

[54] APPARATUS AND METHODS EMPLOYING
ION ANALYSIS APPARATUS WITH
ENHANCED GAS FLOW

3,621,240 11/1971 Cohen et al. 250/41.9 G
3,626,180 12/1971 Carroll et al. 250/41.9 TF
3,697,749 10/1972 Wernlund 250/41.9 G

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[51] Int. Cl. H01j 39/34

[58] Field of Search 250/41.9 TF, 41.9 G, 286,
250/287

[56] **References Cited**

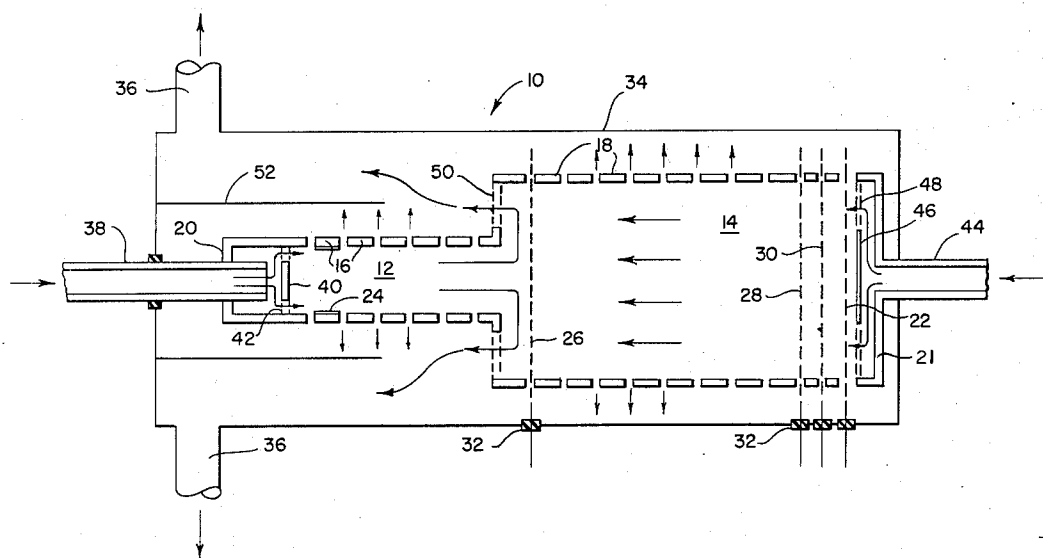
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[57] **ABSTRACT**

Plasma chromatograph response time is decreased by improvement of the gas flow. An ion-molecule reaction region is provided in tandem with a larger diameter drift region, and a gas outlet is provided at the junction of the regions. Sample gas flowing through the ion-molecule reaction region into the drift region is re-directed by a counter-flow of drift gas through the drift region, causing both gases to exit through the outlet and reducing intrusion of the sample gas into the drift region. Diffuse gas flow is employed in both regions, special structures being provided to avoid gas jetting.

42 Claims, 6 Drawing Figures



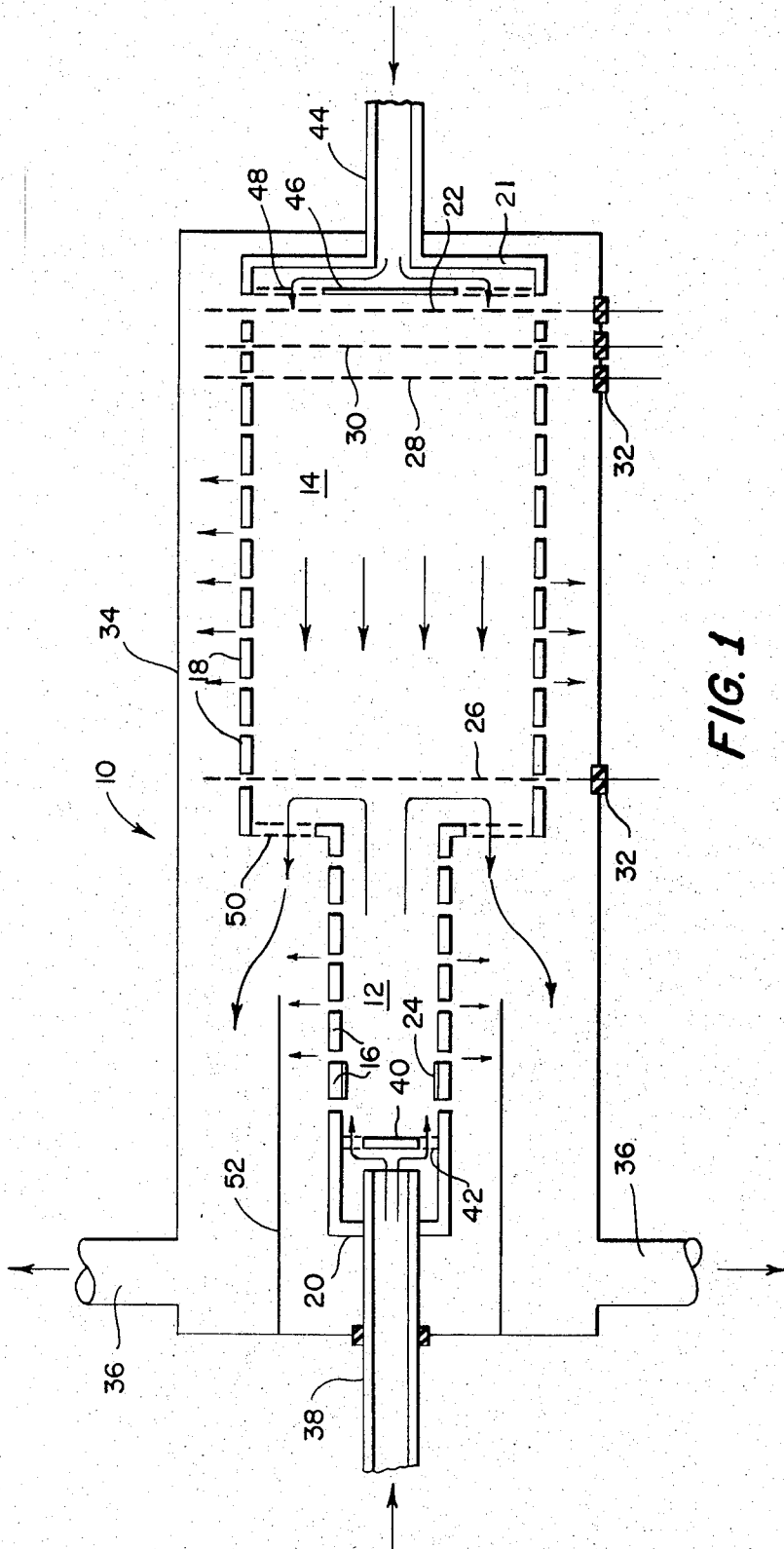


FIG. 1

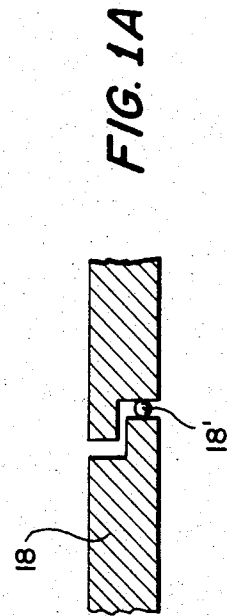
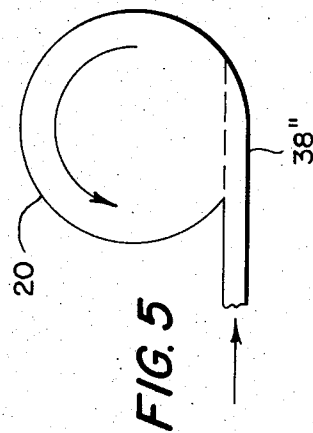
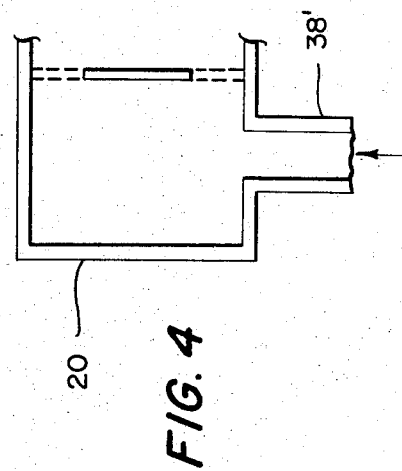
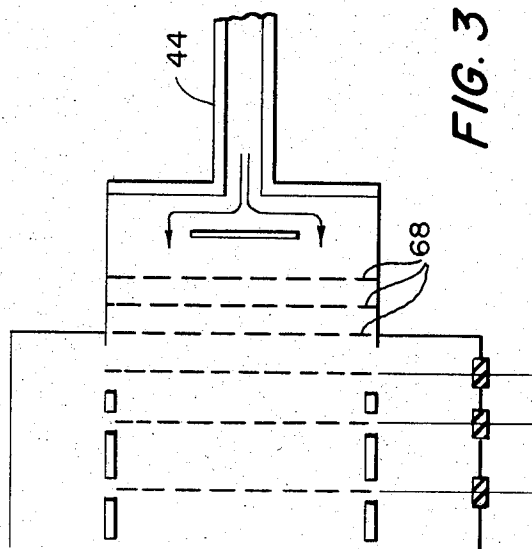
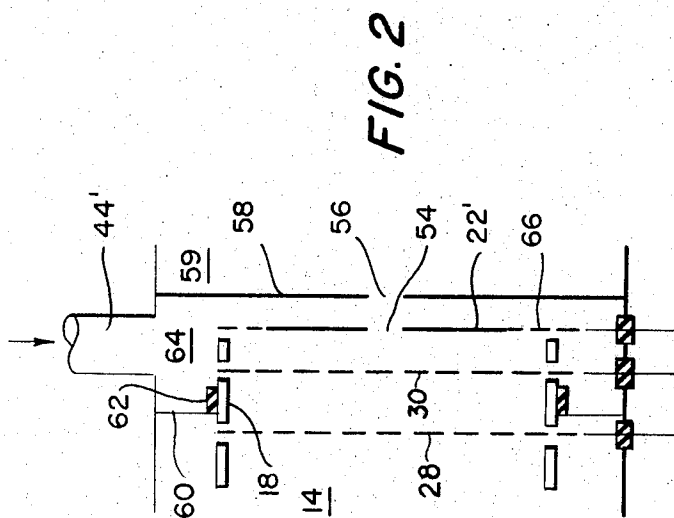


FIG. 1A



APPARATUS AND METHODS EMPLOYING ION ANALYSIS APPARATUS WITH ENHANCED GAS FLOW

BACKGROUND OF THE INVENTION

This invention relates to apparatus and methods for performing measurements upon gaseous samples and is more particularly concerned with improving the response time of trace gas measurement apparatus and methods.

The present invention has special applicability to the field of "Plasma Chromatography," which is described, for example, in U.S. Pat. No. 3,626,180, granted Dec. 7, 1971, and assigned to the same assignee as the present application. It will be apparent to those skilled in the art, however, that certain aspects of the invention have applicability to other fields as well.

Plasma Chromatography involves the formation of primary or reactant ions and the reaction of such ions with molecules of trace substances to form secondary or product ions, which may be concentrated, separated, detected, and measured by virtue of the difference of velocity or mobility of the ions in an electric field. The primary ions may be produced by subjecting the molecules of a suitable host gas, such as air, to ionizing radiation, the ions being subjected to an electric drift field which causes them to move in a predetermined direction through a reaction space into which the sample or trace gas is introduced. The resultant ion-molecule reactions produce the product ions. Plasma Chromatography is performed at a pressure, preferably atmospheric, such that the length of the mean free path of the ions is very short compared to the dimensions of reaction and drift regions, providing efficient generation of product ions and permitting the ions to reach substantially constant, mass-dependent, statistical drift velocity, so that they may be readily segregated for detection as separate ion species.

As set forth in the aforesaid prior patent, it has been proposed to employ a non-reactive or inert drift gas in order to reduce or quench ion-molecule reactions in the drift region. The utilization of such a drift gas reduces interfering ion species and enhances resolution of the desired ion species in the Plasma Chromatogram.

Despite the employment of a non-reactive drift gas in the drift region (with the attendant improvement referred to above), the sample gas intrudes into the drift region to an undesired extent, reducing the effectiveness of the drift gas and increasing the time required to clear the sample and reaction products from the Plasma Chromatograph substantially beyond that which would be required if the drift region were maintained largely free of sample gas.

BRIEF DESCRIPTION OF THE INVENTION

It is accordingly a principal object of the present invention to provide improved ion analysis apparatus and methods.

Another object of the invention is to provide improved gas flow in a Plasma Chromatograph or the like.

A further object of the invention is to provide an improved Plasma Chromatograph structure.

Briefly stated, the present invention employs an ion-molecule reaction region in tandem with a drift region

of larger diameter. At the junction of the regions, a gas outlet is provided. The regions are defined by two series of guard rings, which maintain uniformity of an electric field established between electrodes at the remote ends of the reaction and drift regions. A sample gas is admitted to the reaction region adjacent to an ionizer and is caused to flow diffusely toward the drift region. A drift gas is similarly admitted to the drift region and is caused to flow diffusely toward the reaction region. Both gases pass through the outlet, with the flow of drift gas being sufficient to re-direct the sample gas and to prevent significant intrusion of the sample gas into the drift region. An ion gate shutter grid, located in the drift region adjacent to the gas outlet, assists in this respect. This grid is employed in conjunction with a second ion gate shutter grid in the drift region to pass selected ion species to an ion detector.

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 diagrammatic longitudinal sectional view of one form of the invention;

FIG. 1A is a fragmentary longitudinal sectional view of a detail of the invention;

FIG. 2 is a fragmentary diagrammatic longitudinal sectional view of a modification;

FIG. 3 is a similar view of another modification;

FIG. 4 is a similar view of another modification; and

FIG. 5 is a diagrammatic transverse sectional view of a further modification.

Referring to the drawings, and initially to FIG. 1 thereof, reference numeral 10 designates a Plasma Chromatograph of the type generally disclosed in the aforesaid prior patent. In the present invention, the ion-molecule reaction region 12 and the drift region 14, arranged in tandem, are, in effect, communicating chambers defined in part by two series of guard rings 16 and 18, the guard rings of the latter series being of larger diameter, so that the drift chamber has larger cross-sectional area transverse to a drift field than the reaction chamber. A unidirectional electric drift field is established between a repeller electrode 20 and a further electrode 21, at the remote ends of the chambers, respectively. The drift field has a polarity dependent upon the polarity of the ions to be detected. An ionizer, such as a tritium or nickel-63 film 24, is provided upon one of the guard rings adjacent to electrode 20. The guard rings may be interconnected by a series of resistors (not shown) to maintain the uniformity of the electric field between electrodes 20 and 21.

The drift chamber 14 is provided with a pair of ion gates, such as shutter grids 26 and 28, adjacent to opposite ends thereof. As set forth in the aforesaid prior patent, each grid is a dual grid formed of interdigitated coplanar grid sections, with the sections normally being maintained at equal and opposite potentials with respect to a grid average potential established by the D.C. supply connected to electrodes 20 and 21 and guard rings 16 and 18. Each shutter grid is opened, for the passage of ions therethrough, by driving the grid sections thereof to the grid average potential. A further grid, a unipotential shield grid 30, may be provided between the second shutter grid 28 and a signal electrode 22. The signal electrode 22 is a fine mesh of about

200/in. The grids 26, 28 and 30 have a porosity of about 50/in. Connections to the grids and other electrodes may be made by leads which pass through insulators 32 in the wall of a metal housing or case 34 which surrounds chambers 12 and 14. Gas exhausts 36 are provided at the reaction chamber end of the housing.

Sample gas is introduced into the reaction chamber by an inlet pipe 38 extending axially of the chambers. The inlet pipe passes into the repeller electrode structure 20 and has a mouth facing a wall 40. The entering gas is thus re-directed transversely and then passes through diffusion screens 42 and past the ionizer 24. By this arrangement, the sample gas is prevented from jetting into and through the reaction region and is caused to flow diffusely from inlet 38 through reaction chamber 12 in the direction of the drift field and toward the junction of the reaction region and the drift region.

A non-reactive drift gas, such as nitrogen or dry air, is introduced into the drift chamber by an inlet pipe 44 extending axially of the chambers. The drift gas is re-directed transversely by a wall 46 spaced from the mouth of the inlet pipe 44 and then passes through diffusion screens 48 and the foraminous signal electrode 22, shield grid 30 and second shutter grid 28. By this arrangement, the flow of drift gas in the drift chamber is diffused, as distinguished from a jet, and is counter to the flow of sample gas in the reaction region.

The bending and screening of the gas flow from the inlets 38 and 44 absorbs and decreases linear gas flow velocity and smooths the flow of gas to a substantially uniform one across the entire diameter of the chambers 12 and 14.

It is necessary that adjacent guard rings be insulated from one another in order to perform their electrical functions. This is achieved by the use of air gaps defined by ball insulators 18' (in appropriate depressions) between successive rings, as shown in FIG. 1A. The ring junctions in the present invention are preferably re-entrant or dove-tailed to provide circuitous paths for gas, as shown in FIG. 1A, to reduce the gas flow between the rings. Thus, although there is some leakage between rings, most of the gas in the reaction chamber 12 and the drift chamber 14 flows the full length of the chambers. The grids may be mounted in rings similar to the guard rings and the entire stack of electrodes, guard rings and grids (with the interposition of ball insulators) may be clamped between end plates (not shown) by means of adjustable longitudinal screw-rods, in a well-known manner.

At the junction of the chambers, a gas outlet 50 is provided. This outlet may be constituted by a plurality of openings or by screens or screen sections in a ventilating guard ring which serves as the end ring of each series and is closer to the drift chamber 14 than the inlet 38. The volumetric flow of drift gas is made substantially higher than the flow of sample gas, preferably from 3 to 10 times higher, so that the drift gas effectively re-directs the sample gas at the chamber junction and so that both gases exit through the outlet 50. The first shutter grid 26, which is adjacent to the outlet, assists in re-directing the sample gas and preventing substantial intrusion of the sample gas into the drift region, the net effect being the formation of a planar gas intersection or boundary. A cylindrical baffle 52, which surrounds the inlet end of the chamber 12, and the provision of the gas exhausts 36 at the locations shown, tend

to prevent pockets of gas from remaining as a result of earlier sample flow and to prevent recirculation of output gas into the ion-molecule reaction region. The slight gas leakage between the guard rings assists in ventilating the case 34.

The electrical operation of the Plasma Chromatograph of the present invention is substantially the same as that set forth in the aforesaid prior patent. Product ion species of different mobility are efficiently produced in the reaction chamber 12, at the preferred atmospheric operating pressure, and reach substantially constant statistical drift velocity dependent upon ion mass. The ion species are sorted by successively opening the grids 26 and 28, selected ion species producing signals at electrode 22, which are detected in the usual manner.

FIG. 2 illustrates a modification of the invention which may be utilized when it is desired to employ the Plasma Chromatograph in conjunction with a mass spectrometer, as set forth, for example, in U.S. Pat. No. 3,621,240, granted Nov. 16, 1971, and assigned to the same assignee as the present invention. In this embodiment, the left portion of which is identical to FIG. 1, a signal electrode 22' is provided with a central aperture 54 aligned with an aperture 56 in a wall 58 separating the Plasma Chromatograph from the mass spectrometer 59, which operates under high vacuum conditions. These apertures pass an ion beam to the mass spectrometer. Wall 58 may constitute the electrode of polarity opposite to that of the repeller electrode. A circular baffle 60 (at case potential) connected to one of the guard rings 18 by an insulating washer 62 (of mica or quartz, for example) provides an annular chamber 64 surrounding the adjacent end of the drift chamber 14 and into which the drift gas may be introduced by means of an inlet pipe 44'. The drift gas enters the drift chamber through openings in an outer perforated portion 66 of electrode 22'. Baffle 60 also serves as an electrical shield between the pulsed grid circuits (shutter grids) and the electrometer circuitry which may be connected to electrode 22' for providing an output directly from the Plasma Chromatograph.

FIG. 3 illustrates an embodiment like FIG. 1, except that additional mesh baffles 68 are provided to assist in smoothing the drift gas flow.

FIG. 4 illustrates a modification of the sample gas outlet. In this instance, the sample gas enters the repeller electrode structure 20 transversely, as shown at 38'. As illustrated in FIG. 5, at 38'', the inlet pipe may be oriented tangentially to create a swirling motion of the sample gas, which assists in producing a more moderate, less jet-like gas flow. Similar orientation of the drift gas inlet 44' in FIG. 2 may be utilized for the same purpose.

In a typical apparatus of the invention, the inner diameter of the reaction region may be about ½ inch and that of the drift region 1 ½ inches. Sample gas flow may range between 50–300 cc/min and drift gas flow between 300–1000 cc/min (the ratio of drift gas to sample gas flow preferably being at least three, as stated previously). The sample gas may be constituted by a sample in an inert carrier, for example.

The improved gas flow of the invention provides much faster reaction region clearing, much faster response, high sensitivity, predictable reaction region performance, and better resolution. Sample and drift gas preheaters may be employed to obtain better uni-

formity of gas temperature in the ion drift region, for further improvement.

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. Ion analysis apparatus and the like comprising an ion-molecule reaction chamber followed by an ion drift chamber communicating therewith, means for establishing a drift field along said chambers, means for introducing a sample gas into said reaction chamber through an inlet and causing said sample gas to flow through said reaction chamber toward said drift chamber, means including an ionizer for forming ions in said reaction chamber by ion-molecule reactions, outlet means for said gas substantially at the junction of said chambers and closer to said drift chamber than said inlet, means for introducing a drift gas into said drift chamber in counter-flow to the flow of sample gas in said reaction chamber, and means for detecting ions after they have drifted in said drift chamber.

2. Apparatus in accordance with claim 1, wherein the cross-sectional area of the reaction chamber transverse to said drift field is substantially less than the cross-sectional area of the drift chamber.

3. Apparatus in accordance with claim 1, further comprising means for diffusing the flow of at least one of said sample gas and drift gas.

4. Apparatus in accordance with claim 3, wherein said diffusing means comprises at least one screen.

5. Apparatus in accordance with claim 3, wherein the diffusing means comprises means for causing the gas to be diffused to change direction as it is introduced.

6. Apparatus in accordance with claim 3, wherein the diffusing means comprises means for causing swirling movement of the gas to be diffused.

7. Apparatus in accordance with claim 6, wherein the means for causing swirling movement of the gas to be diffused comprises means for directing that gas substantially tangentially of the chamber into which it is introduced.

8. Apparatus in accordance with claim 1, wherein the reaction chamber has smaller cross-sectional area transverse to said drift field than the drift chamber, and the gas outlet is provided through an end of the drift chamber.

9. Apparatus in accordance with claim 1, each of said chambers being defined in part by a series of electric field guard rings.

10. Apparatus in accordance with claim 9, adjacent rings being insulated from one another and providing controlled gas leakage paths therebetween.

11. Apparatus in accordance with claim 1, said drift chamber having a grid thereacross adjacent to the junction of said chambers.

12. Apparatus in accordance with claim 11, said drift chamber having a further grid thereacross remote from the first-mentioned grid, said detecting means comprising a signal electrode following said further grid, said grids being ion gates for selectively passing ions to said signal electrode.

13. Apparatus in accordance with claim 1, said reaction chamber having smaller cross-sectional area transverse to said drift field than said drift chamber, and

means for diffusing the flow of sample gas substantially throughout said reaction chamber.

14. Apparatus in accordance with claim 13, wherein said means for introducing a drift gas into said drift chamber in counter-flow to the flow of sample gas in said reaction chamber includes means for supplying said drift gas at a volumetric flow rate at least several times the flow rate of the sample gas.

15. Apparatus in accordance with claim 14, further comprising foraminous means for forming a substantially planar boundary between said gases adjacent to said outlet.

16. Apparatus in accordance with claim 1, wherein said means for introducing a drift gas into said drift chamber comprises a chamber surrounding one end of said drift chamber.

17. Apparatus in accordance with claim 1, further comprising a housing surrounding said chambers and having a gas exhaust therefrom.

18. Apparatus in accordance with claim 17, wherein said gas exhaust is located at an end of said housing remote from said drift chamber.

19. Apparatus in accordance with claim 18, said housing having a baffle therein surrounding the end of said reaction chamber remote from said drift chamber.

20. Apparatus in accordance with claim 1, wherein said drift chamber has an electrode therein with an aperture therethrough for the passage of ions to a further chamber for detection.

21. Apparatus in accordance with claim 1, said detecting means comprising a foraminous electrode in said drift chamber, and said means for introducing a drift gas into said drift chamber including means for passing said drift gas through said electrode.

22. Apparatus in accordance with claim 1, further comprising means for maintaining the pressure in said chambers at a level such that the length of the mean free path of ions therein is substantially less than the dimensions of the chambers.

23. Apparatus in accordance with claim 1, wherein said chambers are defined in part by electric field guard rings, said gas outlet being provided through one of said guard rings.

24. A method of ion analysis, which comprises providing communicating ion-molecule reaction and drift chambers in tandem, with the drift chamber having larger cross-sectional area than the reaction chamber and with a gas outlet from the region of the junction of said chambers, causing a sample gas to flow from an inlet to said reaction chamber and along said reaction chamber in a direction toward said drift chamber and said junction, producing product ions from said sample gas by ion-molecule reactions in said reaction chamber, applying a drift field along said chambers in the direction of said sample gas flow and causing said ions to pass from said reaction chamber and then through said drift chamber, detecting at least a portion of the ions in said drift chamber, and causing a drift gas to flow through said drift chamber toward said junction in counter-flow to the flow of sample gas and at a sufficient volumetric flow rate to re-direct said sample gas through the gas outlet.

25. A method in accordance with claim 24, further comprising maintaining the pressure in said chambers at a level such that the mean free path of ions therein

is short compared to the dimensions of said chambers.

26. A method in accordance with claim 24, further comprising segregating the ions in said drift chamber in accordance with their drift velocity.

27. A method in accordance with claim 24, wherein the pressure in said drift chamber is maintained high enough to cause said ions to reach substantially constant statistical drift velocity dependent upon ion mass.

28. A method in accordance with claim 24, further comprising causing said sample gas to flow diffusely through said reaction chamber and into said drift chamber.

29. A method in accordance with claim 28, further comprising causing said drift gas to flow diffusely along said drift chamber.

30. A method in accordance with claim 24, wherein said sample gas is introduced axially of said reaction chamber and is then re-directed.

31. A method in accordance with claim 24, wherein said drift gas is introduced axially of said drift chamber and is then re-directed.

32. A method in accordance with claim 24, wherein at least one of said sample gas and said drift gas is caused to swirl as it flows.

33. Ion analysis apparatus comprising an ion-molecule reaction chamber communicating with an ion drift chamber, means for producing ions by ion-molecule reactions in said reaction chamber, means for establishing a drift field along said chambers for causing ions to move along said reaction chamber and into and along said drift chamber, means for segregating ions in said drift chamber in accordance with their drift velocity, means for detecting at least some of the segregated ions, the cross-sectional area of said reaction chamber transverse to said drift field being substantially less than the cross-sectional area of said drift chamber, and means for introducing a sample gas into said reaction chamber and a drift gas into said drift chamber in counter-flow.

34. Apparatus in accordance with claim 33, further comprising means for causing said gases to flow diffusely in said chambers, respectively, across substantially the entire chamber cross-sectional areas.

35. Apparatus in accordance with claim 33, said chambers being defined at least in part by electric field guard rings.

36. Apparatus in accordance with claim 33, further comprising means for maintaining the pressure in said chambers at a level such that the mean free path of ions in said chambers is short compared to the dimensions of said chambers and such that said ions reach substantially constant mass-dependent statistical drift velocity in said drift chamber.

37. Ion analysis apparatus comprising an ion-molecule reaction chamber communicating with an ion drift chamber, means for introducing a sample gas into

said reaction chamber, means for introducing a drift gas into said drift chamber, means for producing ions by ion-molecule reactions in said reaction chamber, means for establishing a drift field along said chambers for causing ions to drift along said reaction chamber and into and along said drift chamber, means for segregating ions in said drift chamber in accordance with their drift velocity, means for detecting at least some of the segregated ions, means for causing the gases to flow in said chambers, respectively, in counter-flow and means including a gas diffusion screen for causing at least said sample gas to flow diffusely through said reaction chamber and preventing said sample gas from jetting into said drift chamber.

38. Apparatus in accordance with claim 37, further comprising means providing a gas outlet adjacent to the junction of said chambers and means for supplying said drift gas to said drift gas introducing means at a volumetric flow rate sufficient to prevent substantial intrusion of said sample gas into said drift chamber.

39. Apparatus in accordance with claim 38, further comprising means for forming a substantially planar boundary between said gases adjacent to said outlet.

40. Apparatus in accordance with claim 39, the last-mentioned means comprising a grid across said drift chamber.

41. Ion analysis apparatus comprising a chamber, means for introducing a sample gas into said chamber, means for producing ions in said chamber from said sample gas, means for establishing an electric drift field along said chamber, means for detecting at least some of the ions after the ions have moved along said chamber, and a series of guard rings spaced along said chamber for maintaining the drift field along said chamber, said guard rings having circuitous junctions for controlling the leakage of gas therebetween by causing it to flow along circuitous paths.

42. Ion analysis apparatus and the like comprising an envelope having a pair of electrodes spaced apart therein, means for introducing a sample gas into said envelope, means including an ionizer adjacent to one of said electrodes for forming ions of said sample by ion-molecule reactions, means for establishing a drift field between said electrodes and causing said ions to drift toward the other of said electrodes, shutter grid means between said electrodes for segregating ions in the space between said electrodes in accordance with their drift velocity, means adjacent to said other electrode for detecting at least some of the segregated ions, a plurality of guard rings arranged in series between said electrodes and spaced from said envelope, and means including an annular shield extending between one of said rings and said envelope for shielding the detector means from said shutter grids and for introducing a drift gas into said envelope in counter-flow to said sample gas.

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