isolated battery supply. The shaft of the ganged taps 60 and 62 of the potentiometers may be extended with a polystyrene rod to permit adjustment of the grid bias voltage.

The basic structure of the invention can be simplified as has been indicated in FIG. 6, by the elimination of grids G1 and G2. This requires that the electrons attach and form the initial reactant ions close to the cathode. The ion-molecule reaction then follows in the space before shutter grid G3. Depending upon space, size, and sensitivity desired, the region of C to G3, the areas of electrodes, and the size of the equipment have to be designed to maximize the current available and to reduce both space charge and diffusion losses.

The utilization of ion-molecule reactions (in which, for example, an original negative ion formed by electron capture undergoes exothermic chemical reaction to produce a negative product ion) has very definite advantages over apparatus in which the detected trace ions are formed by direct electron attachment. By the ion-molecule method positive primary ions (such as positive oxygen and nitrogen ions) may be formed by ionization, as with a tritium or corona source, and the ion-molecule reaction may produce positive trace ions for detection. Pollution effluents, such as SO_2 and NO_2 , can be detected. Special fluorocarbons, particularly fluorocarbon ethers, can be detected at high sensitivity. This is in contradistinction to the direct electron capture method, which is not as sensitive as the reaction-ion technique of the present invention. Of course, a selection has to be made of trace materials which undergo ion-molecule reactions with the primary ions employed, which may be the ions of a carrier or host gas, and sufficient knowledge must be had of the many ion-molecule reactions which may take place with particular gases in order to permit the detection of the desired trace material. For certain types of samples, pre-treatment may be necessary to produce detectable trace vapors. Thus, carbon-nitrogen compounds may be burned in oxygen, and the resulting NO_2 may be detected as either positive or negative ions.

The level of detection sensitivity in accordance with the invention is such that single ions of the candidate trace vapor can be sorted and measured. Single ion detection can be achieved by a condensation nuclei technique, as illustrated in FIG. 2. Here the Plasma Chromatography cell is shown as a portion of a duct 72 having a section surrounded by a cooling jacket 74 of conventional type, the cooling jacket being located between grid G4 and the anode A. The trace ions M-

that enter this region are caused to form water or other aerosol droplets by providing an atmosphere that is super-saturated in such vapor, the aerosol being formed by condensation about the charged ion nuclei. Under-saturated volatile and gas mixture is inserted through the pipes or nozzles 76 into the duct 72, and aerosol droplets grow about the charged molecules M^- as the gas is cooled by the cooling jacket. Each aerosol particle then becomes large enough for detection by a standard optical scattering device, such as the Royco Model 220 detector or the General Electric concentration nuclei detection head indicated diagrammatically in FIG. 2 by the parallel beam light source 78, the mirrors 80 and 82, and the scattered light detector 84, all of which are well known in the art. Although single particle detection can thus be provided, multiple particle detection is usually sufficient and avoids the statistical errors inherent in the counting of small numbers. A vibrating reed electrometer is sufficiently sensitive to measure the equivalent of 100 nuclei.

The invention can be used to detect a wide range of materials at lower concentrations than those available by any comparable method. The measurement system is virtually instantaneous and can be made specific to a wide variety of compounds. The technique requires neither the high vacuum necessary for mass spectrometry nor the long time required for gas chromatography. In general all electrophilic compounds can be measured with great sensitivity, as well as those compounds which form positive ions. The invention has many applications, both military and commercial. For example, it may be employed in poison gas detection, in the detection of explosive material (nitrates), in trace gas management in confined atmospheres (space craft and submarines), in detecting water in fuel, and as an atmospheric sensor ("sniffer"). It may be employed in the diagnosis of bottled "pure" gases, in the detection of leaks in sealed passages, in meat and fish quality controls, in pollution control, as a chemical analytical instrument, as a meteorological analytic instrument (water analysis) and as a gas chromatography detector.

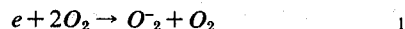
The last-mentioned application of the invention is illustrated in FIG. 3, wherein the PC cell of FIG. 1 is modified for gas chromatography use. The output of the gas chromatograph column 86, which comprises trace gas in an inert carrier gas, is fed to the inlet of the cell, and a reactant gas is fed separately into the cell as shown. The reactant gas may be any suitable gas, such as oxygen, SO_2 , Freon, etc. Except for the separate insertion of the reactant gas, the operation of the PC cell progresses in the manner previously described.

FIG. 4 illustrates the utilization of the ion-molecule reaction principle in the separation and concentration of trace vapors in accordance with the invention. The primary ions may be negative or positive, such as negative oxygen ions or positive oxygen or nitrogen ions. While the separation and concentration of negatively charged molecules is shown, the reversal of potential would permit the use of positive charge.

The concentrator comprises a duct 88 through which a gaseous sample (for example, air containing a trace vapor) is drawn by a fan 90. A section of the duct wall, 92, is insulated from the remainder to form a principal electrode of one polarity, e.g., a cathode. The principal electrode of opposite polarity, e.g., anode, is con-

stituted by the duct wall at 94. Grids G1 and G2, respectively, are provided adjacent to the cathode and the anode. A battery or voltage divider chain is provided at 96 to render the cathode, grid G1, grid G2, and the anode 94 progressively less negative, the anode being connected to ground. A source of ionizing electric charge is provided on the cathode or in the cathode region and may be of the type set forth previously. Electrons from the source produce primary or reactant ions from the oxygen molecules, and the oxygen ions drift from the cathode toward the anode, reacting with the trace molecules M in the main gas stream between the grids. The secondary or product ions M^- so produced drift to the anode and become neutral molecules again. Under the combined influence of diffusion and dynamic air flow, the molecules tend to move back into the air stream to a position near the exit end of the concentrator. The net effect of this process, operating throughout the air volume, is a concentration of M or M^- in the vicinity of the anode as the air approaches the exit of the concentrator. The depleted air is exhausted back into the atmosphere, while the more concentrated sample is pumped through a passage 98 adjacent to the anode at the exit of the duct.

As indicated above, ion-molecule reactions per se are well documented in the literature. To assist in an understanding of the invention the following brief explanation is given. The basic reactions employing oxygen as a primary ion source may be represented as follows:



followed by



where P symbolically represents the trace molecule. The rate of reaction 1, k_a , has been measured and is given by the following equation:

$$k_a = 2.1 \times 10^{-30} \text{ cm}^6/\text{sec.}$$

It can be shown theoretically that electron attachment to oxygen occurs in a thin sheath close to the place of electron formation. In a gaseous air mixture containing very dilute neutral tracer the electrons interact preferentially with the predominantly abundant oxygen, equation (1). If the P^- ion is a relatively more stable configuration for the electron compared to the O_2^- ion, then by equation 2 the O_2^- will be reduced to a very small amount if the drift time is sufficient. From a chemical viewpoint the reaction of equation 2 is exothermic with the formation of P^- , while from a physics point of view P^- has a greater electron affinity than O_2^- . Although the direct electron attachment of the tracer does not have a sufficiently large cross section to form negative ions competitively with O_2 , by means of the reaction cross section the negative tracer ion is formed and permits detection at very low levels.

While preferred embodiments of the invention have been shown and described, it will be apparent to those skilled in the art that changes can be made in these embodiments without departing from the principles and spirit of the invention, the scope of which is defined in the appended claims. For example, a pulsed source of ionizing electric charge, such as pulsed ultra-violet light, may be utilized as a timed reference instead of

G3. The resulting group of primary ions would then react with the tracer molecules and drift toward an ion analysis grid G4.

What is claimed is:

1. A method of detecting a component of a gas, which comprises converting molecules of said component to ions by reaction of said molecules with other ions, applying a drift field to the ions produced by the conversion, segregating said ions in accordance with their drift velocity, the recited steps being performed in a space maintained at a pressure such that the length of the mean free path of said ions is very much less than the dimensions of the space, and detecting at least some of the segregated ions in a manner so as to distinguish them.

2. A method of segregating a component of a body of gas, which comprises providing ions at a first region of said body, reacting said ions with the molecules of said component to form ions of said component, applying a drift field between said first region and a second region of said body for attracting the formed ions to said second region, neutralizing the formed ions at said second region to produce neutral molecules of said component, and extracting said neutral molecules from said second region to a region separated from said body and at which the concentration of said component is greater than in said body, the recited steps being performed in a space maintained at a pressure such that the length of the mean free path of said ions is very much less than the dimensions of the space.

3. A method in accordance with claim 2, further comprising moving said body of gas as a stream during the segregating of said component.

4. A method in accordance with claim 3, wherein the drift field is transverse to the stream movement.

5. A method of detecting a gaseous substance, which comprises forming reactant ions, reacting said ions with molecules of the substance to be detected to form product ions, applying a drift field to said ions to cause them to drift in said field, and selectively gating said product ions to means for detecting the same, the recited steps being performed in a space maintained at a pressure such that the length of the mean free path of said ions is very much less than the dimensions of the space, and detecting at least some of said product ions in a manner so as to distinguish them.

6. A method in accordance with claim 5, wherein a group of said product ions is selectively gated to a first region and then a portion of said group is selectively gated from said first region to said detecting means.

7. A method in accordance with claim 5, wherein said product ions are detected by growing aerosol droplets thereon and detecting the droplets optically.

8. A method in accordance with claim 5, wherein said gaseous substance is a trace vapor in an inert gas effluent of a gas chromatograph and wherein said reactant ions are formed from the molecules of a separate reactant gas.

9. A method in accordance with claim 5, wherein said pressure is substantially atmospheric.

10. A method in accordance with claim 5, wherein the reactant ions are formed substantially continually during the performance of the recited steps.

11. A method in accordance with claim 10, wherein the drift field is applied substantially continuously and unidirectionally during the other recited steps.

12. Apparatus for separating components from a gas, comprising an envelope having means for introducing said gas therein, means for producing reactant ions at a first region of said envelope for reaction with the molecules of said components to form product ions, means for applying a drift field to said ions for causing said ions to drift from said first region toward a second region of said envelope, ion gate means between said regions, and means for opening said gate means for a predetermined interval during the application of said drift field to pass ions of predetermined drift velocity to said second region, and means for maintaining the pressure in said envelope such that the length of the gas collision mean free path is very much less than the dimensions of said envelope.

13. The apparatus of claim 12, said gate means comprising a grid having two interdigitated substantially coplanar sets of grid elements and having means for normally maintaining adjacent elements at equal and opposite potentials with respect to a reference potential, and said means for opening said gate means comprising means for placing all of said grid elements substantially at said reference potential.

14. The apparatus of claim 12, further comprising means for varying the time of opening of said gate means.

15. The apparatus of claim 13, further comprising means for producing an output in response to the ions at said second region.

16. The apparatus of claim 12, said gate means comprising a pair of shutter grids arranged seriatim in the path of said ions.

17. Apparatus for detecting the presence of a substance in a gas, comprising an envelope having means for introducing said gas therein, means for providing reactant ions at a first region of said envelope to form product ions by reaction with said substance at said first region, means for applying a drift field to said ions for causing said ions to drift from said first region toward a second region of said envelope, first and second ion gates arranged serially between said first and said second regions, means for opening the first ion gate at a predetermined time to pass a group of said product ions toward said second ion gate, and means for opening said second ion gate at a predetermined time after the opening of said first ion gate to pass a portion of the ions passed by said first ion gate, means for maintaining the pressure in said envelope at a level such that the length of the gas collision mean free path is very much less than the dimensions of said envelope, and means for detecting at least some of the ions passed by said second ion gate in a manner so as to distinguish them.

18. The apparatus of claim 17, wherein said detecting means comprises an electrometer.

19. The apparatus of claim 17, wherein said detecting means comprises means for producing aerosol particles from the ions passed thereto and means for optically detecting said aerosol particles.

20. The apparatus of claim 17, further comprising means for removing said gas from said envelope continuously as it is introduced into said envelope.

21. Apparatus in accordance with claim 17, each of said ion gates comprising a grid having two interdigitated substantially coplanar sets of grid elements and having means for normally maintaining adjacent

elements at equal and opposite potentials with respect to a reference potential, and said means for opening said gates comprising means for placing all of the elements of a grid substantially at said reference potential.

22. Apparatus in accordance with claim 17, wherein said means for providing reactant ions comprises a continuous ionizing source.

23. Apparatus in accordance with claim 17, wherein said means for applying said drift field comprises means providing a unidirectional drift field continuously.

24. Apparatus in accordance with claim 17, said means for applying a drift field comprising a pair of electrodes at said first and second regions, respectively, and means for providing a DC potential difference between said electrodes continuously, said means for providing reactant ions comprising a continuous ionizing source associated with the electrode at said first region, each of said ion gates comprising a grid having two interdigitated substantially coplanar sets of grid elements and having means for normally maintaining adjacent elements at equal and opposite potentials with respect to a reference potential, and said means for opening said gates comprising means for placing all of the elements of a grid substantially at said reference potential.

25. Apparatus for detecting trace gas components in an inert gas flowing in the conduit, which comprises an envelope, means for introducing said inert gas and said trace gas into said envelope, means for introducing a reactant gas into said envelope, means at a first region of said envelope for producing reactant ions from the molecules of said reactant gas to form product ions from said trace gas as the result of reaction of the molecules of said trace gas with said reactant ions, means for applying a drift field to said ions for causing said ions to drift from said first region of said envelope toward a second region of said envelope, ion gate means between said regions, means for operating said gate means at a predetermined time to pass a portion of said product ions to said second region, means for detecting at least some of the product ions passed to said second region so as to distinguish them, and means for maintaining the pressure in said envelope at a level such that the length of the gas collision mean free path is very much less than the dimensions of said envelope.

26. Apparatus in accordance with claim 25, said means for introducing said inert gas and said trace gas comprising means for feeding those gases to said envelope at the same rate of flow as the rate of flow of those gases in the conduit.

27. A method of segregating a component of a body of gas flowing in a conduit, which comprises ionizing molecules of said component by reaction of the molecules with other ions at a first region of said body, applying a drift field to said body to cause the resultant ions to drift to a second region of said body, neutralizing the resultant ions at the second region to produce neutral molecules of said component, extracting said neutral molecules from said second region to a region separated from said body at which the concentration of said component is greater than in said body, and maintaining the pressure of said body within said conduit at a level such that the length of the mean free path of said ions is very much less than the dimensions of said conduit.

28. A method of detecting a substance in a gaseous sample, which comprises forming ions of said substance in said sample by ion-molecule reactions, applying a drift field to said ions to cause them to drift in said field, selectively gating a group of said ions to a first region at a predetermined time, and thereafter at a predetermined time selectively gating a portion of said group from said first region to means for detecting said portion, the recited steps being performed in a space maintained at a pressure such that the length of the mean free path of said ions is very much less than the dimensions of the space, and detecting at least some of the ions of said portion in a manner so as to distinguish them.

29. A method in accordance with claim 28, wherein the time of the last-mentioned gating relative to the first is varied for plural cycles of operation.

30. A method in accordance with claim 28, wherein said pressure is substantially atmospheric.

31. A method in accordance with claim 28, wherein the ions are formed substantially continuously during the performance of the other recited steps.

32. A method in accordance with claim 28, wherein the drift field is applied substantially continuously and unidirectionally during the other recited steps.

33. Apparatus for concentrating a component of a gas, comprising a duct, means for moving a stream of said gas through said duct, an electrode of one polarity having associated therewith a source of reactant ions at a first region of said duct for forming product ions from the molecules of said component, means including an electrode of opposite polarity at a second region of said duct for attracting and neutralizing said product ions, a passage adjacent to the last-mentioned electrode and separated from said stream for withdrawing molecules of said component to a region separated from said stream and at which the concentration of said component is greater than in said stream, and means for maintaining the pressure in said duct at a level such that the length of the mean free path of said ions is very much less than the dimensions of said duct.

34. The apparatus of claim 33, said electrodes being located at opposite sides of said duct and said passage being located at the downstream end of the second-mentioned electrode.

35. The apparatus of claim 34, there being a first grid adjacent to the first-mentioned electrode and a second grid adjacent to the second-mentioned electrode.

36. Apparatus for detecting a substance in a gas, comprising an envelope enclosing spaced electrodes of opposite polarity and provided with a gas inlet, one of said electrodes having associated therewith means including an ionizing source for producing ions of said substance by ion-molecule reactions, means for establishing a steady unidirectional electric drift field between said electrodes, a pair of ion gates arranged in succession between said electrodes, means for opening said gates in succession, means for detecting ions which drift in said field and are passed by said ion gates in a manner so as to distinguish them, and means for maintaining the pressure in said envelope at a level such that the length of the mean free path of said ions is very much less than the dimensions of said envelope.

37. Apparatus in accordance with claim 36, said detecting means comprising means connected to the other of said electrodes for producing an output dependent upon the ions reaching said other electrode.

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38. Apparatus in accordance with claim 36, further comprising a pair of grids between said one electrode and one of said ion gates.

39. Apparatus in accordance with claim 36, wherein each of said ion gates comprises a grid having two interdigitated substantially coplanar sets of grid elements and having means for normally maintaining adjacent elements at equal and opposite potentials with respect to a reference potential, and said means for opening said gates comprising means for placing all of the elements of a grid substantially at said reference potential.

40. Apparatus in accordance with claim 36, wherein said source is a continuous source.

41. Apparatus for separating a component of a gas stream, comprising a duct, means for passing said stream through said duct, an electrode of one polarity at one side of said duct, means including a source of ionizing energy associated with said electrode for producing ions of said components by ion-molecule

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reactions, means including an electrode of the opposite polarity at the opposite side of said duct for neutralizing said ions, an outlet for said component adjacent to the second-mentioned electrode at the downstream end of said duct and separate from the main flow path of said duct for extracting the neutralized ions to a region separated from said stream and at which the concentration of said component is greater than in said stream, and means for maintaining the pressure in said duct at a level such that the length of the mean free path of said ions is very much less than the dimensions of said duct.

42. Apparatus in accordance with claim 41, further comprising a pair of grids in said duct adjacent to said electrodes, respectively.

43. Apparatus in accordance with claim 42, further comprising means for establishing an electric drift field between said electrodes.

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