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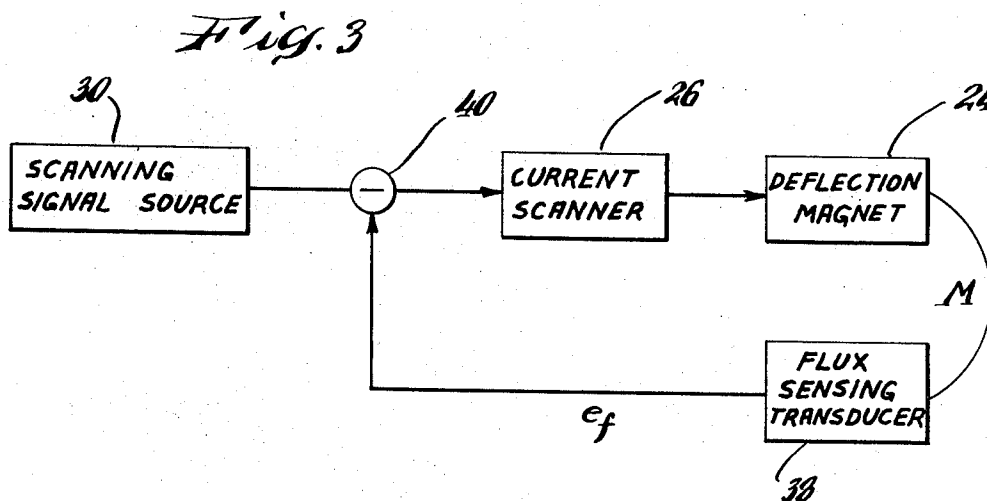
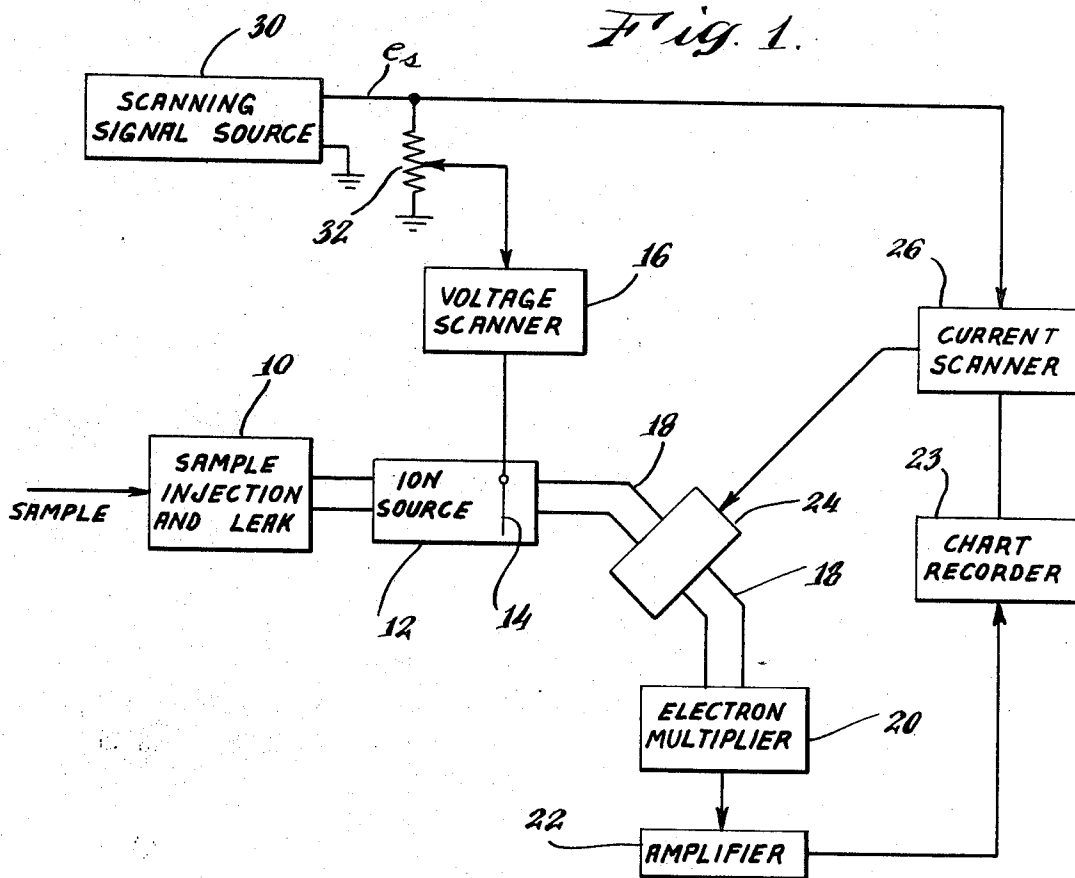
E. B. DELANY

3,527,938

LINEARIZATION OF MASS SCANNING IN A MASS SPECTROMETER

Filed Oct. 16, 1967

2 Sheets-Sheet 1



INVENTOR.
Edward B. Delaney
 BY
Frank J. Thompson
 ATTORNEY.

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E. B. DELANY

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2 Sheets-Sheet 2

Fig. 2

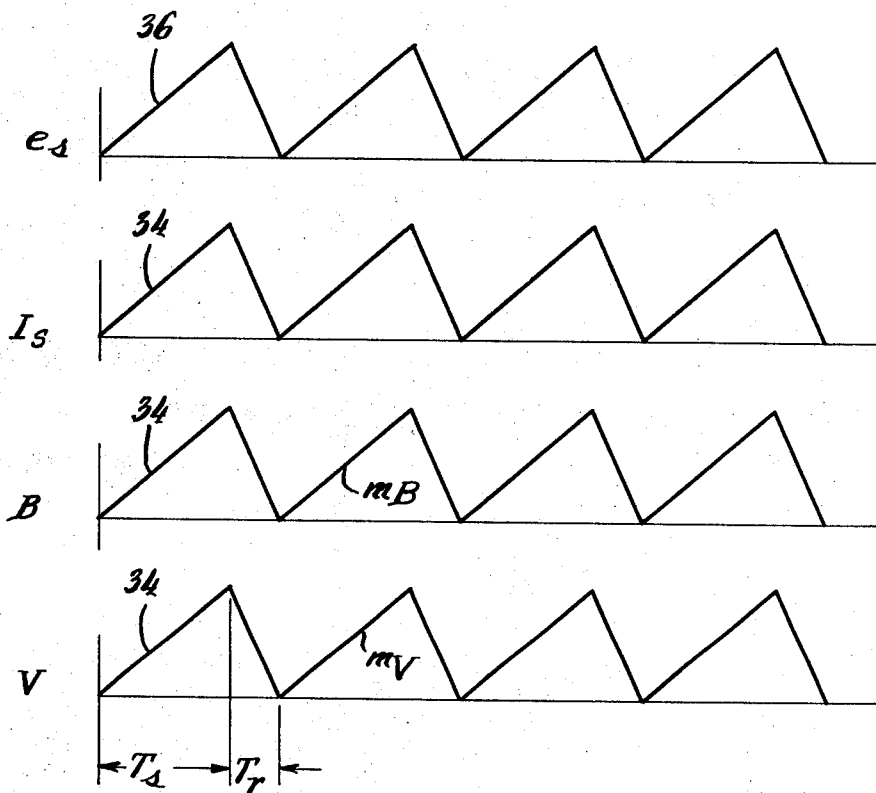
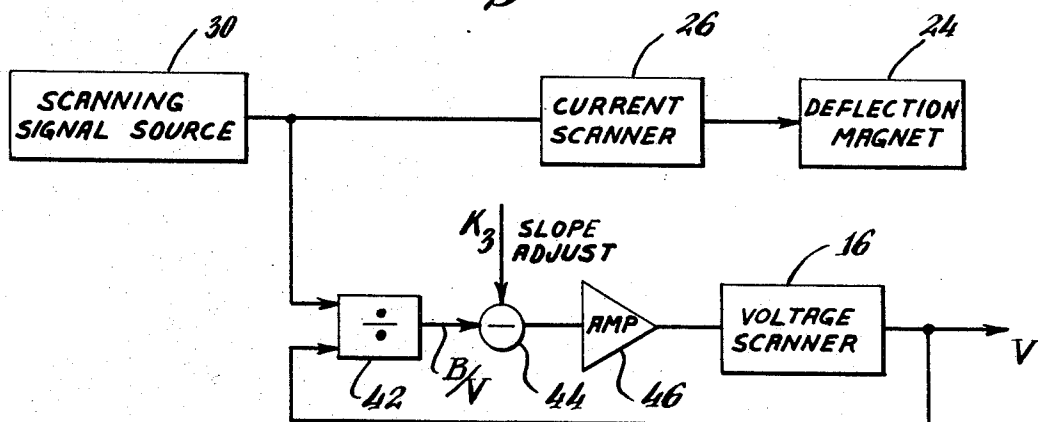


Fig. 4



INVENTOR.

Edward B. Delaney

BY

Frank J. Thompson

ATTORNEY.

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LINEARIZATION OF MASS SCANNING IN A MASS SPECTROMETER

Edward B. Delany, Ridgefield, Conn., assignor to The Perkin-Elmer Corporation, Norwalk, Conn., a corporation of New York

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8 Claims

ABSTRACT OF THE DISCLOSURE

A mass spectrometer includes means for establishing a magnetic scanning field and a simultaneously varying electric, ion accelerating field. The flux density B of the magnetic field and the amplitude of the accelerating field potential V are varied linearly and simultaneously in a manner for providing that a ratio B/V is maintained substantially constant during a scanning interval. Linear presentation in time of mass-charge data thereby occurs while a variation in V results in a varying resolution characteristic providing a substantially constant base width for peaks of differing mass-charge numbers.

This invention relates to mass spectrometers. The invention relates more particularly to an improved scanning arrangement for a mass spectrometer.

In a mass spectrometer, ionized sample particles are accelerated by virtue of an electric field E through a magnetic field ϕ toward an aperture in an output ion collector plate. The magnetic field exerts a force on the ionized particles causing them to follow a curved trajectory and to focus on the collector plate. When the mass spectrometer equation:

$$M/e = 4.82 \times 10^{-5} \frac{R^2 B^2}{V} = k_1 \frac{B^2}{V} \quad (1)$$

is satisfied, particles of a particular M/e focus at the aperture and excite an electron multiplier. In this equation:

B is the magnetic flux density
V is the accelerating potential
R is the radius of trajectory
M is the mass of an ion, and
e is the charge on an ion.

A mass spectrometer having fixed physical dimensions exhibits a constant radius of trajectory R. Mass-charge scanning for an ionized sample is generated in an instrument of this type by varying the magnetic flux density B or the ion accelerating potential V, or both, in a predetermined manner. In general, magnetic scanning provides for scanning over a substantially larger range of M/e values than does electric scanning. It is thus generally desirable to provide a magnetic scanning arrangement for general purpose use.

In practice, a chart recorder has been employed for recording the generated spectrum. The chart drive is synchronized with the spectrometer during a scanning interval and mass-charge abundance data is recorded as ordinate data, for example, while mass-charge magnitude or elapsed time is recorded as abscissa data. This data thus appears as relatively narrow spectrum lines or peaks which represent mass-charge numbers in the range of from 4 to 12 to about 1,000. Some sample substances have spectra including several hundred peaks, any two or more of which may occur with successive mass-charge numbers. The relatively large amount of data which can be generated and the occurrence of substances with successive mass numbers dictates the presentation of recorded data in a manner which facilitates the sample analysis and is not cumbersome to the instrument operator.

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One aspect of data presentation relates to the particular manner in which mass-charge data is recorded. It is generally deemed preferable, that the chart recorder be driven linearly with respect to time. In addition, the magnetic flux density B is a function of time. However, reference to the mass spectrometer Equation 1 indicates that mass-charge data is not presented in a linear manner but rather as an exponential function of time. This data, when recorded by a linearly driven chart recorder, comprises a group of peaks which are not equally spaced and which are bunched near the beginning or near the end of the scan. Insofar as analysis of the recorded data is concerned, this recording arrangement is disadvantageous.

It has been proposed to linearize the recording of data in order to facilitate analysis by modifying the scanning function to provide linear presentation of mass-charge data in time. One arrangement for accomplishing the desired presentation utilizes a magnetic deflection field current function, $I = k \cdot t^{1/2}$. Although the recording of data is thereby linearized, the resolution characteristic of the apparatus, i.e., discrimination between closely adjacent peaks, remains constant. The bandwidth of a linearly scanned system of this type will increase substantially as M/e approaches zero. Thus, the bandwidth of the scanning and peak amplifying components of the spectrometer must be increased substantially with attending and disadvantageous increase in cost and complexity in order to reproduce information peaks throughout the scanning range.

Accordingly, it is an object of this invention to provide an improved form of mass spectrometer.

Another object of this invention is to provide an improved scanning arrangement for a mass spectrometer.

A further object of the invention is to provide an improved form of mass spectrometer adapted for linear presentation in time of mass-charge data.

Still another object of the invention is to provide a mass spectrometer adapted for linear presentation in time of mass data and having a varying bandwidth characteristic.

In accordance with a feature of the present invention, a mass spectrometer includes means for establishing a magnetic scanning field and a simultaneously varying electric ion accelerating field. The flux density B of the magnetic field and the accelerating field potential V are varied linearly and simultaneously in a manner for providing that a ratio B/V is maintained constant during a scanning interval. Since B is linear and $B/V = k_2$, then the mass spectrometer equation becomes:

$$M/e = k_1 \times B \cdot B/V = k_1 \times B \times k_2 = k_3 \times B \quad (2)$$

This equation demonstrates that a linear presentation in time of mass-charge data occurs with linear variations in B and V. In addition, a resulting varying resolution accompanying the variation of V effects a substantially constant base width for peaks of different mass-charge numbers.

These and other objects and features of the invention will become apparent with reference to the following specifications and drawings wherein:

FIG. 1 is a diagram, in block form of a mass spectrometer constructed in accordance with features of the present invention;

FIG. 2 is a diagram of various waveforms occurring in the spectrometer of FIG. 1;

FIG. 3 is a block diagram of a scanning linearity correction means for the spectrometer of FIG. 1; and

FIG. 4 is a block diagram of an alternate scanning arrangement for the spectrometer of FIG. 1.

Referring now to FIG. 1, a magnetic field scanning mass spectrometer is illustrated. The spectrometer includes a sample injector and leak arrangement 10 and an ion source 12. As is well known, a sample is vaporized and contained in an evacuated reservoir from which the sample

molecules leak into the ion source at a desired rate. The ion source operates on the molecules and generates ions therefrom. In one arrangement the molecules are ionized through bombardment by an electron beam.

Means are provided for accelerating the generated ions toward an apertured collector plate positioned in an analyzer section of the apparatus. The mechanical configuration of the ion accelerating means is conventional and is represented in FIG. 1 by an anode 14 to which a time varying potential V is applied from a source 16. The particular waveform of this varying potential is described in more detail hereinafter. The path of the accelerated ions is described generally by the tubulation 18. Ions passing through the collector plate aperture excite an electron multiplier 20 and a signal generated thereby is further amplified by an amplifier arrangement 22 and coupled to a chart recorder 23.

In providing mass selection, ions which are accelerated through the tubulation 18 traverse a magnetic field having a flux density B which varies in time and thereby causes ions of different mass-charge ratios to pass through the aperture in the collector plate. This magnetic field is established by an electromagnet 24 which is energized by a current scanning circuit arrangement 26. A mass spectrum is generated by causing the current in a winding of the electromagnet 24 to vary in a predetermined fashion during an interval of time.

A spectrum of the ions of different M/e numbers passing through the collector plate is recorded by the chart recorder 23. The chart recorder is a conventional mechanically driven chart upon which an indication of mass-charge abundance data is entered along an ordinate in accordance with an output signal from amplifier 22 and time or mass-charge number is represented along an abscissa. The mechanical drive of the recorder is synchronized with the scanning of the spectrometer. As indicated hereinbefore, the chart is preferably advanced linearly in time. With this arrangement, a length of chart (L) passing a recording station during an interval of time (t) is constant during the scanning interval. This form of chart drive is relatively non-complex and eliminates the need for other more complex arrangements when a nonlinear chart drive is employed.

In accordance with a feature of the present invention, circuit means are provided for establishing a time-varying magnetic flux density B and a time-varying accelerating potential V which are adapted for causing a linear presentation in time of mass-charge data. A signal source 30 provides a scanning reference signal e_s which is a linear function of time, $e_s = f(t)$. This signal is applied to the current scanner 26 for causing a linearly varying current I_s to flow in the magnet 24 during a scanning interval. In addition, the scanning signal e_s is also applied via a potentiometer 32 to the voltage scanner 16. A voltage which varies linearly in time is thereby coupled to the ion accelerating electrode 14 and generates an electric field similarly varying linearly in time, $V = f(t)$. The particular circuit arrangements of the current scanner 26, voltage scanner 16, and scanning signal source 30 are well known. Typical arrangements for generating a linear current and voltage ramp function of the desired waveform, as illustrated in FIG. 2, are described in detail in Pulse and Digital Circuits, Millman and Taub, McGraw-Hill, 1956, chapters 7 and 8. Since the current scanner 26 and voltage scanner 16 are driven by a linear signal from a common source 30, the linear waveforms of scanning current I_s and accelerating potential V are of equal slope and of similar polarity during a scanning interval.

As indicated hereinbefore, in the mass spectrometer equation the mass-charge ratio is given by:

$$M/e = 4.82 \times 10^{-5} \frac{R^2 B^2}{V} = k_1 \frac{B^2}{V} \quad (1)$$

Thus a linear variation in the scanning current accompanied by a simultaneous linear variation in the accelerat-

ing potential V will result in the presentation in time of mass-charge data linearly related to the flux density.

FIG. 2 illustrates typical waveforms occurring in the mass spectrometer of FIG. 1. The waveforms for deflection current I_s and the resulting flux density B as well as the accelerating potential V are each shown to include a linear segment 34 synchronized to a linear segment 36 of the scanning signal e_s during a scanning interval T_s . Since both B and V are linear and of equal slope, m_B and m_V respectively, during the period T_s , their ratio B/V will be a constant k_2 . Mass-charge data will then be presented as a linear function of time. In addition, since V varies during the interval T_s , a variation in the resolution of the apparatus also occurs. The bandwidth requirements of the linearly scanned system are thereby lowered.

The linearity of the scanning current I_s and the resulting flux density B can be increased by utilizing means for detecting variations in linearity and applying a correction to the scanning current to compensate for this variation. In FIG. 3, a flux sensing means 38 is illustrated as being inductively coupled to the field generated by the deflection magnet 24. This flux sensing means includes a transducer for converting flux density into a representative voltage. A flux sensing transducer of this type is conventional and it is not believed that the details of its construction need be described further. An output voltage from the transducer 38 is coupled to an adder circuit 40 which is adapted for combining the signal e_s with the signal from the transducer 38 to provide a resultant linearity corrected input signal for the current scanner 26.

An alternative scanning arrangement for the mass spectrometer of FIG. 1 is illustrated in FIG. 4. In this scanning arrangement, the varying electric field voltage generator comprises a closed circuit loop including a dividing network 42 which provides an output voltage representative of the ratio B/V , a slope adjusting circuit 44, and an amplifier 46. The network 44 is adapted for adjusting the slope of the varying accelerating potential V to provide a deviation from a constant ratio between B/V which may result from circuit characteristics changing with time. The linear output signal from the scanning signal source 30 is applied to the current scanner 26 as in FIG. 1. The arrangement of FIG. 4 is advantageous in that it provides relatively high linearity and accuracy with respect to the establishment of the electric field and the adjustment of the constant k_3 .

An improved mass spectrometer has been described wherein the mass data is presented linearly in time while the bandwidth of the apparatus is altered during a scanning interval.

While I have illustrated and described a particular embodiment of my invention, it will be understood that various modifications may be made therein without departing from the spirit of the invention and the scope of the appended claims.

I claim:

1. In a mass spectrometer, an improved scanning arrangement comprising:

means for establishing a magnetic ion scanning field having a flux density B varying linearly as a function of time and means for establishing an ion accelerating electric field having an intensity V varying linearly as a function of time, said means adapted for establishing a constant ratio of B/V during a scanning interval.

2. In a mass spectrometer having an accelerating electrode for accelerating ions toward a target and an electromagnet for deflecting the ions during a scanning interval, an improved scanning arrangement comprising:

first circuit means for causing a current I_s to flow in said electromagnet winding in a manner for causing a magnetic field having a flux density B varying linearly in time to be established by said electromagnet;

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second circuit means for applying to the accelerating electrode a voltage having a magnitude V which varies linearly in time;

said first and second circuit means adapted for providing that a ratio B/V is substantially constant during a scanning interval.

3. The spectrometer of claim 2 including a source of a linear scanning signal e_s , and, means for coupling said linear scanning signal to said first and second circuit means.

4. The spectrometer of claim 3 including recording means having a recording mechanism operated linearly in time, sensing means for sensing the occurrence of ions at the target and means for coupling said sensing means to said recording means.

5. A mass spectrometer comprising :

a source of ions;

a target electrode;

an accelerating electrode for accelerating said ions to said target electrode over a predetermined passage-way;

an electromagnet positioned with respect to said passageway for establishing a magnetic field in a path traversed by said accelerating ions;

sensing means coupled to said target electrode for sensing the occurrence of said ions at said electrode;

recording means including a mechanism operating linearly in time for recording electrical data coupled thereto;

means for coupling said sensing means to said recording means;

current scanning circuit means coupled to said electromagnet and adapted for causing said electromagnet to establish a magnetic field flux density B which varies linearly in time when a signal which varies linearly in time is coupled thereto;

voltage generating circuit means coupled to said ac-

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celerating electrode and adapted for applying a voltage V to said electrode which varies linearly in time when an input signal which varies linearly in time is coupled thereto;

means for applying an input signal which varies linearly in time to said current scanning circuit means and to said voltage generating circuit means; said current scanning and voltage generating circuit adapted for establishing a constant relationship B/V during a scanning interval.

6. The spectrometer of claim 5 wherein a slope m_B of the time varying magnetic field and the slope m_V of the time varying accelerating voltage are equal and of the same polarity.

7. The spectrometer of claim 6 including a flux sensing means inductively coupled to said deflection electromagnet for providing an output signal indication indicative of nonlinearities occurring in the magnetic field intensity during the scanning interval and means for combining the output signal and said scanning signal in a manner for correcting the nonlinearities.

8. The scanning arrangement of claim 7 wherein said voltage scanning circuit means includes means for generating a voltage representative of a ratio between the flux density B and the electric field V , means for adjusting the magnitude, and means for applying said adjusted voltage to a voltage scanning circuit.

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ARCHIE R. BORCHELT, Primary Examiner

A. L. BIRCH, Assistant Examiner