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Wernlund et al.

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[54] **APPARATUS AND METHODS FOR MEASURING ION MASS AS A FUNCTION OF MOBILITY**

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[52] **U.S. Cl.** **250/283**

[51] **Int. Cl.** **H01j 39/34**

[58] **Field of Search** . 250/41.9 TF, 41.9 SE, 41.9 G, 250/41.9 S

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Assistant Examiner—B. C. Anderson
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[57] **ABSTRACT**

Ion mass is determined directly as a function of the drift time in a chamber containing gas at atmospheric pressure. The drift time is a function of approximately the cube root of the ion mass for ion mass greater than the mass of the drift gas and a function of approximately the square root of the ion mass for ion mass less than the mass of the drift gas. A measure of the ion mass may be obtained by recording the ion-current output of the drift tube with the time base adjusted to an exponential function of the drift time. Corrections may be made automatically for variations in temperature, pressure and drift field.

23 Claims, 6 Drawing Figures

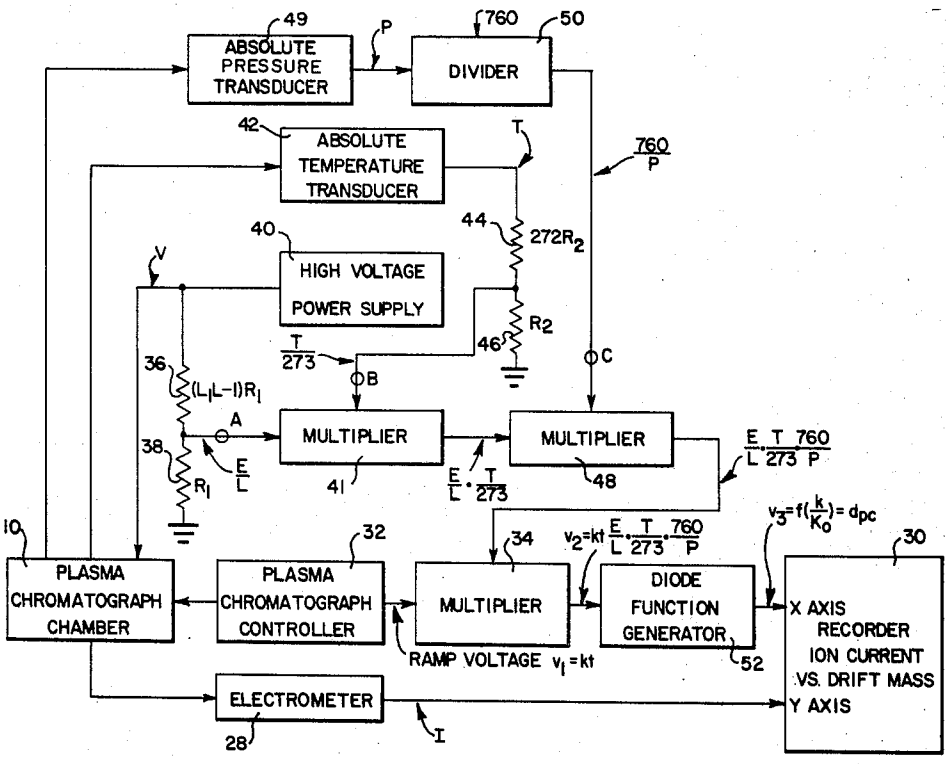
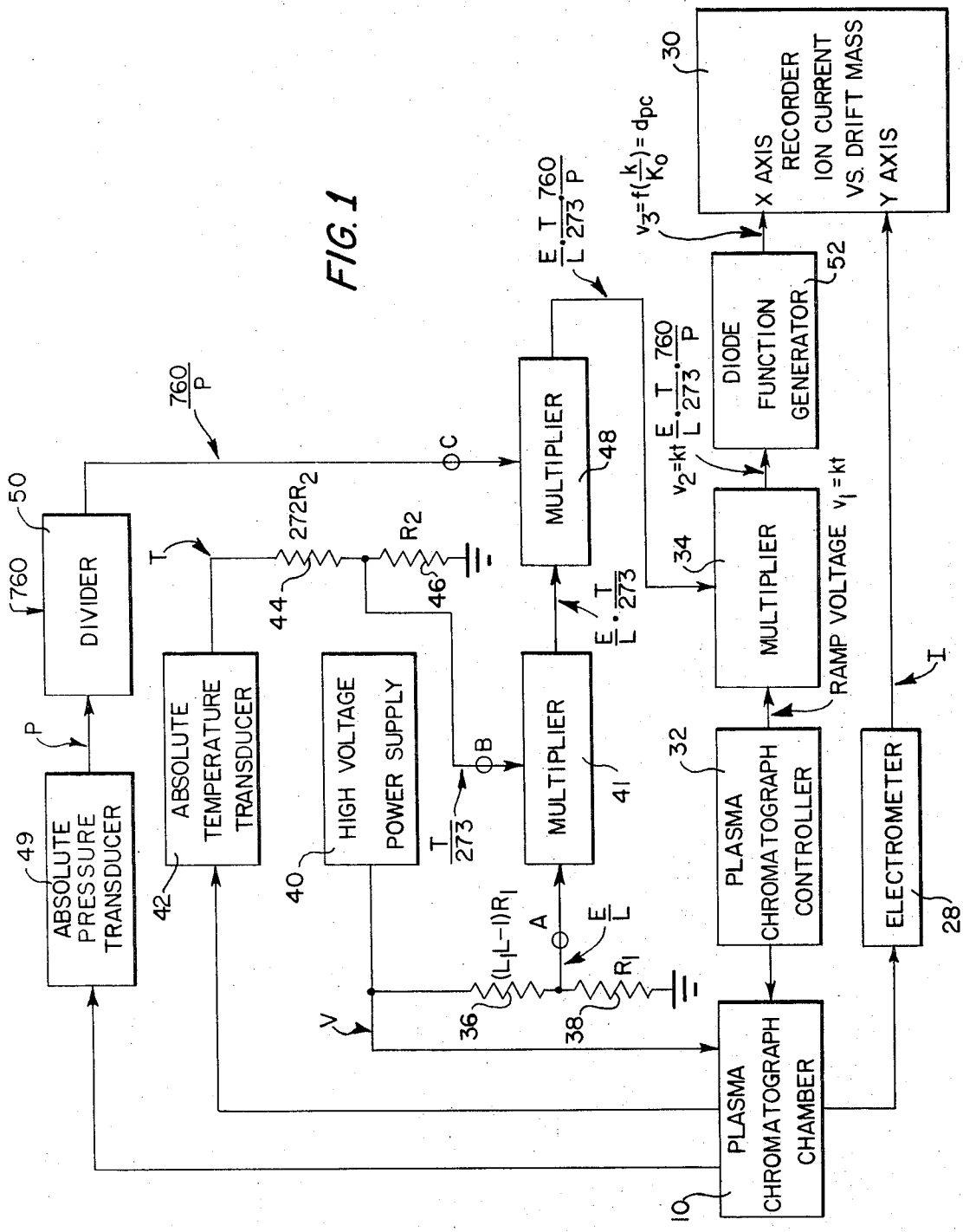


FIG. 1


ABSOLUTE PRESSURE TRANSDUCER
49
P
DIVIDER
50
760
P
760
P
ABSOLUTE TEMPERATURE TRANSDUCER
42
T
272R2
R2
44
46
HIGH VOLTAGE POWER SUPPLY
40
T
273
ΦB
ΦC
MULTIPLIER
41
MULTIPLIER
48
E T 760
L 273 P
E T
L 273
A
E
L
(L1L-1)R1
R1
36
38
V
34
MULTIPLIER
v2=kt E T 760
L 273 P
DIODE FUNCTION GENERATOR
52
RAMP VOLTAGE v1=kt
PLASMA CHROMATOGRAPH CONTROLLER
32
PLASMA CHROMATOGRAPH CHAMBER
10
ELECTROMETER
28
I
v3=f(k/Ko)=dpc
X AXIS RECORDER ION CURRENT VS. DRIFT MASS
Y AXIS
30

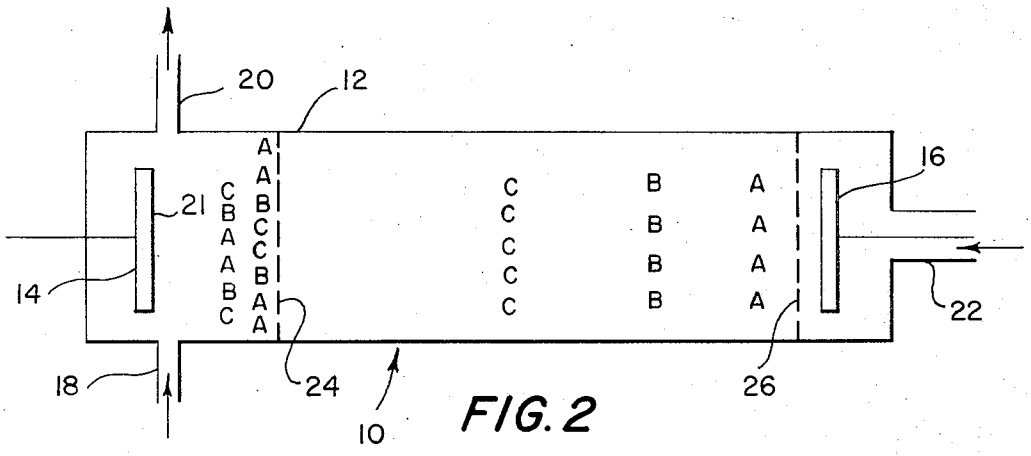

20
12
16
21
14
22
18
24
26
10
A
A
B
C
C
B
A
A
C
B
A
A
B
C
C
C
C
C
B
B
B
B
A
A
A
A

FIG. 2

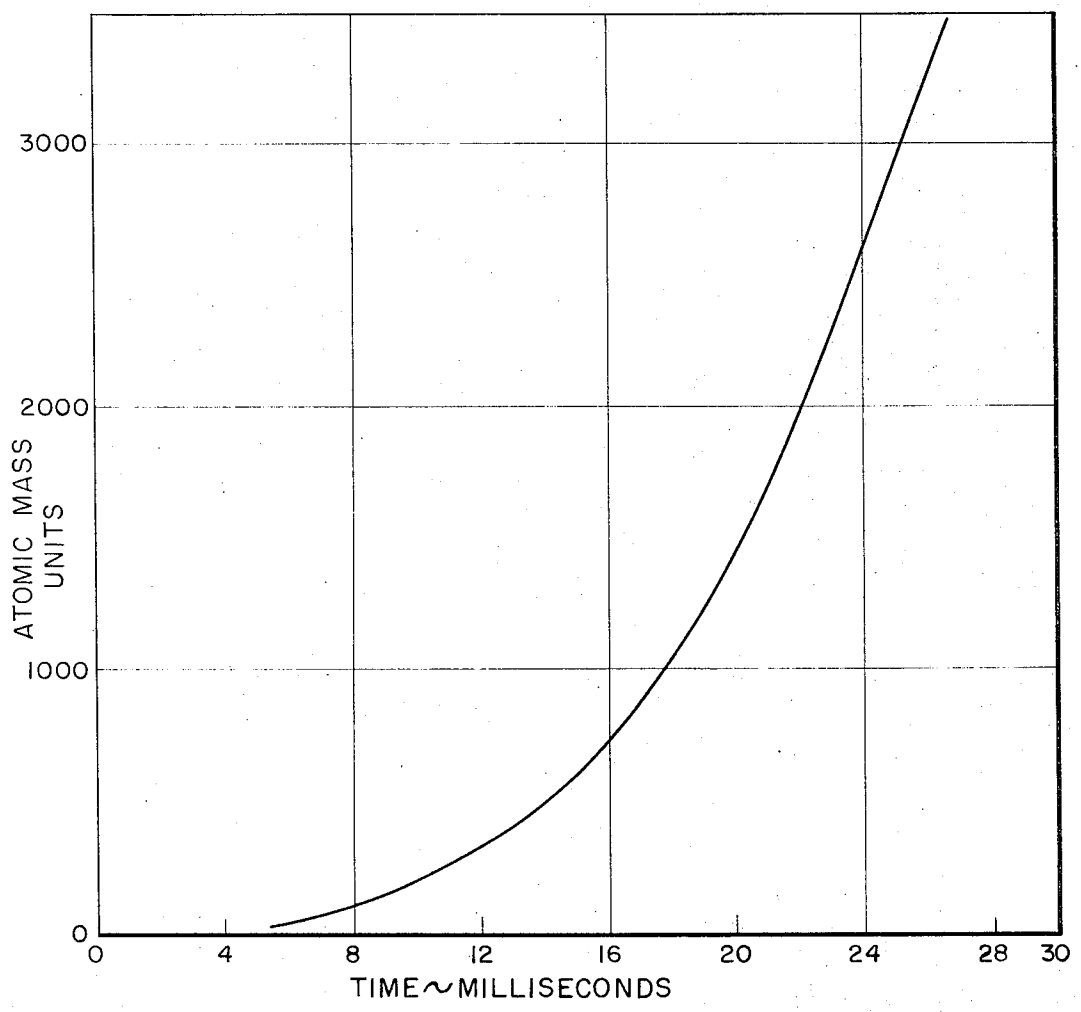

3000
2000
1000
0
ATOMIC MASS UNITS
0
4
8
12
16
20
24
28
30
TIME ~ MILLISECONDS

FIG. 5

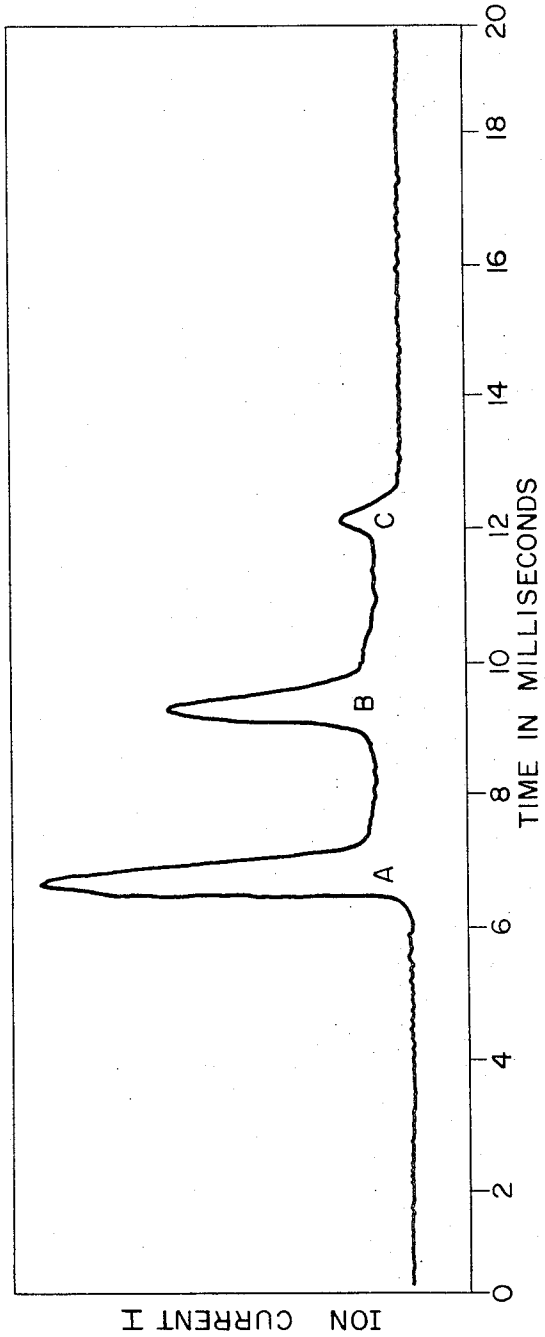

ION CURRENT I
0
2
4
6
8
10
12
14
16
18
20
TIME IN MILLISECONDS
A
B
C

FIG. 3

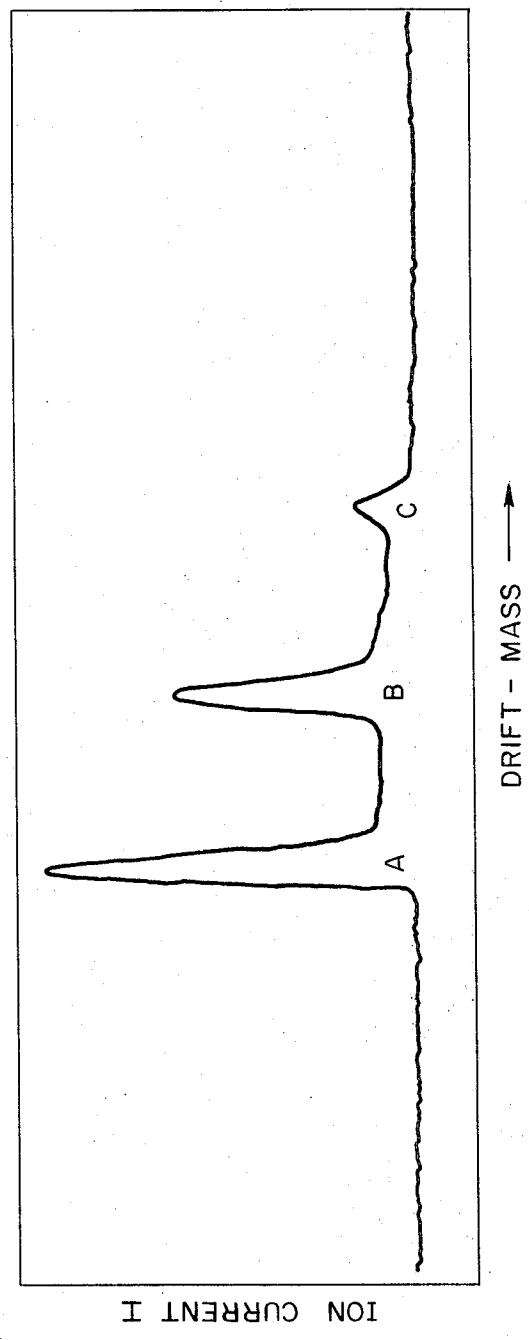

ION CURRENT I
A
B
C
DRIFT - MASS

FIG. 6

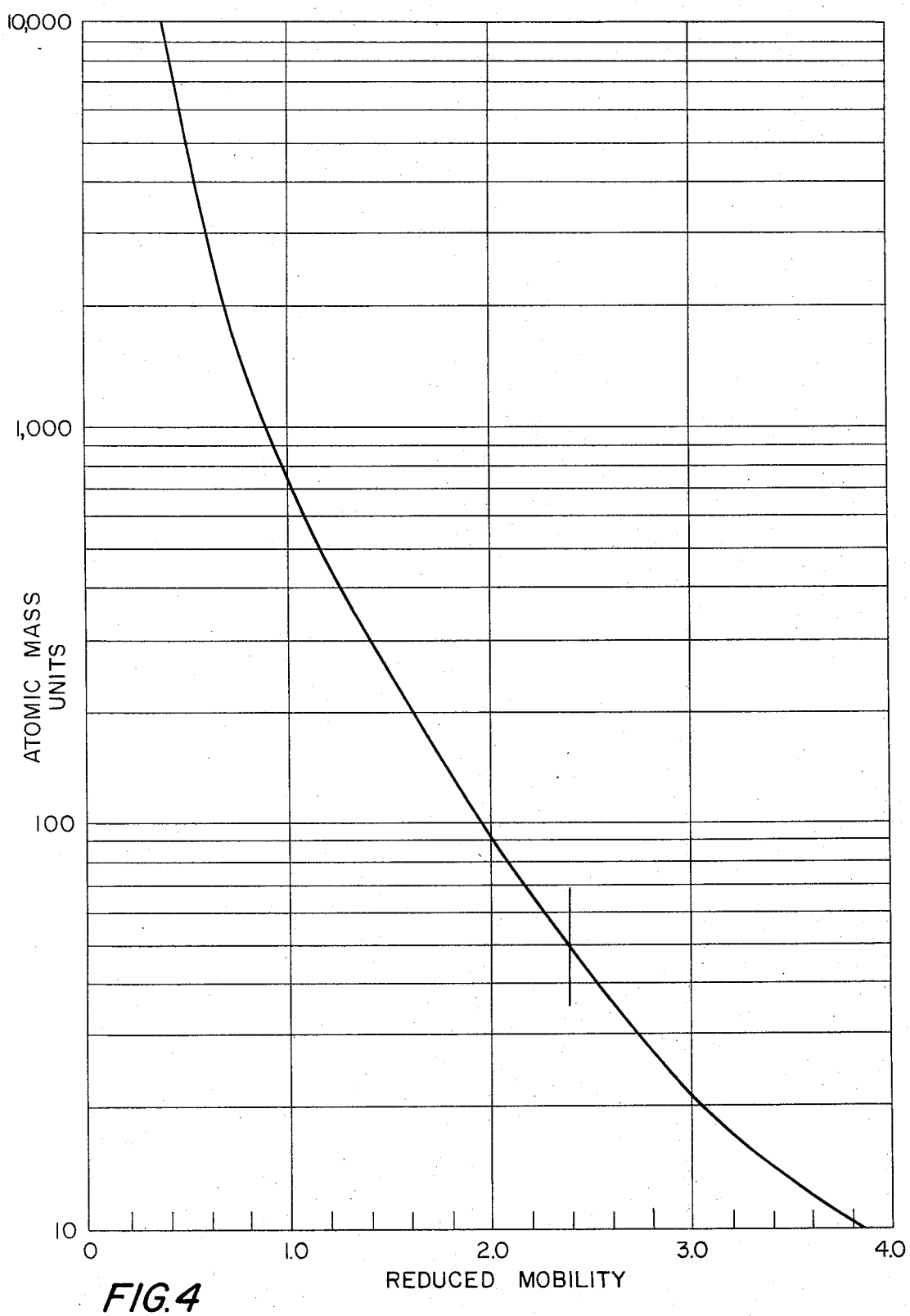

10,000
1,000
100
10
ATOMIC MASS UNITS
0
1.0
2.0
3.0
4.0
REDUCED MOBILITY

FIG. 4

APPARATUS AND METHODS FOR MEASURING ION MASS AS A FUNCTION OF MOBILITY

BACKGROUND OF THE INVENTION

This invention relates to Plasma Chromatography and is more particularly concerned with the measurement of ion mass directly from a Plasma Chromatograph chamber operating at atmospheric pressure.

The basic concepts of Plasma Chromatography are now well-known. See, for example, "The Plasma Chromatograph", *Research/Development*, March, 1970. In the Plasma Charomatograph, which preferably operates at atmopsheric pressure, product ions are produced by ion-molecule reactions, and the ions are caused to drift in an electric field toward a detector, becoming segregated in accordance with their mobility in the drift field. The output of the Plasma Chromatograph may be a recording in which ion species are represented by the peaks of a curve of ion current versus drift time. In order to measure the mass of the ion species, it has been necessary to inject ions from the Plasma Chromatograph chamber into a conventional mass spectrometer (lacking the usual ion source).

BRIEF DESCRIPTION OF THE INVENTION

It is a principal object of the present invention to provide a measure of ion mass directly from the Plasma chromatograph.

Another object of the invention is to provide a method and apparatus for measuring the mass of trace molecules at atmospheric pressure.

Still another object of the invention is to provide apparatus and method for measuring the mass of molecules over a very wide range, and up to the order of 5,000 to 10,000 atomic mass units.

A further object of the invention is to provide simple instrumentation for measuring the mass of molecules on a linear or logarithmic scale.

A still further object of the invention is to provide instrumentation of the foregoing type in which variations due to pressure, temperature, or drift field changes may be compensated automatically or manually.

Briefly stated, in a preferred embodiment of the invention trace molecules are converted to ions by ion-molecule reactions and are subjected to a drift field in a chamber containing a drift gas at atmospheric pressure. The ions are segregated in accordance with their mobility in the drift field and are collected to produce an ion current, pulses of which correspond to ion species of different mobility. By recording these pulses with respect to a time base which varies exponentially as a function of drift time, a direct measure of the mass of the molecules (ions) is obtained.

BREIF 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 block diagram of a system in accordance with the invention;

FIG. **2** is a somewhat diagrammatic longitudinal sectional view of a Plasma Chromatograph drift chamber;

FIG. **3** is a waveform diagram illustrating the output of the Plasma Chromatograph as a function of drift time;

FIG. **4** is a graphical diagram illustrating the relationship of drift-mass and reduced mobility in accordance with the invention;

FIG. **5** is a graphical diagram illustrating the relationship of drift-mass and time of drift in accordance with the invention; and

FIG. **6** is a waveform diagram illustrating the output of an instrument of the invention from which drift-mass can be read directly.

A basic Plasma Chromatograph chamber **10** is shown in FIG. **2** and comprises an envelope **12** containing a pair of spaced electrodes **14** and **16** adjacent to opposite ends of the envelope, the electrodes being separated by several centimeters, for example. An inlet **18** is provided adjacent to electrode **14** for the admission of a sample, and an outlet **20** is provided also. An ionizer **21** is provided adjacent to electrode **14** and may comprise a tritium film supported on the electrode, for example. A sample, which may comprise a host gas, such as air at atmospheric pressure, containing trace molecules, such as DMSO, is admitted by the inlet **18,** passes the ionizer **21,** and leaves the envelope by way of the outlet **20.** Reactant ions of a reactant gas, which may be part of the sample, are produced by the ionizer, and product ions of the trace molecules are formed as the result of ion-molecule reactions involving the reactant ions. The length of the mean free path of the ions is very much less than the dimensions of the reaction region.

An electric drift field is established between electrodes **14** and **16** by a high voltage power supply. The polarity of the field is selected to cause the ions to drift from the reaction region adjacent to electrode **14** toward the collection region at electrode **16.** A non-reactive (inert) gas, such as nitrogen, is admitted to the chamber by an inlet **22,** leaving the chamber by way of outlet **20.** The drift gas fills the drift region between a pair of spaced shutter grids **24** and **26,** the first of which is in the vicinity of the electrode **14** and the second of which is adjacent to the collector electrode **16.** Each grid comprises a pair of coplanar, interdigitated, parallel-wire grid sections, whereby alternate wires of the grid may normally be held at equal and opposite potentials with respect to a grid average potential, which may be applied to the grids from taps of a voltage divider across the high voltage power supply. Uniformity of field between the electrodes **14** and **16** may be maintained by a series of guard rings (not shown) also connected to taps of the voltage divider.

A mixed ion population, represented by the letters A, B, and C in FIG. **2,** is presented to the first shutter grid **24** from the reaction region between electrode **14** and shutter grid **24.** At a predetermined time the shutter grid is opened, by driving each of the grid sections to the grid average potential, and remains open long enough to pass a group of ions to the drift region between the grids **24** and **26.** The various ion species, A, B, and C, become segregated in the drift region in accordance with their mobility, each species reaching substantially constant statistical drift velocity characteristic of the ion species. The separate species may then be passed to the collector **16** by opening the second shutter grid **26** at an appropriately delayed time with respect to the opening of the first shutter grid **24.** The collector may be connected to an electrometer, for example, which integrates the ion current over successive cycles. By scanning the time of opening of grid **26**

relative to grid **24**, substantially the entire ion population within the drift region may produce output pulses as a function of drift time as shown in FIG. **3**.

The Plasma Chromatograph has very high sensitivity for the detection of trace molecules capable of engaging in ion-molecule reactions, but in the past it has been necessary to employ a conventional mass spectrometer in tandem with the Plasma Chromatograph chamber in order to determine the mass of the molecules (ions). In accordance with the present invention, however, it has been discovered that a measure of the mass can be taken directly from the Plasma Chromatograph output, thereby making it possible to perform mass measurements at atmospheric pressure and avoiding the need for the complexity and high vacuum of the mass spectrometer. The term "drift-mass" will be utilized herein to connote the measured ion mass, to account for the fact that in some instances the measured mass may be affected by the molecule configuration. The term "reduced mobility" connotes the measured mobility normalized to standard temperature and pressure conditions.

As shown in FIG. **4**, it has been discovered that there is an exponential relationship between the drift mass (expressed in atomic mass units) and the reduced mobility K_o. When the ion mass M_i is less than the mass of the drift gas M_o, the mobility approaches a Langevin polarization dependence, $K_0 \sim (M_r)^{-1/2}$, where M_r is the reduced mass defined by $1/M_r = 1/M_i + 1/M_0$. For M_i greater than M_o, the reduced mobility K_o approaches an inverse cubic dependence, $K_0 \sim M_i^{-1/3}$. This is illustrated by the curve of FIG. **4** (where drift mass is on a logarithmic scale), the portion to the right of the vertical line being in accordance with the square root relationship and the remainder of the curve, to the left of the vertical line, being in accordance with the cube root relationship. The region where $M_i = M_o$ is a transition region. Where the drift air or nitrogen at atmospheric pressure, it has been discovered that the square root relationship holds up to $M_i \sim 50$ to 100 AMU, and that above this, the cube root relationship exists. Since the time of drift is inversely proportional to the reduced mobility, the same relationship may be shown in terms of drift mass versus time of drift as in FIG. **5** (drift-mass being shown on a linear scale).

FIG. **1** illustrates a system of the invention for obtaining a direct readout of drift mass. In effect, this system converts the drift time axis of FIG. **2** to a drift-mass axis. The Plasma Chromatograph chamber **10** (previously described) has its output connected to the electrometer **28**, which integrates the ion current as described previously. The output of the electrometer is connected to the Y-axis input of an X–Y recorder **30** which is employed to produce the direct readout of ion current versus drift mass as shown in FIG. **6**. In order that the Y-axis ion current pulses from the electrometer **28** may be positioned along the X-axis so as to produce a direct readout of drift mass, d_{pc}, a time base v_3 must be generated in accordance with the equation:

$$v_3 = f(k/K_o) = d_{pc}$$

such that the time base varies as a square function of drift time for M_i less than M_o and as a cube function of drift time for M_i greater than M_o (k being an arbitrary constant). If the mass of the drift gas is low enough, the molecules of interest may have a mass greater than that of the drift gas and the cube function alone may suffice.

The reduced mobility K_o is related to the electric field E (volts per centimeter), drift length L (centimeters), absolute temperature T (degress Kelvin), absolute pressure P (Torr) and drift time t (seconds) by the relationship

$$1/K_o = E/L \times T/273 \times 760/P \times t.$$

Thus, to obtain the voltage v_3, the factors E, L, T, P, and t must be considered.

As shown in FIG. **1**, a ramp voltage $v_1 = kt$ is obtained from the Plasma Chromatograph controller **32**. This is a ramp voltage generator synchronized with the pulse which opens the first shutter grid **24** of the Plasma Chromatograph chamber. Each time the shutter grid **24** is opened, the ramp voltage generator commences the generation of a ramp voltage v_1, the amplitude of which varies as a linear function of time t. The ramp voltage v_1 is applied to one input of a multiplier **34**, the other input of which is a voltage equal to $E/L \times T/273 \times 760/P$. This voltage is obtained as follows: A voltage E/L is derived from a voltage divider comprising reisitors **36** and **38** connected in series across the high voltage power supply **40** from which the drift voltage V is obtained. If the applied voltage to the chamber is V (volts) and the overall length of the chamber between the electrodes **14** and **16** is L_1 (centimeters) then $E/L = V/L_1L$, and resistors **36** and **38** are adjusted in value to produce the voltage E/L at the voltage divider tap. This is applied as one input to a multiplier **41**. The other input is a voltage equal to T/273. This voltage is obtained by applying the voltage output of an absolute temperature transducer **42** to a voltage divider comprising resistors **44** and **46** in series, the values of which are adjusted to produce the voltage T/273 at the divider tap. The absolute temperature transducer measures the absolute temperature of the gas in the Plasma Chromatograph chamber. Any conventional temperature transducer which produces an output voltage which varies linearly with absolute temperature may be employed. The product output of multiplier **41** is a voltage $E/L \times T/273$, and this is applied as one input to a multiplier **48**, the other input of which is a voltage equal to 760/P. This voltage is obtained by applying a voltage P, the output of an absolute pressure transducer **49**, to a divider **50**, the other input of which is a voltage equal to 760. The pressure transducer measures the pressure of the gas in the Plasma Chromatograph chamber and may be any conventional absolute pressure transducer producing an output voltage which varies linearly with pressure.

The product output of multiplier **48** is the voltage $E/L \times T/273 \times 760/P$, which is applied to multiplier **34**.

The product output of multiplier **34** is a voltage $v_2 = kt \times E/L \times T/273 \times 760/P$. This is applied to a diode function generator **52**, which generates the voltage v_3 referred to previously.

The multipliers and dividers referred to above may be operational amplifiers connected to muliply or to divide. The function generator **52** may be an operational amplifier diode function generator, the successive sections of which may be adjusted to approximate many arbitrary functions. The multiplier or the divider may be a Teledyne Philbrick Nexus Model 4450 or

Model 4452, or Burr Brown Model 4029/25 or Model 4030/25. The diode function generator may be a Burr Brown Model 4062/45 or a Teledyne Philbrick Nexus Model SPFX.

The diode function generator may be set empirically so as to produce an X-axis time base which varies in the manner set forth above. Thus, test runs may be made with known ion species and a plot of drift mass (known) versus time of drift (measured) obtained as in FIG. **5**. The function generator **52** may then be adjusted to modify the time base so that the ion current pulses (Y-axis) are produced at times linearly (or logarithmically, if desired) proportional to drift mass, as indicated in FIG. **6**.

If desired, one or more of the functions providing automatic correction of electric field, temperature, or pressure may be replaced by a calibrated potentiometer, which may be manually set to the proper value corresponding to the condition in the plasma Chromatograph chamber, by breaking the circuit at point A, B, or C and substituting the appropriate manually set voltage. The unused portions of the circuit would then be replaced by the appropriate voltage, temperature, or pressure indicator.

From the foregoing, it is apparent that the invention permits a measurement of drift mass by a Plasma Chromatograph directly. Empirically, it has been found that reduced mobility is characteristic of the mass of each ion species when measurements are performed at 760 Torr and E/P~0.5 volts/Torr-centimeter. The relationship between ion mass and reduced mobility extends to very high ion mass values, of the order of 10,000 AMU. The measurement of drift-mass in accordance with the invention produces highly useful data which may be used in conjunction with other data, such as the output of a gas chromatograph or the output of another Plasma Chromatograph drift-mass instrument using a different drift gas. By employment of such a family of instrumentation, chemical identification is possible.

In some instances two molecules of identical mass but of different atomic arrangement may result in different mobility measurements. Where the mass of the ion is the same as or double the drift gas mass, spurious ion-molecule resonance effects can affect the results. Therefore, the ion mass may be considered as lying in a band centered on the drift mass-mobility calibration curve rather than directly on the curve.

Resolution may sometimes be improved by employing a heavier drift gas then a drift gas such as nitrogen, for example. With nitrogen as the drift gas (molecular weight 28), an ion with the molecular weight of 10 times this (280) loses drift-mass resolution from a molecule of, say, 300 AMU, because the curvature of the drift-mass calibration curve at the heavier masses has a steeper slope as compared to the lighter masses, which are near the drift gas mass. If, however, the drift gas is raised in weight to, say, 146 (SF_6), then the same effect on resolution would not be observed until 10 times this weight or mass, or until about 1,500. Resolution of even heavier masses may be possible with the freons as drift gas. Xenon is another suitable drift gas.

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.

The invention claimed is:

1. In a method wherein ions are caused to drift through a drift space containing a drift gas of known mass and at a pressure sufficient to ensure that the length of the mean free path of said ions in said space is substantially less than the dimensions of said space, the improvement for producing a measure of ion mass which comprises producing an output which varies approximately as a cube function of the drift time for ion masses greater than the atomic mass of the drift gas.

2. A method in accordance with claim **1**, wherein said output is produced approximately as a square function of the drift time for ion masses less than the mass of the drift gas.

3. A method in accordance with claim **1**, wherein the ions are produced by ion-molecule reactions in a reaction space maintained at a pressure such that the length of the mean free path of the ions is substantially less than the dimensions of the reaction space.

4. A method in accordance with claim **1**, wherein the pressure is such that the ions reach substantially constant statistical drift velocity in the drift space.

5. A method in accordance with claim **1**, wherein the ions are caused to drift in said space by the application of an electric drift field thereto.

6. A method in accordance with claim **5**, wherein the producing of said output comprises producing an ion current at a time delayed with respect to the commencement of ion drift.

7. A method in accordance with claim **6**, wherein the producing of said output comprises making a recording of said ion current along a time base which varies as an exponential function of the drift time.

8. A method in accordance with claim **7**, wherein the time base varies as a function of the temperature and pressure of the gas in said space and the potential across said space.

9. A method in accordance with claim **6**, wherein said ions are segregated in accordance with their mobility in the drift space and the ion current is produced in response to the segregated ions.

10. A method in accordance with claim **8**, wherein the segregating of the ions comprises gating a group of ions into the drift space and later gating a portion of the group to an ion collector.

11. In apparatus including a drift chamber, means including a pair of spaced electrodes for producing a drift field in said chamber, means providing a drift in said chamber at a pressure such that the length of the mean free path of ions in said chamber is substantially less than the dimensions of the drift space between said electrodes, means for providing ions adjacent to one of said electrodes, means for producing an ion current in response to ions adjacent to the other electrode, the improvement which comprises means for producing an output measure of ion mass in response to said ion current as an exponential function of the drift time.

12. Apparatus in accordance with claim **11**, said function being initially approximately a square function of the drift time and then being approximately a cube function of the drift time.

13. Apparatus in accordance with claim **11**, said function being approximately a cube function of the drift time.

14. Apparatus in accordance with claim 11, said output producing means comprising a recorder having a time base which varies in accordance with said function.

15. Apparatus in accordance with claim 11, wherein said function includes factors corresponding to the temperature and pressure of said gas and the strength of said field.

16. Apparatus in accordance with claim 11, said output producing means comprising means for generating a potential.

17. Apparatus in accordance with claim 16, wherein said potential generating means comprises means for producing a ramp voltage and an exponential function generator controlled by said ramp voltage.

18. Apparatus in accordance with claim 17, wherein said function generator is a diode-type function generator.

19. Apparatus in accordance with claim 17, wherein said drift chamber has means for initiating a drift period synchronously with the commencement of said ramp voltage.

20. Apparatus in accordance with claim 17, further comprising means for producing a voltage proportional to the drift field, means for producing a voltage proportional to the absolute temperature of said gas, means for producing a voltage inversely proportional to the absolute pressure of said gas, and means for obtaining the product of said voltages and controlling the function generator in response thereto.

21. Apparatus in accordance with claim 17, said output producing means comprising a recorder having orthogonal coordinate axes, one of which is a time base axis, means for controlling the time base in accordance with the output of said function generator, and means responsive to the ion current for controlling recording along the remaining axis.

22. Apparatus in accordance with claim 11, wherein said ion providing means comprises means including an ion source adjacent to said one electrode for providing product ions by ion-molecule reactions.

23. Apparatus in accordance with claim 11, wherein said chamber has a pair of ion gates spaced apart between said electrodes and means for opening and gates sequentially, whereby ions produced adjacent to said one electrode are admitted to the space between said gates and become segregated in accordance with their mobility and whereby a portion of the segregated ions is passed by the second gate to the other electrode.

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