March 16, 1965 R. BEHRISCH ETAL 3,174,034

MASS SPECTROMETER

Filed July 2, 1962 4 Sheets-Sheet 1

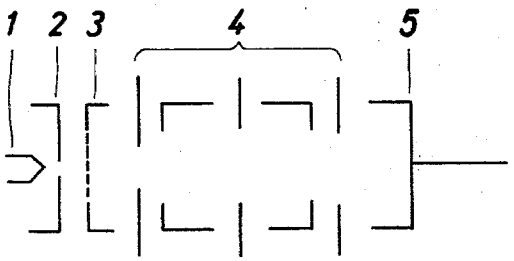


Fig.1

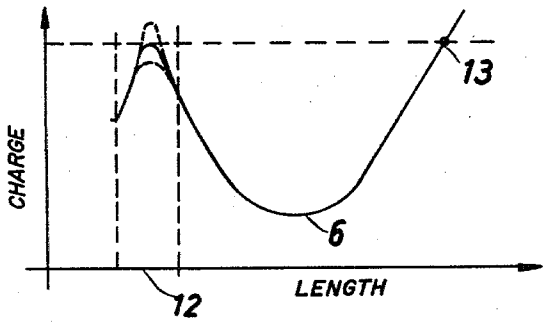


Fig.2

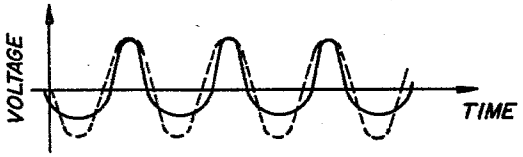


Fig.3

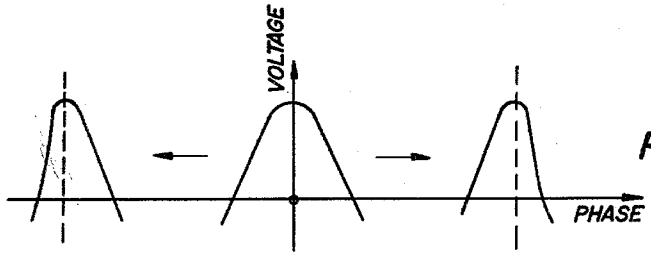


Fig.4

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MASS SPECTROMETER

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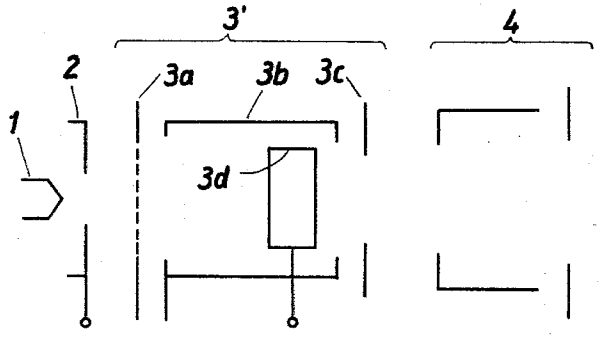


Fig.5

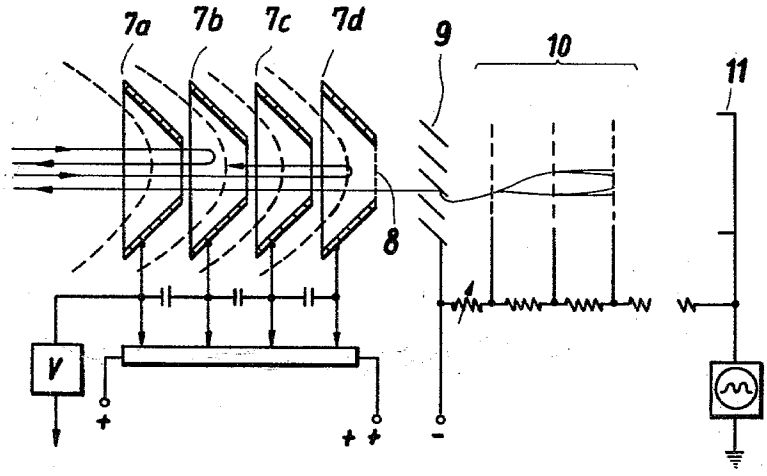


Fig.6

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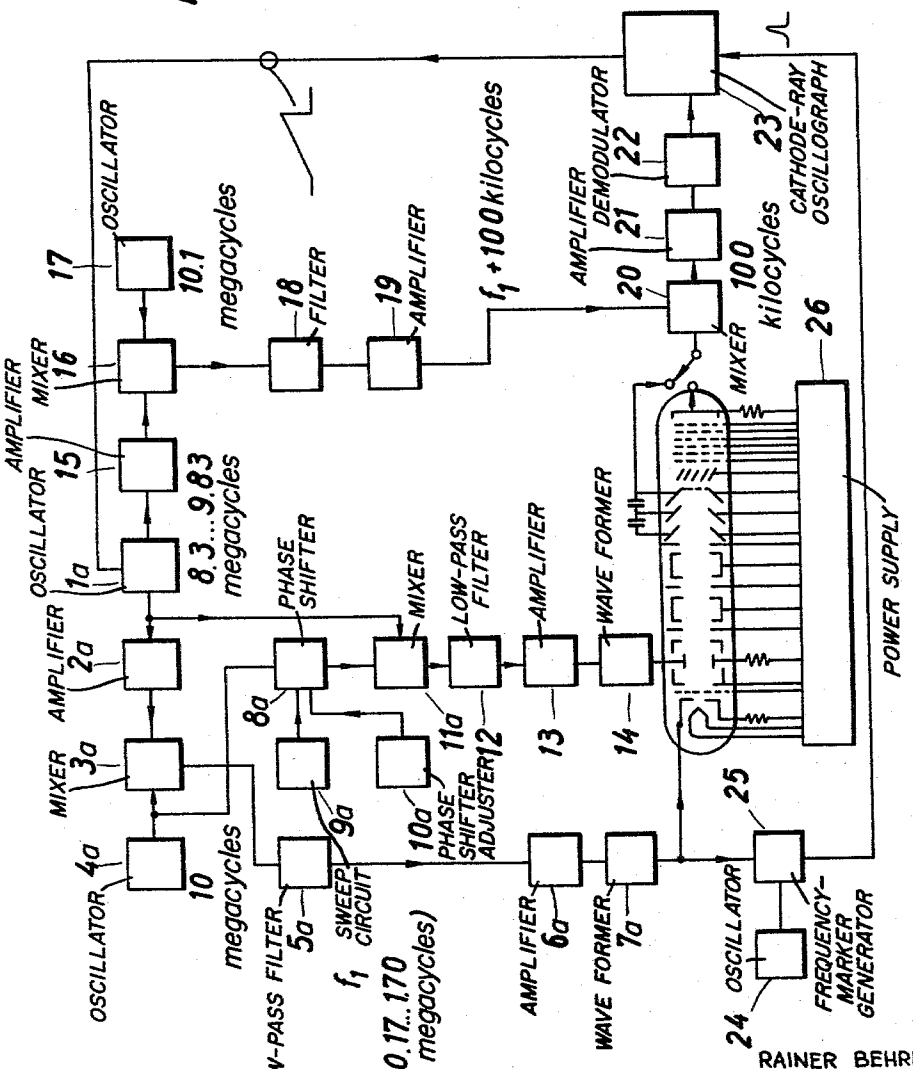
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MASS SPECTROMETER

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Fig. 7



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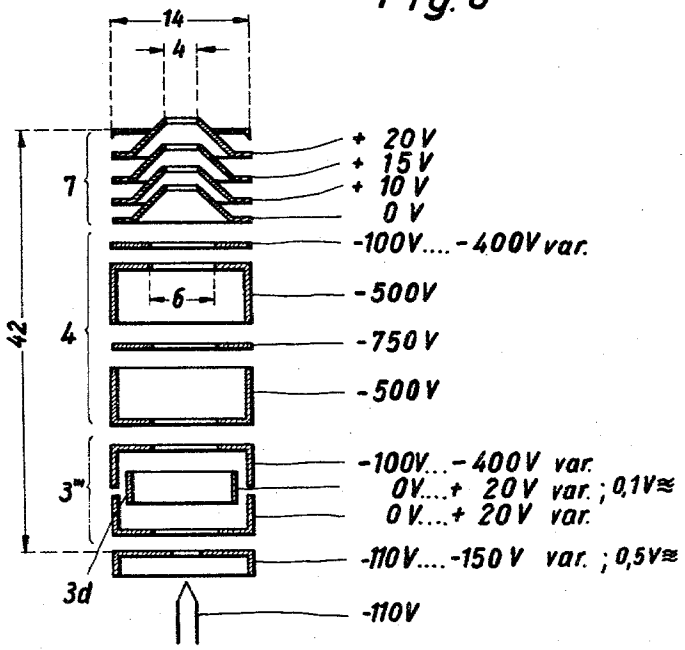
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Fig. 8



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United States Patent Office 3,174,034 Patented Mar. 16, 1965

3,174,034
MASS SPECTROMETER

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Filed July 2, 1962, Ser. No. 206,815
Claims priority, application Germany, July 3, 1961, M 49,548
5 Claims. (Cl. 250—41.9)

This invention relates to a dynamic-functioning mass spectrometer and more particularly to a spectrometer in which the ions perform a motion which is substantially periodic.

All dynamic-functioning mass spectrometers have a similar principle of operation. This principle of operation is that the different ion types are separated on the basis of their different transit times. In mass spectrometers in which the ions undergo a periodic motion, there is a field present which brings ions of different velocities—which are dependent on the masses—(we are not treating here the case of ionization of more than one grade) to stable trajectories where they undergo their reversal in direction of travel. Depending on the principle of operation, this field can be either electric or magnetic.

The selection of ions of a particular type, that is the selection of ions of a particular mass is effected through a periodic variation of suitable parameters of a mass spectrometer. Ions of a particular mass follow the parameter variation in phase synchronization and contribute to an output signal. Ions which cannot follow the parameter variation in phase synchronization, contribute little to the output signal. The ions which perform a motion in phase synchronization with the parameter variation, will be called "resonance ions." This term "resonance ions" does not necessarily coincide with the accepted definition of resonance, as in some cases the selection of a particular ion type may be effected by accumulation.

In a well known mass spectrometer, for example, only ions of one particular mass are accelerated by an alternating voltage. Ions of other masses, however, are unable to gain a significant amount of energy. In another type of mass spectrometer, new ions are produced periodically and if the frequency of ion generation coincides with the oscillation frequency of a particular ion type, an accumulation of ions of this type occurs. In mass spectrometers of this type the ions which are not periodically accumulated constitute an asynchronously oscillating distributed space charge. This space charge significantly reduces the resolution and the minimum detectable concentration sensitivity. If these ions which are not in resonance could be removed from the part of the spectrometer where detection takes place, the performance of the spectrometer could be considerably improved.

It is therefore an object of this invention to improve the characteristics of a mass spectrometer in which the ions undergo an oscillatory movement. The improvement is accomplished by continuously removing ions which are not in resonance, and constitute a space charge, from the resonating ions, without significantly influencing the latter.

A further object of the invention is to provide phase focussing of the resonance ions in a mass spectrometer employing an electrostatic field distribution in which said ions oscillate for improving the sensitivity of said mass spectrometer.

Yet a further object of this invention is to provide an improved mass spectrometer comprising a new electrode arrangement for signal generation by influence.

Still a further object of this invention is to provide an improved mass spectrometer in which both a spectrometer tube and electronic signal detecting means are controlled by a single oscillator.

At least some objects and advantages of the invention are achieved by a method of operating a mass spectrometer in which a field (which may be either of magnetic or electric nature) defines trajectories on which the ions perform at least substantially periodic motions. Said method is charctertized by periodically varying said field and/or periodically superimposing an additional field of like or different nature in such a manner that only ions which are not in resonance will be deflected from their stable trajectories and discharge themsleves. The resulting field distortion shall be such that it takes place in such a part of the spectrometer at such a time that the resonating ions are substantially not influenced.

These and other objects and advantages of the present invention will be set forth in greater detail in the following description and accompanying drawings, and the claims appended thereto.

In the drawings:

FIGURE 1 is a schematic sectional view of an electrode system for an electrostatic-field mass spectrometer tube.

FIGURE 2 is a diagram of the potential distribution for the mass spectrometer tube given in FIG. 1, the scale in axial direction being the same as in FIG. 1.

FIGURES 3 and 4 are diagrams of some voltages applied to the tube shown in FIG. 1.

FIGURE 5 is a schematic view of a portion of an electrode system for a mass spectrometer tube which is somewhat different than that shown in FIG. 1.

FIGURE 6 is an improved signal electrode system for a mass spectrometer such as shown in FIG. 1 or 5.

FIGURE 7 is a block diagram and a schematic view of another embodiment of the invention.

FIGURE 8 is an axial cross-sectional view of an embodiment of an electrode system as practically used.

FIG. 1 shows schematically an electrode system of an essentially well-known mass spectrometer tube (for example, Zs. f. angew. Phys., 11, 1959, pp. 395 to 399). The electrode system consists of a cathode 1, a Wehnelt electrode 2, an anode 3, field electrodes 4, and a collector 5. The electrodes are biased so that the potential distribution which is shown in FIG. 2 is generated. The linear horizontal scale is the same for FIGS. 1 and 2. The electrons which are emitted from the cathode 1 are accelerated toward the anode 3. The anode normally has the form of a grid, so that these electrons may penetrate through the plane of the anode 3 and proceed in the direction of the field electrodes. Since the field electrodes 4 are biased negatively with respect to the anode, the electrons are reflected toward the cathode and again, on encountering a negative potential, are reflected and perform an oscillatory motion. These electrons thus ionize the gas molecules which are present in this part of the mass spectrometer. Here and in the following text, the terms "positive" and "negative" are only relative. In the normal functioning of such a tube, the anode 3 and the collector 5 are approximately at ground potential, whereas the potential minimum 6 is created by biasing the field electrodes 4 to a large negative potential.

The ions which were formed in the space around the anode 3 are accelerated into the potential trough 6 where they, then, oscillate. In the ideal case the potential trough 6 should be parabolic. The oscillation frequency of these ions is dependent on their mass. Ions of a particular mass can be selected by supplying new ions in phase with the oscillation of the already present oscillating ions. This supplying of new ions of a snychronous phase with the oscillations can be caused by modulating

the Wehnelt electrode or control grid **2** with an appropriate periodic voltage. Through summation, these ions can build a large charge cloud which can produce a signal on the electrostatic influence electrode or collector **5** which is larger than the background signal which is produced by the ions oscillating asynchronously. This is the case, because the ions which are not in resonance, in general, do not have a preferential phase. It is obvious, however, that in tubes of this type the space charge caused by the ions not in resonance produces a detrimental effect.

According to the present invention this disturbing space charge is eliminated by applying a voltage to an electrode in synchronism with the oscillations of the resonant ions in such a manner that the ions which are not in resonance are deflected from their stable trajectories, so that they contact an electrode or the wall of the tube and eventually are discharged. This effect can be achieved in several ways:

In a first embodiment of the invention new ions are generated periodically, for example, by applying a radio frequency of appropriate frequency to the Wehnelt grid **2**. The period of generating new ions is made equal to the frequency with which ions of a kind to be detected oscillate. Thus ions of all kinds start oscillating periodically at the same time, and with identical phases. For removing ions the oscillating frequency of which does not coincide with the frequency of ion generation (which ions form the undesired space charge) we also apply an alternating voltage of the same frequency and phase to the anode **3**. Ions of all types begin their first oscillation period with the same phase, and this is when the voltage on the anode has reached its most positive value. It is important to note that the anode is responsible for one side of the trough-like potential distribution **6**. When the ions which are in resonance return to the region of the anode, they find a potential distribution identical to that present at the beginning of their oscillation and therefore perform undisturbed oscillations. The ions which are not in resonance return to the region of the anode at a time before or after that of the resonance ions and therefore find a potential which is not as positive as they experienced at the beginning of their oscillation period. These ions are, therefore, not reflected by the positive anode potential, but rather continue to travel in the direction of the cathode and are discharged there. The ions which are in resonance theoretically can have arbitrarily many oscillation periods. The ions which are not in resonance are discharged after one oscillation period.

The synchronous modulation of the anode and the Wehnelt electrode can be accomplished when the anode is isolated from ground for high-frequency signals. The anode, then, receives a high-frequency voltage because of capacitive coupling to the Wehnelt electrode. The phase of the voltage on the anode is, however, somewhat different from the voltage present on the Wehnelt electrode because of the time constant of the capacitive coupling and the coupling effect of the electron beam which is in antiphase to the capacitive coupling. However, despite these non-ideal conditions, a significant improvement in the operation of the mass spectrometer is achieved.

The resolution of the spectrometer can be further improved by allowing ions to be generated only over a very small part of the oscillation period. This can be accomplished by applying a pulse-shaped voltage to the Wehnelt electrode. This can be accomplished simply by shaping the sine-wave modulation applied to the Wehnelt electrode, so that it resembles the curve shown in FIG. 3. The electrons will then be delivered to the anode only when the voltage applied to the Wehnelt electrode lies above the axis. By restricting the ion generation process to a small portion of the oscillation period, we affect, practically, only the ions which are not in resonance, so that the sensitivity of minimum detection of the spectrometer is not changed significantly through this process.

Known mass spectrometer tubes of the type described perform satisfactorily in the pressure range between 10^{-5} and 10^{-8} mm./Hg. Making use of the invention as described here, satisfactory measurements have been made in the pressure range between $5 \cdot 10^{-4}$ and $5 \cdot 10^{-11}$ mm./Hg.

Besides getting rid of the undesired ions, the high-frequency voltage on the anode also can perform a phase focussing of the resonance ions when the potential distribution in the tube is properly chosen. In order to achieve this phase focussing, it must be established that the force due to the electric field increases in magnitude more slowly than linearly with increasing distance. That is, the frequency of the oscillation of the ions is amplitude-dependent. This causes oscillations of larger amplitude to have a longer period than oscillations of smaller amplitude. That is, the ions shall demonstrate an underlinear type of oscillation. The phase focussing takes place because the leading ions which arrive too soon at the anode receive additional enargy, due to the increasing electric field of the anode, and therefore have a larger amplitude during the next half cycle. This causes these ions to arrive at the anode at the end of their period somewhat later. Lagging ions, i.e., ions which arrive too late at the anode encounter a decreasing electric field and therefore give up some of their energy. This causes them to have a smaller amplitude of oscillation and arrive at the anode at the end of this cycle somewhat sooner. This requirement that the electric field increases in amplitude at a rate less than linear with distance must only be fulfilled in one part of this tube. The electric field preferably is made symmetrical to the potential minimum and underlinear in the region where the oscillation amplitude maximums occur. This requirement needs only be fulfilled in the space where the oscillating ions are actually present.

The sensitivity and resolution of the spectrometer system can be increased even further by refining the phase focussing. This can be accomplished by sweeping the shape and/or the phase of the voltage applied to the anode. (Phase is, with reference to the voltage, applied to the Wehnelt electrode and in fact with ion generation.) Sweeping of the form is to be understood as an increasing of the absolute value of the slope of the voltage applied to the anode, alternately ahead of and behind the positive maximum. Wave-shape modulation, phase modulation, and phase relation are chosen in combination with the sweep frequency, so that the focussing effect is larger than the defocussing effect.

FIG. 4 shows the case where the normally sine voltage applied to the anode has undergone a phase modulation as well as a shaping. When the instantaneous phase deviation is zero, the sine voltage is undistorted, that is symmetrical. At the maximum of the instantaneous phase deviation in one direction, the slope ahead of the voltage maximum is increased; at the maximum of the instantaneous phase deviation in the other direction, the absolute value of the slope of the voltage behind the maximum is increased. The amplitude of the voltage and the wave form in the immediate vicinity of the maximum should not be changed by this shaping process.

In order to keep the coupling between the Wehnelt electrode and the anode as small as possible, it has been found advantageous to insert a screen grid between these electrodes which is grounded for high-frequency signals.

For an effective phase focussing an adequately underlinear oscillation must be established which is symmetrical in the space during the time when the ions are being generated. In order to make a good approximation to this, it is useful to apply the high-frequency voltage to a separate electrode within the anode, as shown, for example, in FIG. 5. The anode **3** of this spectrometer system consists of the electrodes **3***a*, **3***b*, **3***c*, and **3***d*. The electrode **3***b* is biased to a potential somewhat less positive than the electrodes **3***a* and **3***c*. The high-fre-

quency modulation voltage is applied to the somewhat ring-formed electrode 3*d* which is located inside the substantially cylindrical-formed electrode 3*b*. The electrodes 3*a*, 3*b*, and 3*c* are grounded for high-frequency signals. The underlinearity must only be guaranteed during the injection of new ions, as this is the only time when the resonating ions are in the vicinity of the anode. An appropriate field distribution shall be established in the region of the opposite signal electrode or collector that no defocussing occurs there.

For the mass spectrometer tube shown in FIG. 1 or 5 an alternating voltage whose frequency is continuously variable between 0.17 and 1.70 megacycles per second is required in order to cover the range of masses between approximately 2 and 200. The output signal of the mass spectrograph tube must be amplified by a high-sensitivity amplifier. An improvement is obtained when a selective heterodyne-type amplifier is used, as the ions oscillating at wrong frequencies are then not measured. The image frequency could, if desired, be removed by a selective high-frequency amplifier stage which would synchronously be tuned with the local oscillator. This expense, however, is generally not required. For phase focussing via phase modulation a signal is necessary whose phase can be changed by about ±45° with respect to the reference signal.

The apparatus depicted as block diagram in FIG. 7 fulfills the above mentioned requirements. The frequency of the variable oscillator 1 is periodically variable between 8.3 and 9.83 megacycles per second. The variation is conveniently synchronized with line frequency. The output voltage of this oscillator 1*a* is amplified in amplifier 2*a* and mixed in mixer 3*a* with a fixed 10 megacycles per second signal from oscillator 4*a*. The output of the mixer stage is processed through a low-pass filter 5*a*. The output of the low-pass filter is a sine wave whose frequency varies between 0.17 and 1.70 megacycles per second. This signal is then amplified in block 6*a* and processed by an adjustable wave forming stage 7*a*. The output of block 7*a* which is shown in FIG. 3 is then applied to Wehnelt or control electrode 2 (FIG. 5).

The anode 3 or 3*d* requires a signal whose phase, with respect to the signal applied to the Wehnelt electrode, is frequency-dependent. This signal is generated in a separate mixer stage 11*a*. The inputs to this mixer 11*a* are the output of the variable oscillator 1*a* and the output of the fixed-frequency oscillator 4*a*. The output signal of the fixed-frequency oscillator is, however, not applied directly to the mixer stage, but rather processed through a phase shifter 8*a*. The phase shifter can be adjusted manually (block 10*a*) and swept by block 9*a*. The output voltage of mixer 11*a* is then passed through a low-pass filter (block 12). This resulting signal is frequency-coherent with that applied to the Wehnelt electrode, but can be statically and dynamically phase-modulated. This signal is further amplified in stage 13 and processed by an adjustable wave forming stage 14 before being applied to the anodes 3 or 3*d* (FIGS. 1 and 5, respectively).

A small voltage is received at the output electrode (influence electrode, collector, or multiplier). The frequency of this signal is obviously the difference between the variable oscillator 1*a* and the fixed-frequency oscillator 4*a*. A constant IF-frequency of 10 megacycles per second can be produced by mixing the signal from the output electrode with the output signal of the variable oscillator 1*a*.

When very good selectivity is desired, one can provide an arrangement, as shown in FIG. 7. The output signal of the mass spectrometer tube is mixed with a signal whose frequency differs from the received signal by a small, but constant amount. This can be accomplished by amplifying the output signal of oscillator 1*a* in stage 15 and mixing this signal in stage 16 with a signal from oscillator 17. The frequency of oscillator 17 was chosen at 10.1 megacycles per second. The output of the mixer 17 is applied to a filter 18 and then to an amplifier 19 before being applied to the final mixing stage 20. The other signal applied to the mixing stage 20 is that signal produced by the signal electrode of the mass spectrometer tube. The signals applied to the mixer stage 20 have a constant frequency difference of 100 kilocycles per second. The output of mixer stage 20 is amplified in a selective 100 kilocycles per second IF-amplifier 21, demodulated in the demodulator 22, and then applied to the vertical deflection means of a cathode-ray oscillograph 23. The time-base voltage generated in the oscillograph is also used to derive the frequency sweep voltage for oscillator 1*a*. The synchronization of the oscillographic display is thereby assured.

The reactance element in oscillator 1*a* is preferably a capacitance diode. By choosing the frequency of the variable oscillator 1*a* under the frequency of the fixed oscillator 4*a* we are better able to utilize the display capability of the oscillograph. This follows because of the diode characteristics which cause the higher frequency, that is, maximum frequency difference between oscillators 1 and 4, to be compressed on the oscillograph. This is desirable, as the difference between the masses at this end of the mass spectrum is relatively large. The other end of the mass spectrum is therefore relatively enlarged.

A frequency-marker generator is useful for calibration purposes. The signal from a calibrated oscillator 24 is combined with the signal applied to the Wehnelt electrode or anode in stage 25. Stage 25 produces an impulse when the frequencies of the two applied signals coincide. This impulse is used to intensity-modulate the electron beam of the cathode-ray oscillograph 23.

A power supply 26 supplies the necessary D.C.-voltages for operation of the spectrometer tube. This power supply unit 26 may be of known kind and, therefore, is not described in detail.

Another method of getting rid of the undesired space charge will now be described: At a time when the resonating ions are at a turning-around point of their trajectory, preferably inside the collector, a short intensive negative impulse is applied to an electrode spaced preferably as far as possible from the collector or the other point where the ions are at this moment. The ions which are near that pulse electrode, at the time of the impulse, experience a field which causes them to deviate from their stable trajectories and contact one of the electrodes or the wall of the tube envelope. The resonating ions, however, due to the screening effect of the collector, are immune to the effect of this impulse and remain in their stable trajectories.

In known mass spectrographs of the type described the presence of ions can be detected either by an electrostatic detector or a multiplier detector. It has been found that both methods of detection can be significantly improved when an increase in the sharpness of the resonance curve is achieved due to the removal of the unwanted space charge.

In an electrostatically operating signal electrode charges are induced by the oscillating ions during their turn-around motion. These induced charges constitute the output signal of the signal electrode. In known tubes the electrostatic electrode 5 shown in FIG. 1 has a fixed potential. Only ions of a very small energy range are then able to deliver a maximum-induced charge. Ions which have too much energy hit the collector and are discharged, whereas ions with too little energy are not able to approach the detector closely enough to produce a significant influence effect. These disadvantages are overcome by this invention in that a signal detector as shown in FIG. 6 is used. This signal detector comprises, according to this invention, a series of axially-aligned apertured electrodes. The apertured electrodes are preferably of frusto-conical shape, the larger opening being directed to the side from which the ions enter. The elec-

trodes are coupled together for high-frequency signals, but are biased at different, preferably adjustable, D.C.-voltages. The electrodes are biased so that the potentials of the electrodes become progressively more positive if one proceeds from the side into which the ions coming from the ion source first enter to the end of the electrode arrangement farthest away from the ion source. The biasing is chosen to produce a series of equipotential surfaces such as those shown by the dotted lines in FIG. 6. The ions penetrate the influence electrode system to a depth which is determined by their energy and are able to deliver a maximum of signal without being discharged. A directional focussing of the ions takes place because of the preferred funnel form of the electrodes. The electrostatic detector can be simultaneously used with a multiplier detector. It is often desirable to be able to utilize either of the detectors or both simultaneously. At higher pressures an electrostatic detector is generally preferable, whereas a multiplier detector is often overloaded. At lower pressures a multiplier detector is generally preferable. For this purpose we have left an opening in the last influence electrode 7*d* which is covered by a net 8. The Venetian blind-shaped electrode 9 is built in behind the influence electrode system 7*a* to 7*d*. When in use, this electrode is biased to a very large negative potential. The rest of the multiplier electrode system can be any normal arrangement with dynodes 10 and an anode 11. Ions which have sufficient energy pass through the grid 8 and are accelerated to the electrode 9 where they cause electron emission. These electrons, then, are multiplied at the dynodes and proceed to the anode where they are collected.

With known mass spectrograph systems of the type described, the use of a multiplier detector is very difficult. This is easily seen from the potential curve shown in FIG. 2. The ions are generated substantially in a region 12 between the dotted lines. The first electrode of the multiplier system shall have the potential 13. Either the ions are generated at a potential less than that of the multiplier, and in which case, without additional energy, they are unable to reach the multiplier, or they are generated at a potential equal to or higher than the multiplier potential in which case they reach the multiplier after only a half of an oscillation period. Many periods of oscillation are necessary, however, for a good selection of the ions. Additional energy can be supplied to the ions through accelerations of a high-frequency field. This, however, brings the disadvantage that the ions which were generated at the highest potential perform considerably less oscillations than the ions which were generated at the lowest potential. Because the entrance potential of the multiplier electrode system must be about equal to the highest potential of the anode electrodes, approximately half the ions exceed the potential maximum of the anode and fall into the electron source. These ions are not only lost, but deteriorate the cathode.

According to this invention, these disadvantages can be avoided by changing the shape of the potential distribution in the electron gun. The approximately parabolic potential is extended, on the side opposite the multiplier, to a potential which is higher than the entrance potential of the multiplier. The electrons which cause ionization are then injected at an angle to the axis of the tube and at a point where the potential is less than the entrance potential of the multiplier. A high-frequency voltage is then applied to a pair of symmetrical electrodes lying in the vicinity of the potential minimum. In a known manner, the ions then receive additional energy through this high-frequency field.

If an electrostatic electrode is placed in the potential minimum 6, an output signal can be derived by influence without disturbing the ions during the turn-around point of the oscillation cycle.

The method of removing space charges according to this invention can also be used for mass spectrographs operating in the method described above, that is, where the energy of the ions is increased through a high-frequency field. The D.C.- and A.C.-voltages applied to electrode 3, or 3*d*, shall be such that the average potential of this electrode shall be somewhat higher than the entrance potential of the multiplier. The phase and amplitude of the high-frequency signal applied to electrode 3, or 3*d*, shall be such that the resonating ions experience a parabolic potential distribution, whereas the ions which are not in resonance experience a potential maximum which they can exceed and therefore, discharge themselves. The positively biased electrodes which are modulated generally would not be connected with the anode of the electron beam generating systm. In the case of angular electron injection (that is, the ionizing electron beam is crossing the tube axis), intensity modulation equivalent to that shown in FIG. 3 is also possible.

Using the following arrangement a better parabolic potential distribution can be obtained than is possible with the electrodes 4. A cylinder with a variable resistance along its axis is used. The resistance shall be a maximum in the middle of the cylinder and decrease linearly toward the ends. Connections to the cylinder are made by ring-formed electrodes placed in the middle and at both ends. The voltage applied to the electrodes is more negative in the middle than at the ends. Such a variable resistance can be formed by a vacuum-evaporated film layer. Instead of such a cylinder with a variable resistance, a cylinder of homogeneous resistivity can be used whereby the thickness of the cylinder wall decreases linearly toward the ends.

Phase focussing can also be used in a mode of operation where the energy of the ions is increased through a high-frequency field. The parabolic form of the potential distribution must, however, in this case be exceedingly good, so that the method of phase focussing through sweeping, such as implied in FIG. 4, is no longer practical. One can, however, achieve a phase focussing by adjusting the phase of the high-frequency field with respect to the resonance ions. The electrodes for the high-frequency field are, as described above, located symmetrical to the potential minimum. Normally the phase difference between the accelerating voltage and the oscillating ion is about $\pi/2$. In order to achieve a phase focussing, this phase difference is chosen larger than $\pi/2$, up to a maximum of $3\ \pi/4$.

Besides eliminating the unwanted space charge through methods as described it may also be desirable to employ a longitudinal magnetic field. This magnetic field reduces the loss of ions due to motions perpendicular to the oscillation direction, that is, perpendicular to the axis of the spectrometer tube.

The principles described in this invention and explained in conjunction with a pure electrostatic-field functioning mass spectrometer can, of course, be applied to other mass spectrometer types in which the ions perform a periodic motion. In the case of a magnetic-field functioning mass spectrometer with the name "Chronotron" (G. R. Rieck, "Einführung in die Massenspektroskopie," VEB Deutscher Verlag der Wissenschaften, Berlin, 1955, page 161 ff.), for example, a negative defocussing impulses can be applied to the grid at a time when the ions of the sought after mass are in the space near the ion source and collector. Appropriate screens can be applied, so that the resonating ions are not affected by this defocussing field.

FIG. 8 is a sectional view of a practical embodiment of an electrode system for a mass spectrometer tube according to this invention. Dimensional values are given in millimeters and operating voltages in volt. The suffix "var" following a voltage value means that this specific bias voltage is made adjustable, so that the optimum value can be adjusted during operation. FIG. 8 is self-explanatory and therefore not described in detail.

Various changes and modifications in the methods and devices of the present invention may be made by those skilled in the art without, however, departing from the spirit and scope of this invention. The invention is by no means limited to the specific embodiments described.

What is claimed is:

1. In a mass spectrometer, the combination which comprises: a vacuum-tight envelope, a periodically modulated ion source, and means for producing a trough-like electric potential distribution in that envelope and incorporating, a substantially cylindrical electrode, means for positively biasing said cylindrical electrode with respect to the minimum of said potential distrbution, an electrode in said cylindrical electrode, and means for applying a radio-frequency voltage to said electrode positioned in said cylindrical electrode.

2. An influence electrode arrangement for a dynamic mass spectrometer in which at least one group of ions having the same mass-to-charge relationship oscillate between a first region in the vicinity of the influence electrode arrangement and a second region which is spaced apart from said first region, thereby to induce in the influence electrode arrangement a signal whose frequency is equal to the oscillation frequency of the ions, said arrangement comprising, in combination: a plurality of aligned apertured electrodes which, in the direction of the oscillation of the ions, are arranged one behind the other and are spaced from each other, said electrodes being capacitatively coupled to each other and to a signal output terminal, each electrode being provided with a terminal for applying an individual D.C. potential to each respective electrode.

3. The arrangement defined in claim 2 wherein said electrodes are funnel-shaped.

4. The arrangement defined in claim 2, further comprising means connected to said terminals for applying to said electrodes a D.C. bias which becomes progressively more positive in the direction from said second region to said first region.

5. In a mass spectrometer in which at least one group of ions having the same mass-to-charge relationship oscillate between spaced apart first and second regions, the combination which comprises: an influence electrode arrangement located at said first region in consequence of which there is induced in said influence electrode arrangement a signal whose frequency is equal to the oscillation frequency of the ions, said influence electrode arrangement incorporating a plurality of aligned apertured electrodes which, in the direction of the oscillation of the ions, are arranged one behind the other and are spaced from each other, said electrodes being capacitatively coupled to each other and to a signal output terminal, each electrode being provided with a terminal for applying an individual D.C. potential to each respctive electrode; and means for applying, in the space where the ions reverse their direction of motion, an underlinear potential distribution, thereby to decelerate leading ions and to accelerate lagging ions and thus to obtain sharper focussing.

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