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PULSE TYPE MASS SPECTROMETER WHEREIN IONS ARE SEPARATED BY
OSCILLATIONS IN AN ELECTROSTATIC FIELD

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2 Sheets-Sheet 1

Fig.1

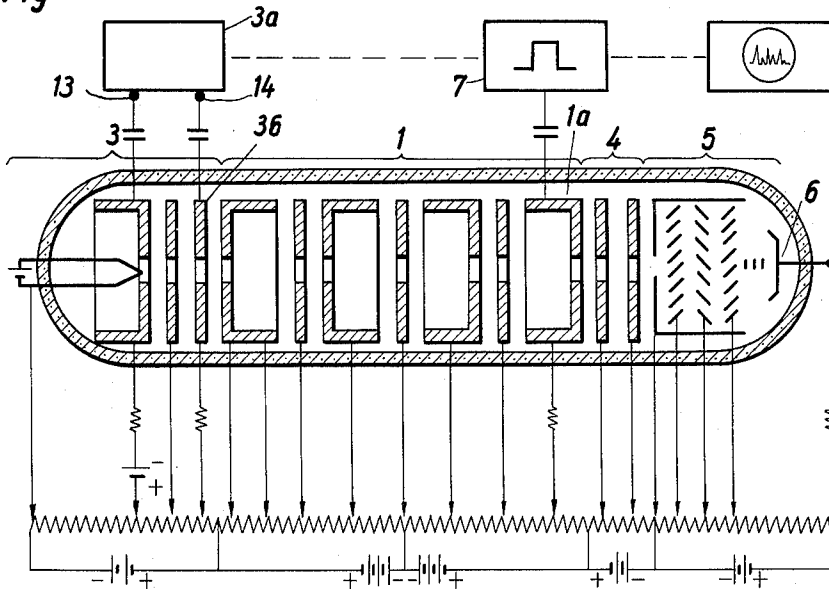
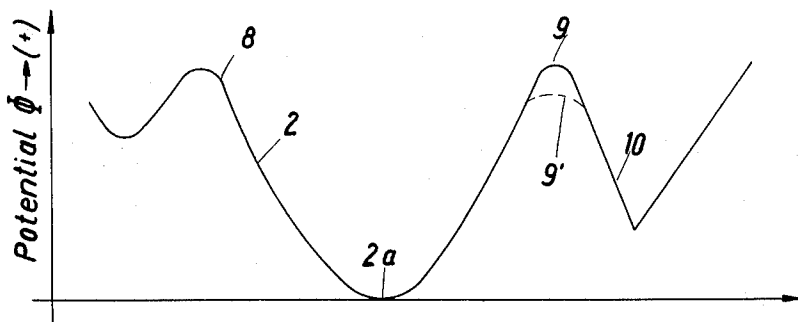


Fig.1a



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Fig. 2

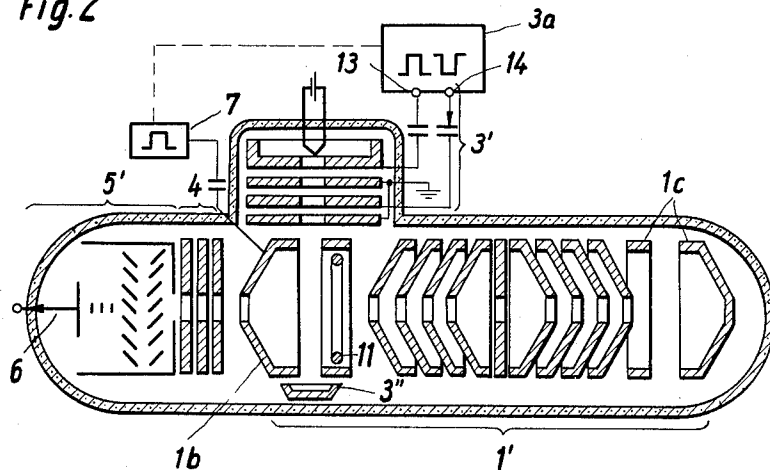
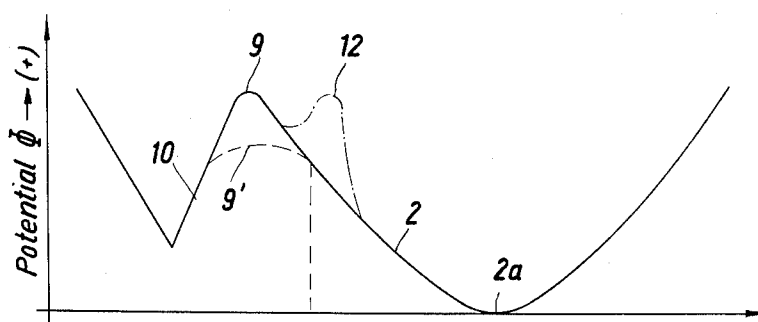


Fig. 2a



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PULSE TYPE MASS SPECTROMETER WHEREIN IONS ARE SEPARATED BY OSCILLATIONS IN AN ELECTROSTATIC FIELD

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The present invention relates to mass spectrometers and in particular to measuring apparatus in which ions exhibiting different ratios between charge (e) and mass (m) pass through a trajectory with a speed depending on the e/m ratio and are consequently separated. Since the ions are produced in pulse and not continuous fashion, apparatus of this sort is also frequently given the name "pulse" mass spectrometer, another name is travel-time mass spectrometer.

In order to achieve good separation between the different types of (i.e., ion having different e/m ratios) ions, the trajectory of the ions must be made relatively long. With mass spectrometers exclusively employing electric fields, this leads to large and cumbersome proportions. True, the dimensions of the apparatus can be reduced by using magnetic fields to make the ions describe circular trajectories; however, the necessary magnets are heavy and expensive.

An object of the invention is, therefore, a pulse-type mass spectrometer which is small and compact but nevertheless enables relatively good separation between the ions to be achieved.

Another object of the invention is to provide a mass spectrometer which is relatively inexpensive and which employs a small spectrometer tube which may be without difficulties incorporated in various kinds of vacuum equipment.

The advantages of the invention stem from the fact that the ions, produced during a first short time interval in pulse fashion, are caused to reciprocate along an axis of a spectrometer tube during a second substantially longer time interval without being subjected to accelerating or decelerating alternating fields, this spectrometer tube containing a number of electrodes arranged along the axis and provided with coaxial holes. In practice, the electrodes are so biased that along the tube axis a trough-shaped preferably parabolic potential distribution is produced, having a relatively negative minimum. The ions are produced at one end of this potential distribution, i.e., at a point of relatively positive potential, and then describe periodic oscillations in the potential trough. The frequency of these oscillations and consequently the mean velocity with which the ions move backwards and forwards along the tube axis, is dependent upon the form of the potential trough, in particular the potential difference between the starting point of the ions and the potential minimum, as well as upon the e/m ratio of the ions. Thus, during the backwards and forwards oscillatory movement, the ions of different e/m ratio separate from one another. Consequently, at a certain time after the pulse-like ion production, the potential trough contains a number of separate groups of oscillating ions, the ions in each group having the same e/m

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ratios. After the ions have oscillated for a specific time interval and have consequently separated, a detection device is activated, this serving to detect the separate groups of ions. The sequence of the individual processes, i.e., ion production, separation during oscillation and detection, can be repeated at a relatively fast rate, e.g., at the mains frequency, so that rapid alteration in the composition of the analysed gas or vapor can be monitored.

The difference between the distances passed through by the different sorts of ions during the backwards and forwards oscillating motion, are naturally greater the longer the time which elapses between the ion production and detection. Since, however, the motion of the ions in the potential trough is periodic, the time elapsing between ion production and detection should not become too long for otherwise the oscillations of the individual sorts of ions would become displaced with respect to one another by more than one cycle and this could lead to ambiguity. Additionally, the number of oscillating ions is continually decreased as a result of collisions with the residual gas and of recombination.

The detection of the ions can be made in a variety of ways. An electrostatic inductive collector can be arranged at one end of the tube and a signal tapped off there corresponding to the oscillating accumulated ions. Detection can also be made by means of a signal induced into one of the electrodes in the center of the electrode arrangement. In a specific embodiment of the invention, a secondary electron multiplier is employed which is arranged beyond the electrode arrangement as an extension of the same. In this embodiment, the bias voltages on the different electrodes are so controlled that at least a part of the ions produced cannot escape from the electrode arrangement but are reflected in the manner described above by the positive potentials at the ends. After the ions have oscillated backwards and forwards for a specific time interval and the optimum separation has been achieved, the potential on the electrodes at the end of the electrode arrangement adjoining the multiplier is reduced until the oscillating ions are no longer reflected and can pass into the multiplier. Before entry into the multiplier, the electrons are preferably accelerated once more. The individual separated ion groups then pass into the multiplier one after the other and there, in known fashion, produce a signal constituted by a series of pulses whose chronological sequence and intensity correspond to the type and quantity of the different ions respectively.

The invention will now be explained making reference to nonlimitative exemplary embodiments in conjunction with the drawing.

FIGURE 1 shows a simplified representation of a first embodiment of a periodically operating travel time or pulse type mass spectrometer in accordance with the invention; the spectrometer tube is shown in section and the corresponding circuit arrangement is for some part represented as a block diagram.

FIGURE 1a shows a diagram of the potential distribution along the axis of the spectrometer tube illustrated in FIGURE 1.

FIGURE 2 shows a simplified representation of a second embodiment of the invention.

FIGURE 2a shows a diagram of the potential distribution along the axis of the spectrometer tube illustrated in FIGURE 2.

The mass spectrometer illustrated in FIGURE 1 has a more or less tubular vacuum vessel containing a number

of electrodes 1 which are preferably solids of rotation and possess central apertures lying on a common axis. The electrodes are provided with connection leads which pass in vacuum-tight fashion out of the vacuum vessel to a voltage divider situated below the spectrometer tube, as shown in FIGURE 1. The voltage divider is in turn connected to different voltage sources which for purposes of demonstration are illustrated as batteries.

Voltage divider and voltage sources are so dimensioned that in operation, in the region of the electrodes 1, along the axis of the tube, a basin-shaped preferably parabolic potential 2 (FIGURE 1a) with a relatively negative minimum point at 2a, is produced.

At one end of the potential electrodes 1, an electron-gun system 3 of conventional construction is situated, this producing an axial electron beam.

As far as it has been described, the mass spectrometer tube is similar to known types, as marketed for instance under the trade name "Farvitron," so that no further detailed description is necessary.

At the end of the potential electrode arrangement 1 opposite to the electron-gun system 3, are situated accelerating electrodes 4 and a multiplier arrangement 5. The multiplier arrangement 5 can contain a number of dynodes of "Venetian blind" type although for the sake of simplicity, only three of these are shown. At one anode 6 of the multiplier, the output signal from the tube can be picked up.

To the electron-gun system 3, a pulse generating source 3a is connected and during operation the gun system 3 produces only short beam-pulses so that corresponding ion pulses result. Ion pulse sources of this sort are known per se so that further explanation is unnecessary.

In accordance with the invention, the last potential electrode 1a in the potential electrode arrangement 1 is connected to a pulse source 7 which enables the potential on the electrode rapidly to be reduced to a more negative value than normal, i.e., than during the separation interval.

To the anode 6 of the multiplier, an indicating instrument, preferably an oscilloscope, is connected. The pulse source 3a for the electron-gun system, the pulse source 7 and the oscilloscope, are preferably synchronised with one another this being indicated by the broken line between the corresponding diagram blocks, pulse sources 3a and 7 may be combined and may then comprise a single pulse source and time delay and pulse forming networks, e.g., monostable multivibrator circuits, the same being true also for the embodiment described later in connection with FIGURES 2 and 2a.

The arrangement described works in the following manner.

The pulse source 3a causes the gun 3 to produce an electron beam pulse so that during a short time interval (in practice e.g., 1×10^{-7} sec.) ions are produced. The ions develop more or less in the vicinity of the electrode (in the potential electrode arrangement 1) situated farthest left in FIGURE 1, this corresponding more or less to the point 8 in the potential curve illustrated in FIGURE 1a. The positive ions are now accelerated along the axis of the tube in the direction towards the potential minimum 2a (FIGURE 1a) situated at the center of the electrode arrangement 1. They oscillate beyond the minimum into the region of the maximum 9 at the other end of the electrode arrangement 1, where they come to a standstill and then return in the direction of the point 8 at which they were produced. The frequency with which the individual ions oscillate in the potential trough 3, is dependent upon the ratio of the ion charge e to the ion mass m . In the course of the oscillations, the ions therefore separate into different "packets" each corresponding to a particular e/m value. A specific interval after the production of the ions, the potential on the electrode 1a is made more negative so that the potential barrier or threshold 9 is reduced approximately to the

value 9' (FIGURE 1a). The oscillating ions are therefore able to surmount the now lower potential threshold 9' so that they emerge from the electrode arrangement 1 through the opening in the electrode 1a in the direction of the multiplier 5. The ions are then accelerated by the potential 10 (FIGURE 1a) applied to the electrodes 4, and enter the multiplier 5 where they produce secondary electrons which are multiplied in known fashion and ultimately collected by the anode 6. Since the ions of different sort have been separated during oscillation in the potential trough 2, a series of pulses therefore appears at the anode or output electrode 6, the time positions of which are a measure of the e/m ratio and the amplitude a measure of the number of ions formed during the electron beam pulse.

The embodiment of the invention illustrated in FIGURE 2, is slightly different in construction from that illustrated in FIGURE 1, but works on the same principle. To simplify the drawing, in FIGURE 2 only the electrode arrangement and the pulse sources have been shown, all other parts are as FIGURE 1.

With the embodiment of the invention as illustrated in FIGURE 2, the electron-gun system 3-4 producing the ionising electron beam and the multiplier 5' for detection, are arranged at the same end of the tube. Consequently, the electron beam is injected perpendicularly to the axis of the potential electrode arrangement 1' and picked up by a collector electrode 3''. As with the exemplary embodiment described earlier, the ions in the potential trough 2 (FIGURE 2a) execute periodic oscillations. The oscillating accumulated ions can as required be detected by the tapping off of an induced voltage at electrodes 1c, in this event both of said electrodes preferably are coupled by individual capacitors (not shown) to an oscilloscope (not shown). However, detection is preferably made by means of the multiplier 5' and to this end to the left potential electrode 1b at the end of the electrode arrangement 1' facing the multiplier, after a specific time has elapsed since the production of the ions, a more negative voltage is applied by the pulse source 7 so that the potential maximum 9 (FIGURE 2a) is reduced to the value 9'. The ions oscillating in the potential trough 2 can surmount this lower potential threshold and after acceleration by the potential applied to the electrodes 4 pass into the multiplier 5'.

It is not difficult to see that the resolving power of mass spectrometers of this type is better the shorter the time interval during which the ions are produced, i.e., the narrower the ion pulse. For a given electron beam current, however, the number of ions produced per pulse decreases with decreasing pulse time. If fewer ions are produced per pulse, then self-evidently the signal strength for a given concentration in the gas or vapor being examined is correspondingly reduced. The resolving power of the mass spectrometer is also better the stricter the adherence to the requirement that the ions all start simultaneously with zero velocity and zero momentum.

The requirements of adequate signal strength and reduction of pulse time seem to conflict but this difficulty can be overcome by an ingenious artifice.

In accordance with a further characteristic of the invention, during the production of the ions by the injection of an electron beam, the potential 2 (FIGURE 2a) is so distorted by an additional electrode 11 that the ions produced within the maximum 9 cannot pass towards the potential minimum 2a. To this end, the electrode 11 has fed to it, during the period of ion production, a positive pulse derived from a pulse source which is not shown, so that a small potential peak 12 (FIGURE 2a) results, which the ions cannot surmount since at the instant of creation they have but very low velocities. Only when all the ions have been produced, i.e., only when the electron beam pulse produced by the electron-gun system has ceased, is the potential on the electrode 11 reduced once more to the normal value so that the

ions collected in the small potential trough between the maximum points 9 and 12 all begin to move simultaneously. This way, the operating time of the ion source can be made relatively long without causing any undesirable widening of the output pulses. The electrode 11 can, for example, take the form of a ring inside the electrode 1b or can also be an adjacent potential electrode.

If the pulsating ion production is based upon an electron beam, a beam pulse is normally produced by the application of a pulse voltage to an electrode in the electron-gun system, for instance the modulating electrode or an accelerating electrode. It has been found that these pulse voltages in the electron-gun system exert an undesirable influence on the ions created in the tube, this being manifested by the imparting to the ions of undesired and uncontrollable momentums. As a consequence, the fulfillment of the above mentioned condition that the ions should start with zero velocity and zero momentum, is made difficult if not impossible. In order to overcome the disturbing influence of the electric fields arising in connection with beam production, in accordance with a further characteristic of the invention an additional apertured (iris-type) electrode (compensating electrode) between the electron-gun system and the region in which the ions are produced has fed to it a pulse voltage which is more or less in antiphase with the pulse voltage modulating the beam. Amplitude and phase of the voltage supplied to the compensating electrode are so adjusted that the fields produced by the modulating electrode (Wehnelt cylinder, anode) of the electron-gun system and by the compensating electrode at least substantially cancel each other out at the point of ion production.

An arrangement of this sort is schematically illustrated in FIGURE 1. The pulse source 3a in this case delivers a positive pulse voltage to a first output terminal 13 for the normally negatively biased modulating electrode (control grid) and a compensating pulse voltage to an output terminal 14 for an additional apertured electrode 3b. The pulse source 3a can contain an attenuator and a phase-shifting network by means of which amplitude and phase of the compensating pulse voltage delivered at the terminal 14 can be adjusted.

Between the compensating electrode 3b and the modulating electrode on the one hand and/or the point of production of the ions within the extreme left electrode of the potential electrodes 1, electrodes, for instance of the iris type and preferably earthed in A.C. fashion, are inserted.

Neither the above described exemplary embodiment nor the exemplary embodiments to be described in the following are limited to the use of an electron beam for the production of ions. Instead of a pulse-operated electron-gun system, other well known ion sources of the pulse type can be employed, e.g., plasma ion sources. The above mentioned compensation principle can be employed with all types of ion sources in which objectionable electric stray fields occur.

In a practical embodiment of a mass spectrometer of the above sort, the potential difference between the maximum 8 and the minimum 2 (FIGURE 1a) amounted to about 1000 v. The duration of the ion producing electron beam pulse was 1×10^{-7} sec. The cycle time, i.e., the time interval between ion production pulse and activation of the means used for detecting the separated spaced ion groups (e.g., by applying a negative pulse to the electrode 1a (FIG. 1) between the electrode system 1 and the multiplier 5) amounted to about 2×10^{-5} seconds and the length of the potential electrode arrangement 1 was about 5 to 10 cm. In this case, a resolving power of 100 was obtained.

We claim:

1. A mass spectrometer comprising a vacuum tight envelope with means for the introduction of a vapor or gas to be analysed, ion source means in said envelope for ionizing, during an initial short time interval, a part of

the gas or vapor to be analysed; a number of spaced apertured electrodes in said envelope; energy source means connected to said electrodes for producing, along an axis of said electrodes, only a trough-shaped D.C. potential having a relatively positive value at the point of ion production, a relatively negative value at a point a certain distance along said axis extending from the point of ion production, and a relatively positive value at a point along the axis which is situated further from the ion source than the point of relatively negative potential, the last mentioned positive potential being at least equal to the positive potential at the ion source to provide, during a period of time following said short time interval, oscillations of ions disposed between the two points of positive potential; means for detecting groups of ions which have separated during oscillations along said axis between the point of ion production and the opposite point of positive potential; and means activating said detecting means for detecting separated groups of ions a specific time interval after the production of these.

2. Mass spectrometer in accordance with claim 1, characterized in that potential trough is at least approximately parabolic in shape.

3. Mass spectrometer in accordance with claim 2, characterized in that the potential trough is produced by means of a number of electrodes arranged along an axis and possessing coaxial holes, together with a D.C. voltage source connected to these electrodes and supplying them individually with variously stepped voltages.

4. Mass spectrometer in accordance with claim 3, characterized in that forming the extension of one end of the electrodes (1) serving to produce the potential trough, a multiplier (5) is provided; in that the electrodes (1) and the multiplier (5) are so biased that between the potential minimum (2a) of the potential trough (2) and an input electrode in the multiplier (5) a positive potential threshold (9) is created; and in that an electrode (1a in FIGURE 1; 1b in FIGURE 2) situated at the location of the positive potential threshold (9) is connected with an arrangement (7) which enables the potential of this electrode to be reduced to a more negative value (9').

5. Mass spectrometer in accordance with claim 1, characterized in that the ion source contains an electron-gun system producing an electron beam which intersects the tube axis approximately perpendicularly.

6. Mass spectrometer in accordance with claim 5, characterized in that the electron-gun system (3') is arranged at the end of the potential arrangement (1') at which the multiplier (5') is situated.

7. Mass spectrometer in accordance with claim 4, characterized by accelerating electrodes (4) between the potential electrodes (1, 1') and an input electrode in the multiplier (5, 5').

8. Mass spectrometer in accordance with claim 5, characterized by an electrode (11) situated between the point of ion production and the potential minimum (2a) of the potential trough (2) and by means for supplying to this electrode during ion production a positive potential of such magnitude that the ions created cannot pass into the potential trough.

9. Mass spectrometer in accordance with claim 1 wherein said ion source means includes an electrode which is fed with a pulse voltage for the purpose of producing an ion pulse, characterized in that between the electrode to which the pulse voltage is fed and the point in the spectrometer tube at which the ions are produced, a compensating electrode is provided and in that this electrode is connected to means (3a) supplying it with a pulse voltage of equal duration whose phase and amplitude are so selected that the electric fields produced by the former and latter electrodes substantially cancel each other out at the point of production of the ions.

10. Mass spectrometer in accordance with claim 9, characterized in that between the compensating electrode and the point of production of the ions, an electrode is provided which is grounded for A.C. voltages.

11. Mass spectrometer in accordance with claim 5, characterized by accelerating electrodes (4) between the potential electrodes (1, 1') and an input electrode in the multiplier (5, 5').

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