Trace components of a gaseous sample are separated at atmospheric pressure in a drift cell by producing ions of the trace gases through ion-molecule reactions and by separating the resultant product ions in accordance with drift velocity. A molecular beam, including product ions from the drift cell, passes through a transition region, where the ions are focused and separated from neutral molecules, to a mass analyzer. In the analyzer, the product ions are separated in accordance with mass and selectively passed to an ion counter. The mass analyzer and ion counter are maintained at high vacuum.
APPARATUS AND METHODS FOR DETECTING AND IDENTIFYING TRACE GASES

BACKGROUND OF THE INVENTION

This invention relates to apparatus and methods for detecting and identifying either positive or negative ions of trace gases in an ambient sample. Prior techniques for the analysis of trace gases, such as gas chromatography or mass spectrometry, are deficient in one or more of the following respects: (1) the necessity of obtaining discrete samples of the gas to be analyzed, (2) fragmentation of the parent material, (3) the requirement of long measurement times.

The copending application of Martin J. Cohen, David I. Carroll, Roger F. Wernlund, and Wallace D. Kilpatrick, Ser. No. 777,964, filed Oct. 23, 1968, and entitled "Apparatus and Methods for Separating, Concentrating, Detecting, and Measuring Trace Gases", discloses a technique, termed "Plasma Chromatography", by which measurements upon trace gases can be performed continuously at atmospheric pressure, without collecting discrete samples and without modification of the parent materials. Moreover, the measurements can be performed very rapidly (in seconds) and at high sensitivity (of the order of one part in 10^6, for example). Succinctly stated, the system of that application involves the formation of primary or reactive ions from a reactant gas and the reaction of the primary ions with molecules of trace substances to form secondary or product ions, which can be measured, detected, and measured by virtue of the velocity or mobility of the ions in an electric field. A significant advantage of the system is that measurements are preferably performed at or about atmospheric pressure. The resolution of the apparatus described in the copending application is, however, not as great as that of gas chromatography, for example, and therefore, some ambiguity may exist where it is desired to identify particular trace gas constituents of the sample.

BRIEF DESCRIPTION OF THE INVENTION

It is accordingly a principal object of the present invention to provide apparatus and methods for measuring trace gases at atmospheric pressure, such as in ambient air, and yet to identify the gas components with far greater accuracy than has heretofore been possible.

A further object of the invention is to provide apparatus and methods of the foregoing type which do not require the collection of discrete samples, which avoid modification of parent materials, and which operate rapidly and at high sensitivity.

Briefly stated, the present invention is concerned with a measurement technique in which ions of trace gases are formed as the product of ion-molecule reactions in a drift cell operated at atmospheric pressure. The primary ions are separated in accordance with their drift velocity and are passed in a molecular beam to a mass analyzer, operated at a high vacuum, via a transition region at which the ions are focused and the neutral molecules of the molecular beam are separated from the ions. Ions selected by the mass analyzer are counted or otherwise detected.

BRIEF DESCRIPTION OF THE DRAWING

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

FIG. 1 is a diagrammatic perspective view of one form of the invention.

FIG. 2 is a diagrammatic longitudinal sectional view of a second form of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1 of the drawing, apparatus in accordance with the invention comprises a Plasma Chromatograph 10, a mass analyzer 12 connected to the Plasma Chromatograph via a transition section 14, and an ion detector 16. The Plasma Chromatograph, which is shown quite diagrammatically in FIG. 1, is illustrated in greater detail in FIG. 2. Such apparatus is disclosed in the aforesaid copending application, and, in an improved form, in the copending application of David I. Carroll, Martin J. Cohen, and Roger F. Wernlund, Ser. No. 780,851, filed Dec. 3, 1968, and entitled "Apparatus and Methods for Separating, Detecting, and Measuring Trace Gases with Enhanced Resolution".

Broadly, the "Plasma Chromatography" technique involves the production of primary ions by subjecting the molecules of a host gas, such as air, to ionizing radiation, for example. The primary ions are subjected to an electric drift field, causing them to migrate in a predetermined direction through a reaction space into which the sample or trace gas is introduced. The resultant collisions between the primary ions and the trace gas molecules produce secondary ions of the trace gas in much greater numbers than can be produced by mere electron attachment, for example, to the trace gas molecules. The secondary or product ions are also subjected to the drift field. Because the drift cell of the Plasma Chromatograph is operated (preferably at atmospheric pressure) so as to maintain the mean free path of the product ions much smaller than the dimensions of the drift cell, the ions reach statistical terminal velocity in the drift field dependent upon their mass and may be sorted in accordance with their velocity or mobility.

Specific systems of the copending applications employ a pair of successively-arranged ion shutter grids or gates for segregating the ion species in accordance with their drift time. The opening of the first gate is timed to pass a group of ions, which may comprise unreacted primary ions as well as secondary or product ions, and the opening of the second gate is timed to pass a portion of the group to an ion detection means.

In the Plasma Chromatography apparatus illustrated in FIG. 2 of the drawing (representative of FIG. 1), a drift cell is employed which comprises part of an envelope 11, of metal for example, having a sample inlet 13 and an outlet 26. The envelope contains a series of spaced electrodes, which may have parallel plane geometry, for example, and which may include a pair of principal electrodes C and A and a pair of shutter grids or ion gates G1 and G2. If the apparatus is to be employed to detect negative ions, electrode C will be the cathode and electrode A will be an anode, while if positive ions are to be detected, the polarities will be reversed. The electrodes may be spaced-apart distances of the order of a few centimeters or less (for example, cathode to anode spacing of about 10 centimeters) and may have suitable lead wires passing through the envelope by means of insulators (not shown).

Electrode C or the region of the envelope near this electrode is provided with an ionizing means, such as a photo emission source, a radioactive source, a multiple point or wire array (corona) source, or an RF ionization source. In the form shown, the ionizer I is a radioactive source, such as tritium foil. The foil may be placed at the end of the inlet tube 13 which exits through an opening in electrode C.

The grids G1 and G2 may be of the parallel wire type. Alternate wires of each of the grids are connected together to form two separate groups, so that each shutter grid comprises two interdigitated subgrids of parallel wires. Adjacent elements of each grid are normally maintained at equal and opposite potentials relative to a grid average potential, 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 contained within the block 17. The components of this block are effective to drive the adjacent elements of each shutter grid to the same potential, the grid average potential, at predetermined instants. The grids per se and the circuits for driving the same are known in the art and need no further elucidation.

Electrode A would, in the Plasma Chromatograph of the type disclosed in the aforesaid copending applications, serve as a collector plate connected to an output divider. In the present invention, this electrode also serves as an apertured
3,621,240

partition to permit ions to exit from the drift chamber 18 in the envelope 11, the electrode being provided with a central aperture 19 for the passage of a molecular beam.

An electric drift field is provided between electrodes C and A. In the form shown, the source of drift field is a battery 20 connected across a resistor chain 22, taps of which provide static potentials for the electrodes contained within chamber 18. In the embodiment of the invention illustrated in FIG. 2, electrode A is connected to ground, as is the positive side of the battery 20, and the negative side of battery 20 is connected to electrode C. The grid average potential for grid G1 is provided by connecting each subgrid through a series resistor (not shown) to the same point on the resistor chain 22. The grid drive potentials are applied to the junctions of the series resistors and the subgrids, respectively. Grid G2 is similarly supplied. A series of guard rings 24 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 resistor chain. Suitable supports and spacers, such as quartz rods and tubes, may be employed to support the various electrodes within the envelope. The apparatus of the invention also preferably includes an additional inlet 15 through which a nonreactive gasser such as, as nitrogen, may be introduced into the envelope as described in copending Application Ser. No. 780,851.

In an illustrative operation of the Plasma Chromatograph 10, air carrying a suitable ionizable gaseous trace substance, such as methane or SF₆, flows into the chamber 18 by means of the inlet 13 and is ionized through the outlet 26. Any suitable source of flow pressure, such as a fan, may be employed to move the carrier gas containing the trace substances. In the region adjacent to the ionizer I, ions of the carrier or host gas or one or more of the main constituents thereof, such as oxygen, are formed under the influence of the radiative source at this region. The primary ions may be negative oxygen ions, for example, formed by direct attachment of electrons to the oxygen molecules. The ions drift toward electrode A under the influence of the drift field. In the region between electrode C and grid G1, the primary ions formed at electrode C react with molecules of the trace vapor to convert these molecules to product ions. Further ion-molecule reactions are quenched by the nonreactive gas supply by inlet 15.

During operation of the apparatus, shutter grid G1 is periodically opened to sample the products of the reaction and any other ions present. The opening of grid G1 at a predetermined time and for a predetermined duration (for example, milliseconds) initiates a time-dependent process during which a group of ions is passed into the ion mobility analysis region between G1 and G2. As the ions drift from G1 to G2 they become grouped or classified in accordance with the velocity (a function of ion mass) in the drift field. Because the mean free path of the ions in chamber 18 is much less than the chamber dimensions (by virtue of the relatively high-atmospheric pressure), statistical terminal velocity is reached. At a predetermined time, delayed relative to the opening of grid G1, grid G2 is opened for a predetermined duration to select a portion of the ion mobility spectrum within the region G1 to G2 for passage toward electrode A. Those ions which impinge upon electrode A produce an output current which may be measured by an electrometer (not shown). The output current varies in time according to the characteristic drift time of each species as the various species traverse the drift cell. The ions are normally detected as pulses and thereby permit a time display for the ion species present. By scanning the time of opening of grid G2 relative to G1, the entire drift spectrum may be displayed.

Returning now to FIG. 1, the Plasma Chromatograph 10 is assumed to be constructed and to operate like that of FIG. 2, rings 28 being a diagrammatic representation of the grids G1 and G2 and the guard rings 24 of FIG. 2. The product ions passed toward electrode A are sampled by the aperture 19, a sample of the ions being passed through the aperture as part of a molecular beam or jetstream containing neutral gas molecules and product ions. The aperture operates under the viscous flow conditions, the neutral gas flow being augmented by the aperture being small compared to the aperture diameter.

The thickness of the thin wall-sampling aperture is less than the aperture diameter in order to minimize wall interaction with the ions transported through the aperture. The transition section 14 of the envelope 11 comprises a chamber 30 connected by a pipe 32 to a vacuum system for pumping out the chamber (to a vacuum of say 0.5 to 2 Torr). There is thus a supersonic expansion of the jetstream at the aperture 19 from the high-pressure (760 Torr) conditions in chamber 18 to the vacuum conditions in chamber 30.

The transition section transposes ions from an ambient pressure region to a substantially lower pressure region without substantial modification either of the quantity of the ions transferred or the species of the ions transferred. The centrally apertured electrodes 34 (aperture diameter 0.005 to 0.015 inch, for example) in the transition section are diagrammatic representations of conventional ion-focusing electrodes for focusing the product ions into a beam and for preventing dispersion of the ions within the transition region. Neutral gas molecules in this region are separated from the ion beam by virtue of the vacuum pumping. The series of apertures is radially transparent to gas velocities in the molecular beam and opaque to ion velocities in the molecular beam. Ion Species of the Plasma Chromatograph are preserved at all times, so that mass analysis is not subject to the extensive fragmentation found in conventional ion-source spectrometers. Further, the maximum number of ions present in the ambient atmosphere is extracted and introduced efficiently into the mass analyzer. High trace gas sensitivity is provided by concentration (focusing) of the charged carriers, but the fields are kept low enough to avoid changes in ion species.

The beam of ions passes from the transition region 14 to the mass analyzer 12 through an aperture 36 in an electrode A' upon the wall of chamber 38, which constitutes a further portion of the envelope 11, an accelerating potential being applied between electrodes A and A'. The input potential to the mass analyzer is set for the dual purpose of setting the ion velocity and reducing ion losses (analog to ion focusing). The mass analyzer is of a conventional type. The preferred quadrupole type (readily adapted to both positive and negative ions as well as ion counting), comprising the usual rectangular arrangement of elongated electrodes 40 is shown, although other types, such as time-of-flight, magnetic deflection, or RF separator, may be employed. An accelerating potential is applied between electrodes A' and A'' at opposite ends of chamber 38. By virtue of the conventional operation of the mass analyzer, including variation of electrical parameters, as is well known in the art, the product ions are separated in accordance with their mass, and selected ions are passed to the ion detector 16 through an aperture 42 in electrode A'' upon the wall of the detector chamber 44, which forms a further section of the envelope 11. Both the mass analyzer and detector sections are maintained at high vacuum by connection of the pipes 46 and 48 to a high-vacuum system. The pressure in chamber 38 may be 10⁻⁴ Torr or less to reduce ion scattering. The mean free path of ions in chamber 38 is much longer than that in chamber 18 and is preferably substantially longer than the dimensions of the mass analyzer structure, so that the mass analyzer operates under molecular flow conditions. Fast pumping speeds for the neutral gas in the mass analyzer are essential. However, the sampling technique removes such small quantities of gas from chamber 18 that measurements in the Plasma Chromatography drift cell can be accomplished under essentially static conditions.

In order to maintain high sensitivity, the detector preferably an ion-counting device capable of registering 1 to 10,000 counts per second. In the form shown, the detector employs an electron multiplier including a series of dynodes 50 in a conventional arrangement for producing secondary
The charged particles detected may be charged atoms or clusters, as well as charged molecules, and the terms "ion" and "ion-molecule reactions" are intended as comprising such particles.

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. A method of detecting trace gas which comprises forming primary ions at a localized region of a first chamber, forming product ions of different mobility at a further region of said first chamber by ion-molecule reactions involving said primary ions and molecules of said trace gas, applying a drift field to said ions and causing them to drift toward a second chamber, maintaining the pressure in said first chamber at a high enough level such that the mean free path of the ions in said first chamber is very small compared to the dimensions of said first chamber and such that said ions reach substantially constant statistical terminal velocity in said first chamber dependent upon their mass and charge in accordance with their mobility, passing said product ions to said second chamber, main-
taining the pressure in said second chamber at a substantially lower level than that in said first chamber such that the mean free path of the product ions in said second chamber is substantially longer than the mean free path in said first chamber, analyzing said product ions in said second chamber in accordance with their mass, and detecting at least some of the analyzed ions.

2. A method in accordance with claim 1, in which the pressure in said first chamber is maintained at a substantially lower level than that in said second chamber.

3. A method in accordance with claim 1, in which a gas inert and nonreactive with respect to said ions is introduced to said first chamber.

4. A method in accordance with claim 1, in which the product ions are formed into a beam before being passed to said second chamber.

5. A method in accordance with claim 1, in which the product ions are detected in a third chamber.

6. A method in accordance with claim 5 in which said product ions are detected in said third chamber by generating secondary electrons in response thereto.

7. A method in accordance with claim 5, in which said product ions are accelerated in passing from said second chamber to said third chamber.

8. A method in accordance with claim 5, in which said product ions are detected individually in said third chamber.

9. A method in accordance with claim 1, in which the product ions formed in said first chamber are divided by ion gating.

10. A method in accordance with claim 1, in which the product ions are focused into a beam before being passed to said second chamber.

11. A method in accordance with claim 1, in which said product ions are transposed from said first chamber to said second chamber as part of a supersonic jetstream molecular beam, and in which the neutral molecules of said beam are separated from product ions of said beam before said product ions are passed to said second chamber.

12. A method in accordance with claim 1, in which said product ions are detected by producing scintillations therefrom.

13. A method in accordance with claim 1, in which said primary ions are formed by ionizing a reactant gas.

14. A method in accordance with claim 13, in which said trace gas and said reactant gas are supplied to said first chamber as a gaseous sample.

15. Apparatus for performing ion measurements, which comprises an envelope having successive chambers, means within the first of said chambers for forming primary ions at a localized region of said first chamber and for forming different mobility product ions at a further region of said first chamber by ion-molecule reactions involving said primary ions and molecules of a sample gas, means for subjecting said ions to a drift field and causing them to drift toward a second chamber of said envelope means for maintaining the pressure in said first chamber at a high enough level such that the mean free path of said ions in said first chamber is very much smaller than the chamber dimensions and such that said ions react substantially constant statistical terminal velocity in said first chamber dependent upon their mass and separate in accordance with their mobility, means for passing product ions from said first chamber to said second chamber, means for maintaining the pressure in said second chamber substantially lower than the pressure in said first chamber such that the mean free path of said product ions in said second chamber is substantially longer than that in said first chamber, means for separating said product ions in said second chamber in accordance with their mass, and means for detecting at least some of the last-mentioned product ions.

16. Apparatus in accordance with claim 15, said means for passing said product ions from said first chamber to said second chamber comprising an intermediate chamber having means for maintaining the pressure therein at a level between the pressures of said first and second chambers.

17. Apparatus in accordance with claim 16, said intermediate chamber having means associated therewith for forming product ions into a beam.

18. Apparatus in accordance with claim 16, said intermediate chamber having means associated therewith for passing product ions thereto from said first chamber as part of a supersonic jetstream molecular beam and having means for separating neutral molecules of said beam from said product ions.

19. Apparatus in accordance with claim 16, said intermediate chamber being coupled to said first chamber by a various flow aperture.

20. Apparatus in accordance with claim 16, said intermediate chamber having a series of ion-focusing electrodes therein.

21. Apparatus in accordance with claim 15, wherein said first chamber has means for producing primary ions by ionizing a reactant gas.

22. Apparatus in accordance with claim 15, wherein said first chamber has means for introducing therein a gas inert and nonreactive with respect to said ions.

23. Apparatus in accordance with claim 17, said separating means in said second chamber comprising a mass analyzer.

24. Apparatus in accordance with claim 23, said mass analyzer being of the quadrupole type.

25. Apparatus in accordance with claim 15, said ion-detecting means comprising an electron multiplier actuated by said product ions.

26. Apparatus in accordance with claim 15, said first chamber having ion-gating means for passing a group of ions from a first region of said first chamber to a second region thereof and having further ion-gating means for passing a portion of the group of ions from the second region to a third region of said first chamber.

27. Apparatus in accordance with claim 15, said first chamber having a pair of electrodes adjacent to opposite ends thereof and having means for applying said drift field between said electrodes.

28. Apparatus in accordance with claim 15, said means for passing said product ions from said first chamber to said second chamber comprising at least a pair of apertured electrodes.

29. Apparatus in accordance with claim 15, said means for passing said product ions from said first chamber to said second chamber comprising an apertured electrode which diverges from said first chamber toward said second chamber.

30. Apparatus in accordance with claim 15, said means for detecting said product ions comprising a scintillation detector actuated by said ions.

31. Apparatus in accordance with claim 15, further comprising means for accelerating product ions from said first chamber to said second chamber, and means for accelerating product ions from said second chamber to a third chamber for detection.

32. Apparatus in accordance with claim 15, further comprising viscous flow apertured electrode means for decelerating said product ions as the ions pass from said first chamber toward said second chamber, and further comprising means for thereafter accelerating said ions.

33. Apparatus in accordance with claim 15, wherein said detecting means comprises a scintillator and a photomultiplier coupled thereto by an insulating light conductor.

34. Apparatus in accordance with claim 15, wherein said means for subjecting said ions to a drift field comprises a pair of spaced electrodes in said first chamber, said means for forming primary ions comprises a continuous radioactive source adjacent to one of said electrodes, and said means for passing product ions from said first chamber to said second chamber comprises a viscous flow aperture in the other of said electrodes, said further region of said first chamber in which said ion-molecules reactions occur being located between said electrodes.