# United States Patent

[11] 3,629,574


[72] Inventor **David I. Carroll**
**Lantana, Fla.**



[21] Appl. No. **794,742**
[22] Filed **Jan. 28, 1969**
[45] Patented **Dec. 21, 1971**
[73] Assignee **Franklin Gno Corporation**
**West Palm Beach, Fla.**


[54] **APPARATUS AND METHODS FOR SEPARATING ELECTRONS FROM IONS**
**24 Claims, 4 Drawing Figs.**


[52] **U.S. Cl.** ..... **250/41.9 TF,** 250/41.9 G, 250/41.9 DS
[51] **Int. Cl.** ..... **H01j 39/34,** B01d 59/44
[50] **Field of Search** ..... 250/41.91, 41.92, 41.93, 41.9 SB, 41.9 SE, 41.9 G, 43.5 R; 313/63



[56] **References Cited**
UNITED STATES PATENTS

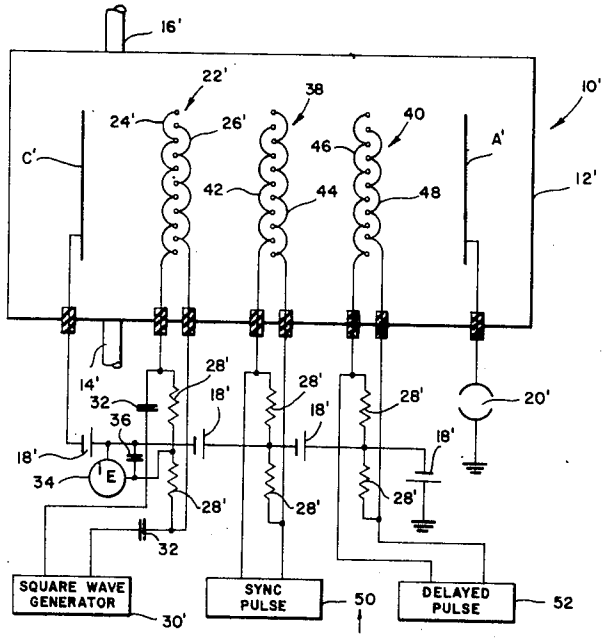
| | | | |
|---|---|---|---|
| 2,772,364 | 11/1956 | Washburn | 250/41.9 |
| 3,154,680 | 10/1964 | Greene | 250/43.5 R |



*Primary Examiner*—James W. Lawrence
*Assistant Examiner*—C. E. Church
*Attorney*—Raphael Semmes



**ABSTRACT:** Electrons are separated from ions by subjecting these charged particles to a drift field to cause them to move from a first region toward a second region and by interposing an electron filter in the drift field between said regions, the filter comprising a pair of grid members to which high-frequency alternating voltages are applied. This principle is applied to an electron capture detector and to a device which separates and detects ions in accordance with their mobility.

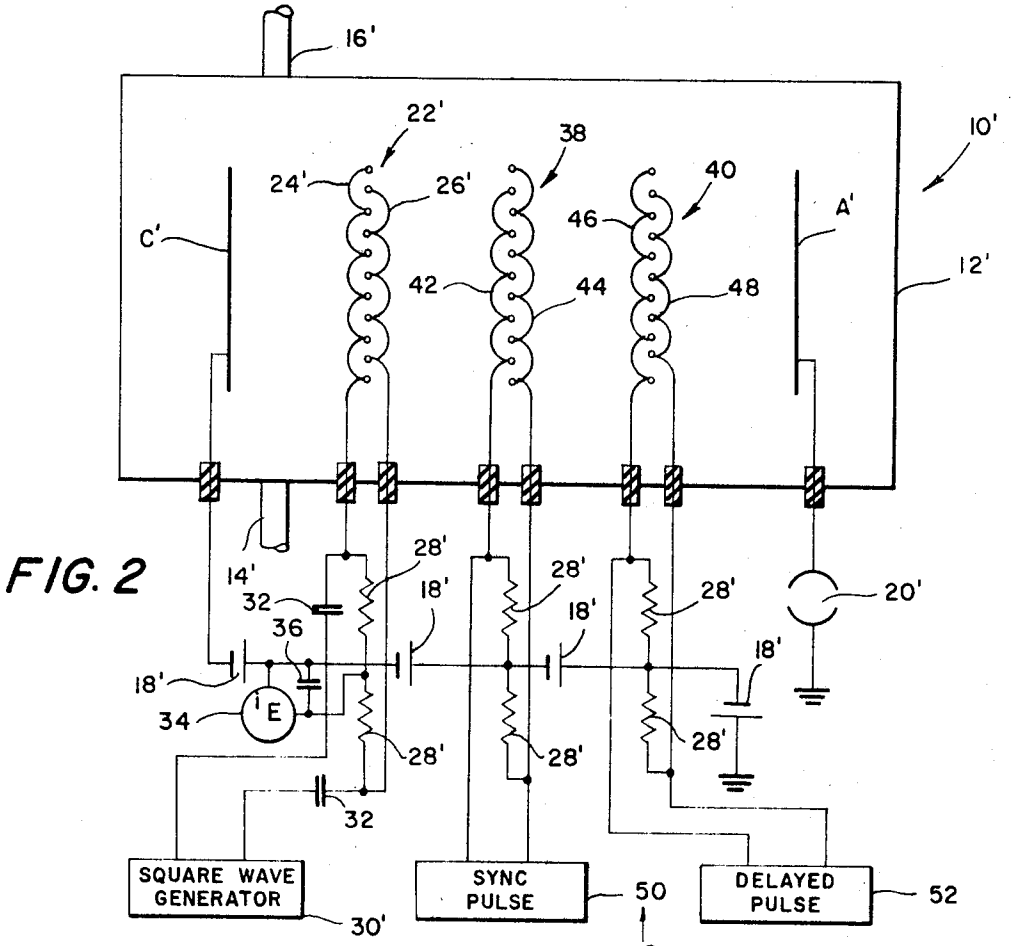



FIG. 2

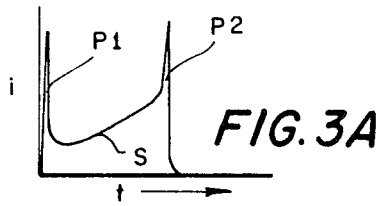



FIG. 3A

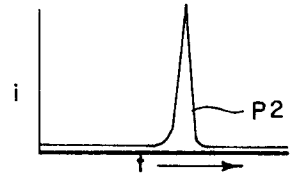



FIG. 3B

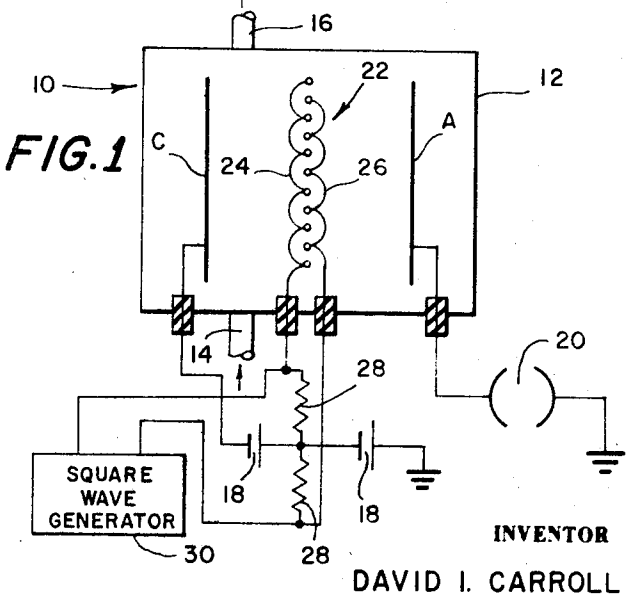



FIG. 1

INVENTOR
DAVID I. CARROLL
BY Raphael Semmes
ATTORNEY

# APPARATUS AND METHODS FOR SEPARATING ELECTRONS FROM IONS

## BACKGROUND OF THE INVENTION

This invention relates to apparatus and methods for separating charged particles of different mass and more particularly is concerned with the separation of electrons from ions.

The electron capture detector (ECD) currently in use depends upon a decrease in the total electron current to detect a substance. This decrease is due to both attachment and recombination. The large electron current "noise" can, in principle, be cancelled out, except for statistics, by bridge techniques, but there will be considerable drift with gas temperature changes. In other types of apparatus, as well as ECD, it is desirable to filter out or separate electrons from ions. For example, 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 "Plasma Chromatography" systems involving the formation of primary or reactant ions and reaction of the primary 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 to ionizing radiation, such as beta rays. Electrons which are not utilized in the production of primary ions may produce a peak in the output current of "Plasma Chromatography" apparatus and may produce interfering ion responses which confuse or obscure peaks produced by ions which it is desired to detect.

## BRIEF DESCRIPTION OF THE INVENTION

It is accordingly a principal object of the present invention to provide improved apparatus and methods for separating charged particles of different mass, and more particularly, for separating electrons from ions.

A further object of the invention is to provide an improved electron capture detector and improved Plasma Chromatography apparatus.

Briefly stated, preferred embodiments of the apparatus and methods of the invention subject the particles to be separated to an electric drift field, so that the particles drift from a first region toward a second region. Interposed between these regions is a filter comprising a pair of grid members to which high-frequency alternating voltages are applied. The relatively fast particles of low mass respond to the alternating potentials and are captured by the grid members, while the relatively slow particles of high mass "see" only the average grid potential and pass through the grid members.

## 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 somewhat diagrammatic schematic view of an electron capture detector in accordance with the invention;

FIG. 2 is a similar view of a Plasma Chromatograph in accordance with the invention; and

FIGS. 3A and 3B are graphs showing output current versus time for the apparatus of FIG. 2 under operating conditions without and with the invention, respectively.

## DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawing, and initially to FIG. 1 thereof, an electron capture detector **10** in accordance with the invention comprises an envelope **12** having a gas inlet pipe **14** and a gas outlet pipe **16** through which samples to be analyzed, such as the effluent of a gas chromatograph, may flow. Principal electrodes C and A are spaced apart in the envelope. An electric drift field is applied between electrodes C and A. In the form shown, the drift field is supplied by a chain of batteries **18**, the negative end of the chain being connected to electrode C and the positive end of the chain being connected to ground. Electrode C or the region of the envelope near this electrode is provided with an ionizing source of electrons, such as a tritium foil. Electrode A is an output electrode connected to a suitable measuring device, such as an electrometer **20**, and is connected to ground through the input circuit of the electrometer.

In accordance with the invention, a filter **22** is interposed in the drift field between electrodes C and A. The filter may comprise a dual shutter grid constituted by two sets of interdigitated parallel wires, alternate wires of grid being connected together to form a pair of interdigitated grid members, **24** and **26**. The grid members **24** and **26** are connected to a reference potential on the battery chain **18** by means of resistors **28**. A source of high-frequency (RF) alternating voltages, such as the square wave generator **30** (or a source of sine waves) is connected to the grid members **24** and **26**, so that the potentials of the grid members alternate oppositely with respect to the grid average potential established by the battery chain **18**. The frequency of the alternating voltages may be in the range from substantially 1 MHz to substantially 10 MHz, for example.

If now a source of ionizable gas to be analyzed is inserted into the envelope **12** from pipe **14**, some of the electrons produced at electrode C will collide with the molecules of the inserted gas and produce negative ions, as by electron attachment. The ions and any remaining electrons will drift in the field toward electrode A. The electrons, which are of light mass relative to that of the ions, will respond to the alternating voltages applied to the grid members **24** and **26** and will be captured by the respective grid members. The slower ions will "see" only the average potential of the grid **22**, however, and will pass through the grid to electrode A and produce a current in the output. The electrons will thus be filtered from the ions, and only the ions will produce an output current in the electrometer **20**. If desired, suitable measuring means may be inserted in the connection between the junction of resistors **28** and the battery chain so as to measure the electron current.

FIG. **2** illustrates the application of the principles of the invention to a Plasma Chromatograph of the type set forth in the above mentioned copending application. The Plasma Chromatograph **10'** comprises an envelope **12'** having an inlet tube **14'** and an outlet tube **16'**. Electrodes C' and A' are spaced apart in the envelope as shown. Again, the electrode C' or the region of the envelope adjacent thereto is provided with an ionizing source of electrons, such as a tritium foil, and the electrode A' is connected to an output current measuring device, such as an electrometer **20'**. Again, a chain of batteries **18'** produces an electric drift field between electrodes C' and A'. In this instance, however, three dual shutter grids are employed. The first grid **22'**, comprising grid members **24'** and **26'**, is identical to that described in connection with FIG. **1**, the grid members being connected through capacitors **32** to the square wave generator **30'**. (Similar capacitors may be employed in the embodiment of FIG. **1** and may form a part of the wave generator **30**.) Measuring device **34**, bridged by capacitor **36**, is connected between the junction of resistors **28'** and the battery chain and measures the electron current $i_E$.

Dual grids **38** and **40** are similar to grid **22'**, comprising interdigitated grid members **42**, **44** and **46**, **48**, respectively, connected to the battery chain through resistors **28'**. Grids **38** and **40** are ion gates, the function of which is described in detail in the aforesaid copending application. A source of sync pulses **50** is connected to grid members **42** and **44**, and, at predetermined times, drives all of the grid wires to the grid average potential established by the battery chain. Normally, grid members **42** and **44** are held at equal and opposite potentials relative to the grid average potential by sources of DC incorporated in block **50**. A source **52** of pulses delayed with respect to the sync pulses from source **50** is connected to grid

members 46 and 48. The delayed pulses drive grid members 46 and 48 to the grid average potential established for grid 40 by the battery chain. Normally, grid members 46 and 48 are also maintained at equal and opposite potentials relative to the grid average potential by DC sources incorporated in block 52. As described in the aforesaid copending application, when the grid members constituting a shutter grid are at equal and opposite potentials, the shutter grid is closed to the passage of ions, but when the grid members are driven to the same potential, the shutter grid is open to the passage of ions.

A sample comprising a host gas, such as air, and a trace gas to be detected, such as Ethion, is introduced into the envelope 12' through pipe 14'. Molecules of the host gas, such as oxygen, will be preferentially ionized by electrons from the source of ionizing radiation at electrode C', and the resulting primary ions will react with the molecules of the trace substance to produce secondary ions. The primary ions, secondary ions, and any unused electrons will drift toward the electrode A' (assuming negative ions and a drift field of appropriate polarity). The electrons will be captured by grid 22', as described in conjunction with FIG. 1, and will produce a resultant current in meter 34. The primary and secondary ions, on the other hand, will pass through grid 22'. At the appropriate moment grid 38 will open to permit the passage of a selected group of ions to the region between grids 38 and 40. In drifting toward the electrode A', the ions will become separated in space in accordance with their relative mass. At the appropriate delayed time relative to the opening of grid 38, grid 40 will be opened to permit a selected species of ions to pass to the detection region between grid 40 and electrode A'. The ions impinging upon electrode A' will produce an output current in the electrometer 20'. By scanning the time of opening of grid 40 relative to the opening of grid 38, a drift time spectrum of the ion population can be obtained in the output and recorded to produce an output curve (current v. drift time). This permits the various secondary ion species to be separated and identified.

FIG. 3A illustrates a representative output curve in the absence of the electron filter of the invention. The first peak P1 is due to the electrons and the second peak P2 is due to the ions formed prior to the first shutter grid 38. The slope S is due to ions formed in the region between the first and second shutter grids 38 and 40 because of the presence of electrons in this region. With the application of the electron filter of the invention, the output curve will assume the form indicated in FIG. 3B, assuming that ion-molecule reactions are completed before grid 38 is passed. Only the second peak P2 is present, and overloading and masking by the electron peak and the resultant slope S are avoided.

As described in the aforesaid copending application, the time between the successive grid opening pulses applied to grid 38 may be of the order of 10 to 100 milliseconds, and grid 38 may be open for a period within the range of about 0.1 to 1 millisecond. The pulses applied to grid 40 may have similar, but delayed, timing and similar duration. A series of guard rings may be spaced along the length of envelope 12' to maintain the uniformity of the drift field, the guard rings being connected to appropriate taps on the battery chain. The total distance between electrodes C' and A' may be of the order of 10 centimeters, with the various electrodes and grids spaced of the order of a few centimeters or less. The apparatus may operate at atmospheric pressure, for example, with sensitivity of the order of one part in $10^{12}$.

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. Apparatus for separating first charged particles from second charged particles of substantially higher mass, comprising means for causing said particles to move from a first region toward a second region, a pair of adjacent grid members interposed transversely to paths between said first region and said second region, and means for applying alternating voltages between said grid members at a rate sufficiently great to cause the second particles to be unaffected by the instantaneous potential of said grid members and to pass therethrough but to permit the first particles to respond to the instantaneous voltages of said grid members and to be captured thereby.

2. Apparatus in accordance with claim 1, wherein said means for causing said particles to move from said first region toward said second region comprises means for applying a drift field between said regions.

3. Apparatus in accordance with claim 1, further comprising a source of electrons for providing said first particles and a source of ions for providing said second particles.

4. Apparatus in accordance with claim 1, further comprising means for producing an output current in response to the particles which pass through said grid members.

5. Apparatus in accordance with claim 1, further comprising means for producing an output current in accordance with the particles captured by said grid members.

6. Apparatus in accordance with claim 1, wherein said means for applying alternating voltages between said grid members comprises means for applying alternating voltages at a frequency between substantially 1 and substantially 10 MHz.

7. Apparatus in accordance with claim 1, wherein said means for applying said alternating voltages comprises a source of sine waves.

8. Apparatus comprising an envelope, a pair of electrodes spaced in said envelope, a source of electrons adjacent to one of said electrodes, means for introducing a substance to be ionized by said electrons in said envelope, means for applying a drift field between said electrodes to cause said electrons and ions resulting from the ionizing to move toward the other of said electrodes, and filter means for capturing said electrons but permitting said ions to pass therethrough, said filter means comprising a pair of adjacent grid members interposed transversely to paths between said electrodes and means for applying high frequency alternating voltages between said grid members.

9. Apparatus in accordance with claim 8, wherein said means for applying said alternating voltages to said grid members comprises means for applying sine waves to said grid members.

10. Apparatus in accordance with claim 8, wherein said grid members are interdigitated.

11. Apparatus in accordance with claim 8, wherein said means for applying said alternating voltages to said grid members comprises means for applying square waves to said grid members.

12. Apparatus in accordance with claim 8, wherein the frequency of said alternating voltages is between substantially 1 and substantially 10 MHz.

13. Apparatus in accordance with claim 8, further comprising means for measuring a current flowing in said other electrode as the result of ions impinging thereon.

14. Apparatus in accordance with claim 8, further comprising a pair of ion gates spaced between said filter means and said other electrode, and means for opening said ion gates sequentially.

15. Apparatus in accordance with claim 8, further comprising means for measuring the current flowing in said other electrode as the result of ions impinging thereon.

16. Apparatus in accordance with claim 8, further comprising means for measuring the current flowing in said filter means as the result of electrons captured thereby.

17. Apparatus in accordance with claim 8, wherein said means for introducing said substance in said envelope comprises means for introducing said substance at substantially atmospheric pressure.

18. Apparatus in accordance with claim 1, wherein said means for applying said alternating voltages comprises a source of square waves.

19. Apparatus in accordance with claim 1, wherein said grid members are interdigitated.

20. Apparatus in accordance with claim 1, wherein said means for causing said particles to move from said first region toward said second region comprises means for applying a DC potential between a pair of electrodes at said regions, respectively, and wherein said grid members are interposed transversely to paths between said electrodes and have means for applying a DC potential thereto intermediate the potentials of said electrodes and with respect to which said alternating voltages are applied.

21. Apparatus in accordance with claim 14, wherein the grid members of said filter means are interdigitated and wherein each of said ion gates comprises a pair of interdigitated grid members provided with means for maintaining the grid members at equal and opposite potentials with respect to an average potential and means for temporarily driving the grid members of each ion gate to the average potential.

22. A method of separating first charged particles from second charged particles of substantially higher mass, which comprises subjecting said particles to a drift field to cause them to move from a first region toward a second region, interposing in said drift field transversely to paths between said regions a pair of adjacent grid members, and causing the potential between said grid members to alternate rapidly enough to render the second particles insensitive to the variations and to permit such particles to pass through said grid members but to cause said first particles to be attracted to said grid members and captured thereby.

23. A method in accordance with claim 22, wherein said second particles are formed by ion-molecule reactions, and further comprising segregating said second particles which pass through said grid members in accordance with their mobility, the foregoing steps being performed substantially at atmospheric pressure, and detecting at least some of the segregated particles.

24. A method in accordance with claim 22, wherein the segregating includes gating of at least some of said second particles from a first location to a second location in the drift field.

* * * * *