

Oct. 18, 1966

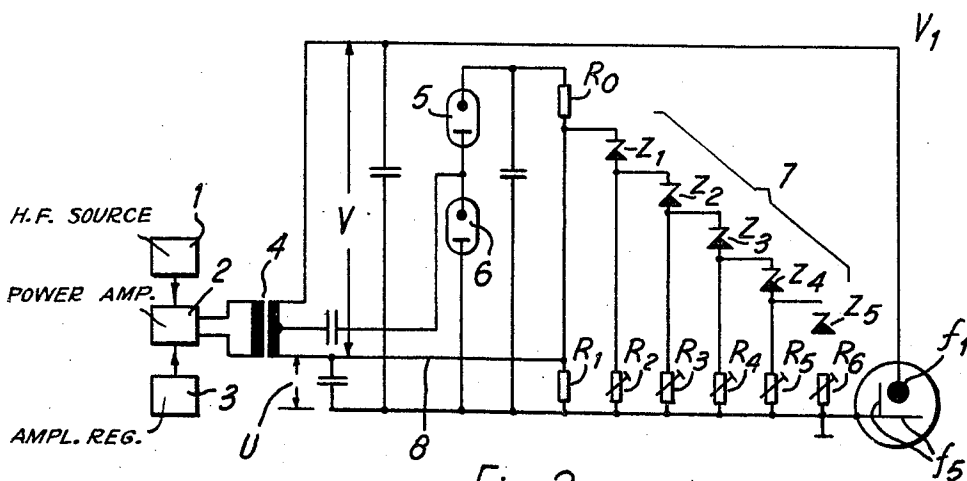
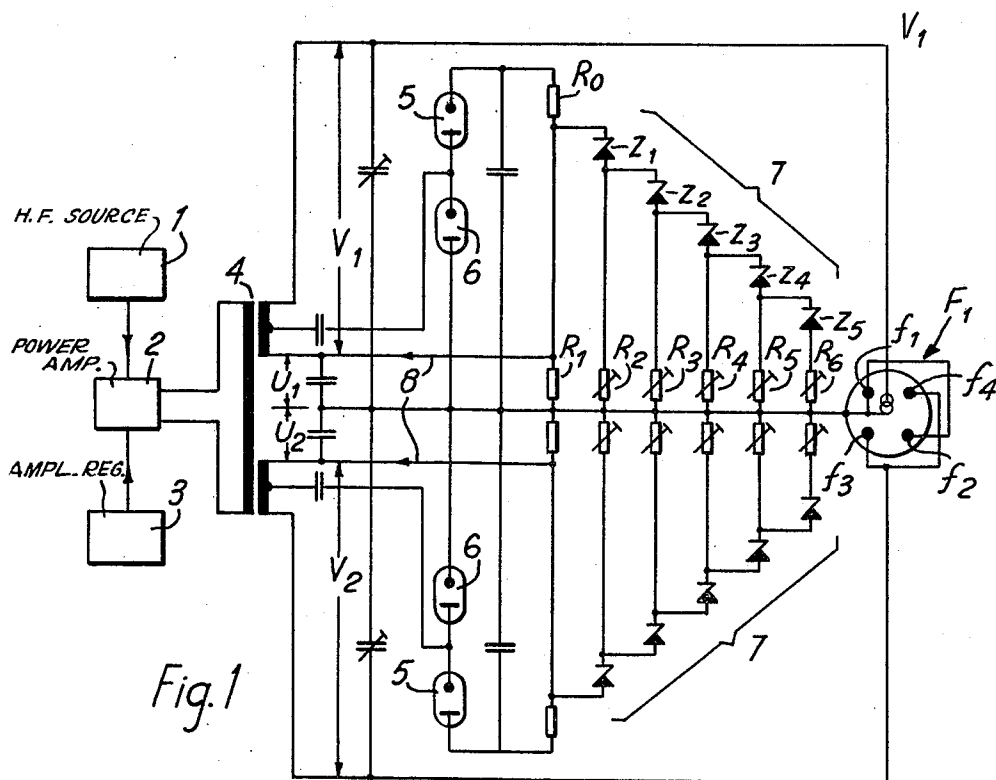
C. BRÜNNÉE ETAL

3,280,325

MASS FILTER WITH PARTICULAR CIRCUIT MEANS CONNECTED TO THE
ELECTRODES FOR ESTABLISHING THE ION DEFLECTING FIELD

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2 Sheets-Sheet 1



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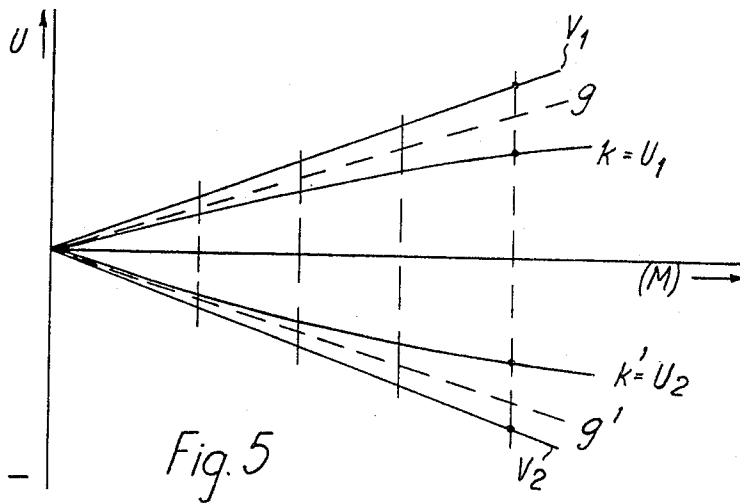
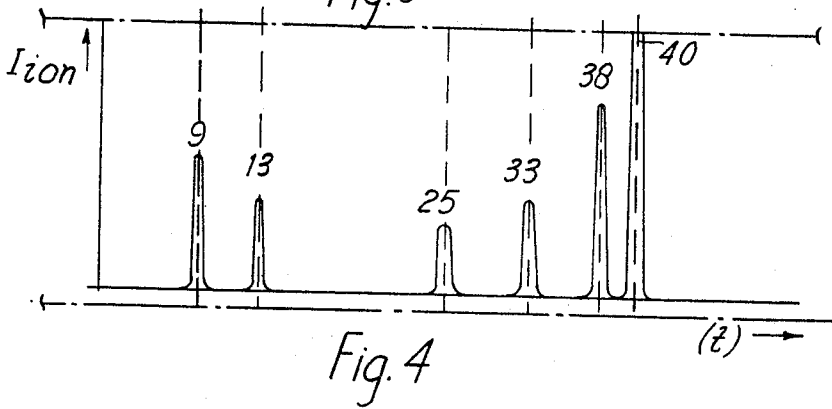
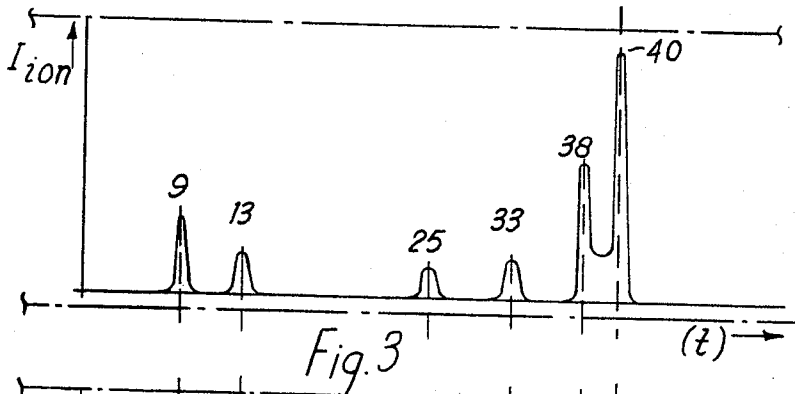
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MASS FILTER WITH PARTICULAR CIRCUIT MEANS CONNECTED TO THE ELECTRODES FOR ESTABLISHING THE ION DEFLECTING FIELD

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3 Claims. (Cl. 250—41.9)

This invention relates to a method of separating ions of different masses by means of a mass filter, for example a Paul's quadrupole filter or Zahn's monopole filter, wherein the ions are shot in the form of an ion beam into an electric field which is produced by one or more alternating voltages $V_1, V_2, \dots$ with superimposed direct voltages $U_1, U_2, \dots$, which are subjected to a continuous variation of magnitude in order to pass through the entire mass range. If the variation in time of the magnitude of the direct voltages U_1, U_2 and the alternating voltage amplitudes V_1 and V_2 is effected in such a manner that the ratios U_1/V_1 and U_2/V_2 respectively are kept constant, the disadvantage is incurred that the line width increases with increasing mass number. Since the line spacing is constant, the resolution is thus reduced.

In order to obviate this shortcoming, according to the invention the ratios U_1/V_1 and U_2/V_2 are adjusted in dependence on the voltages $V_1, V_2, \dots$ in such a manner that they are related by the predetermined functions

$$\frac{U_1}{V_1} = f_1(V_1), \quad \frac{U_2}{V_2} = f_2(V_2) \dots$$

where $V_1, V_2, \dots$ are proportional to the mass number. The functions $f_1(V_1), f_2(V_2)$ can be so selected that a constant resolving power or a constant transmission of the filters is obtained. However, other functions could also be adjusted.

For the purpose of carrying out this method it is possible for the direct voltage U to be derived from the rectified alternating voltage V by means of a voltage divider and to combine the latter with a potentiometer resistor the effective resistance of which is a predetermined function of the alternating voltage amplitudes V_1, V_2 . It is however very difficult to perform this operation accurately, since the necessary function of the resistance cannot, as it has hitherto been attempted to do, be derived accurately from the simple stability criterion. In an actual apparatus the work is also done with beams outside the filter axis and with a finite angle of incidence.

Since the other influencing factors, such as for example the finite angle of incidence, variations of the filter from the ideal form, amplitude-dependent sinusoidal distortions, and also the rectifier characteristic and other similar properties of the apparatus have a considerable influence on resolving power, an alternating voltage/direct voltage function derived from the simplified theory hitherto taken as basis has no great practical importance.

In order to permit an assimilation of the $U-V$ function corresponding to influences which cannot be calculated in advance, according to the invention this function is obtained empirically in direct dependence on the resolving power to be recognised during the measurement or on the transmission of the filter, and utilised in the manner indicated above. This procedure is preferably carried out in such a manner that high frequency amplitudes V_1 and V_2 rise linearly with time, while the direct voltages U_1 and U_2 run in accordance with the functions $f_1(V_1)$ and $f_2(V_2)$. An arrangement which is particularly advantageous and suitable for rapid scanning of the mass spectrum is

2

achieved by obtaining the direct voltages U_1, U_2 with the aid of a voltage divider with electrically adjustable non-linear resistors.

In order that the invention may be more readily understood, reference is made to the accompanying drawings which illustrate diagrammatically and by way of example two embodiments thereof, and in which:

FIGURE 1 shows a circuit arrangement for carrying out the method according to the invention with the aid of a Paul's quadrupole filter,

FIGURE 2 a circuit arrangement for carrying out the method when using a Zahn's monopole mass filter,

FIGURE 3 shows the example of a mass spectrum when applying a linear $U-V$ function corresponding to the broken straight line g, g' in FIGURE 5,

FIGURE 4 shows the mass spectrum illustrated in FIGURE 3 after adjustment of the circuit arrangement shown in FIGURE 1 or 2 to uniformly good sensitivity with the aid of a non-linear $U-V$ function according to the curve k, k' in FIGURE 5, and

FIGURE 5 shows the diagram of a rectilinear and a curved $U-V$ function.

The measurement of the mass spectrum by Paul's method according to German patent specification No. 944,900 is carried out with a so-called quadrupole filter F_1 , in which ions are shot axially into an electric four-pole field in the form of an ion beam from an ion source not illustrated in the drawing. For the purpose of forming this four-pole field, four poles in the form of cylindrical bars f_1, f_2, f_3 and f_4 disposed axially parallel are provided symmetrically about the axis of the cylindrical high vacuum chamber which coincides with the direction of entry of the ions. The voltages serving to form the electric four-pole field are applied in each case to two poles lying diametrically opposite one another. These voltages consist in each case of an alternating voltage

$$V_1 \cdot \cos \omega t \text{ or } V_2 = -V_1 \cdot \cos \omega t$$

and of a superimposed direct voltage

$$U_1 \text{ or } U_2 = -U_1$$

With a determined magnitude of the alternating voltage applied and with a magnitude of the direct voltage dependent thereon, only ions of a determined mass number m/e can pass through the 4-pole field and encounter the ion collector at the end of the field. The ions of all other mass numbers, on the other hand, are excited to perform vibrations of increasing amplitude and thus diverted out of the ion beam. By varying the high frequency amplitude and the direct voltage dependent thereon in synchronism, the ions of the different mass numbers are brought in succession to the collector and hence indicated.

In order to produce the field voltages a high frequency generator 1 is provided which through a power stage 2 with HF amplitude regulation 3 transmits an HF alternating voltage to an HF transformer 4 of amplitude rising strictly linearly with time. From two symmetrically disposed secondary coils of the HF transformer the positive phase $+V_1$ and the negative phase $-V_2$ of the HF alternating voltage are transmitted to the poles f_1, f_2 and f_3, f_4 respectively of the quadrupole filter F_1 . At the same time a direct voltage $+U_1$ and $-U_2$ derived respectively from these two voltage phases by rectification are transmitted through lines 8, 8 to the poles of the filter. For this purpose a rectification of the HF voltage is first effected in rectifiers 5, 5 and 6, 6, and thereupon a voltage division is effected in a voltage divider arrangement 7, 7 in order to derive the desired field direct voltage

$$U_1 \text{ or } U_2 = -U_1$$

The voltage divider 7 works with electrically adjustable non-linear resistors. For this purpose a plurality of shunt resistors (5 in the example illustrated) for the resistor R_1 are allocated to a voltage divider having ohmic resistors R_0 , R_1 , and are composed of adjustable ohmic resistors R_2 , R_3 , R_4 , R_5 , R_6 and of Zener diodes Z_1 , Z_1+Z_2 , $Z_1+Z_2+Z_3$, $Z_1+Z_2+Z_3+Z_4$, and

$$Z_1+Z_2+Z_3+Z_4+Z_5$$

connected in series therewith in a cascade arrangement. By selecting the Zener voltages, that is to say those voltages at which the Zener diodes pass through the break of their resistance characteristic, and by selection of the magnitudes of the resistances R_0 to R_6 it is possible, as will be immediately apparent, to adjust any desired curvature of the U-V function k , k' according to FIGURE 4. By connecting the voltage divider 7 with the resistance R_2 to R_6 in parallel to R_0 , a reverse curvature of the curve k and k' referred to the linear U-V function g and g' is obtained.

The adjustment of the circuit arrangement is effected in the following manner: A measurement is first made with a linear U-V function, that is to say without the electrically nonlinear parallel resistors. This would result in a mass spectrum of the type illustrated in FIGURE 3, which shows an undesirably great line width and hence poor resolving power. The HF amplitude is thereupon slowly adjusted upwards from zero and the nonlinear resistance, consisting of the Zener diode Z_1 and the adjustable ohmic resistance R_2 , is first so adjusted that the mass corresponding to the respective voltage magnitude is indicated with optimum resolving power. In the same manner the following nonlinear resistances are adjusted with increasing HF amplitude up to the last nonlinear resistance combination Z_5 , R_6 . Once this adjustment has been made, it can normally be retained; if, however, variations of the factors influencing the resolving power should occur during operation it is at any time possible to effect a re-adjustment in a simple manner.

The circuit arrangement illustrated in FIGURE 2 corresponds in all essential points to the circuit arrangement illustrated in FIGURE 1, except that the Paul's quadrupole mass filter is replaced by a Zahn's monopole mass filter F_2 (The Review of Scientific Instruments, vol. 34, No. 1, January 1963, "Monopole Spectrometer, a New Electric Field Mass Spectrometer," by Ulf von Zahn) is provided, which is substantially simpler both in its actual construction and in the corresponding circuit arrangement. In the monopole mass filter only a part of the electric field required in the quadrupole mass filter is produced, only one of the four pole bars f_1 provided in the latter being required, while the three missing pole bars f_2 , f_3 , f_4 are replaced by an angle electrode f_5 .

The invention is not restricted to the example illustrated, but on the contrary various modifications and other embodiments are possible. In particular, the electrically nonlinear resistances may be formed by other electric elements. The Zener diodes, which in the above-described circuit arrangement act mainly as switching elements, may also be replaced by other switches working in dependence on the voltage applied, for example diodes having a control electrode. In addition, series connections of simple diodes, ohmic resistors, and ad-

justable auxiliary voltages could also be used. Instead of electronic means it is also possible to use mechanical means, for example motor-driven potentiometers for passing through the predetermined function. The invention can of course also be appropriately applied when the field direct voltage is not derived from the HF voltage but from another voltage.

We claim:

1. Apparatus for separating ions of different masses comprising,
 - mass filter having electrode means for establishing an electric ion deflecting field and an ion source and an ion detector positioned at opposite ends of said electrode means,
 - a source of an alternating voltage of varying amplitude V ,
 - means applying said alternating voltage to said electrode means for establishing a first component of said electric ion deflecting field,
 - nonlinear circuit means responsive to said alternating voltage varying amplitude V for providing a direct voltage U that is a nonlinear function of said varying amplitude V for establishing the resolution of said mass filter substantially independent of said varying amplitude V ,
 - and means applying said direct voltage U to said electrode means for establishing a second component of said electric ion deflecting field whereby the resolution of mass filter is substantially independent of the magnitude of said electric ion deflecting field,
 - said nonlinear circuit means comprising,
 - rectifying means for providing a high direct potential representative of said varying amplitude V ,
 - and potential dividing means for attenuating said high direct potential by a factor dependent upon said varying amplitude V to provide said direct voltage U ,
 - said potential dividing means comprising,
 - a plurality of resistive means and a corresponding plurality of unilaterally conducting devices in series with a respective one of said resistive means to form a corresponding plurality of series combinations,
 - and means for direct coupling each of said series combinations between said rectifying means and said electrode means,
 - the number of said unilaterally conducting devices then conductive being related to the magnitude of said high direct potential.
2. Apparatus for separating ions of different masses in accordance with claim 1 wherein said mass filter comprises a quadrupole mass filter.
3. Apparatus for separating ions of different masses in accordance with claim 1 wherein said mass filter comprises a monopole mass filter.

References Cited by the Examiner

UNITED STATES PATENTS

2,939,952	6/1960	Paul et al.	250—41.9
2,950,389	8/1960	Paul et al.	250—41.9

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