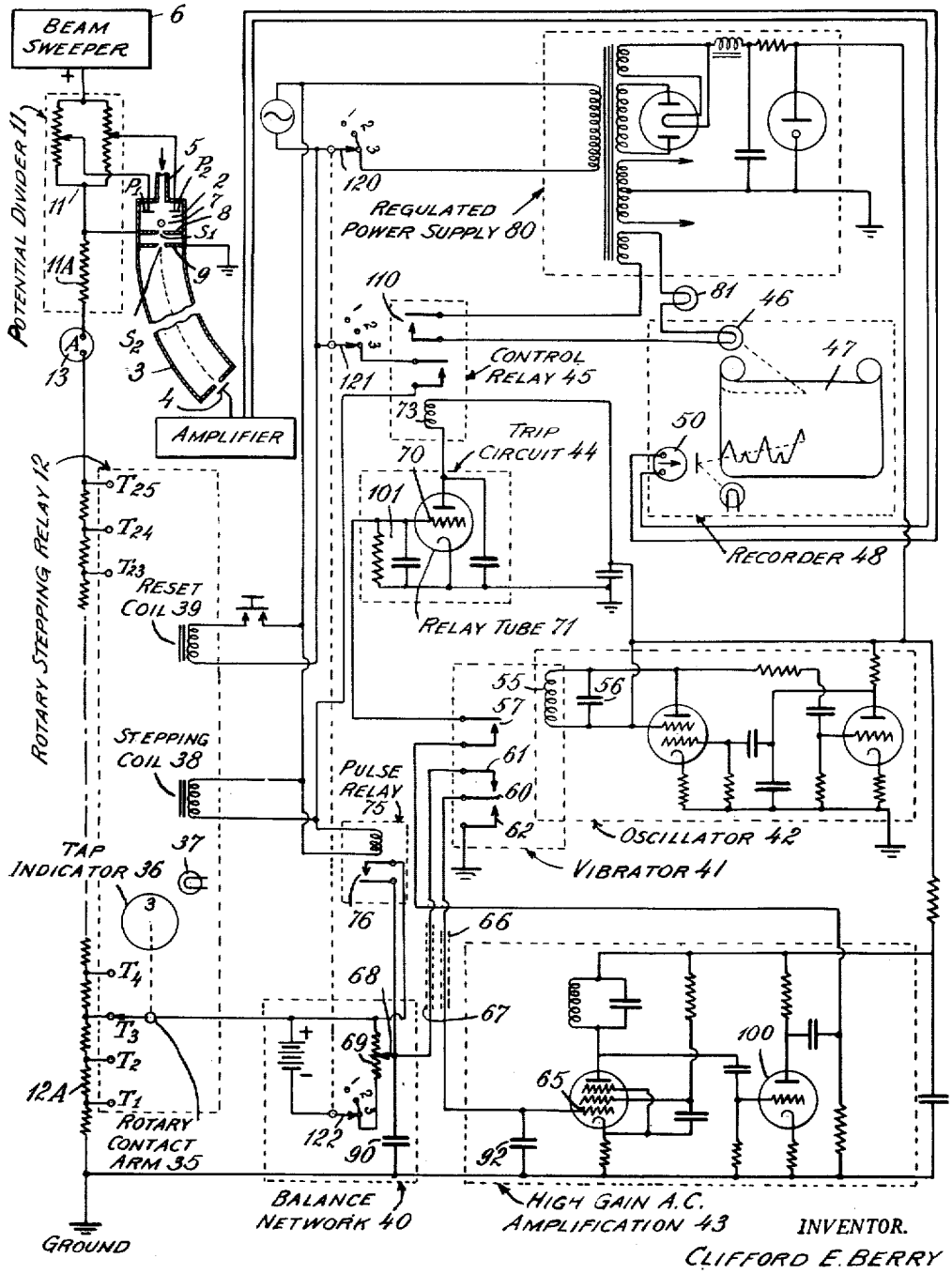
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MASS SPECTROMETRY

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MASS SPECTROMETRY

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6 Claims. (Cl. 73—18)

This invention is concerned with mass spectrometers and provides improved mass markers for such instruments.

A mass spectrometer is an apparatus for sorting ions according to the ratio of the mass of the ion to the charge that it carries (this ratio being referred to hereinafter as "specific mass") and can be employed for various purposes, including qualitative and quantitative analyses of mixtures containing different kinds of molecules, determination of isotope ratios, etc.

A common form of mass spectrometer includes an ionization chamber in which molecules of the mixture to be analyzed are converted into ions, an analyzer tube in which a heterogeneous beam of the ions is separated by an electric or magnetic field into a plurality of diverging homogeneous beams of ions (the ions of the same specific mass being included in a single beam), an ion collector, means (referred to here as a beam sweeper) for bringing the several beams successively into contact with the collector and means for indicating separately the currents collected from the several beams.

A record of the separately collected currents is a mass spectrogram, which may take any one of several forms. For example, it may be a graph on which the magnitudes of the currents corresponding to the several collected ion beams are represented by the heights of a series of peaks projecting from an abscissa axis. Such a record can be produced on a laterally moving sheet of photographic paper, or the like, by a recording galvanometer. For some purposes, such a mass spectrogram is entirely adequate, but in many cases, for example in the quantitative analysis of a mixture of hydrocarbons containing a number of different kinds of molecules some of which crack in the ionization chamber to form a plurality of different kinds of ions, it is necessary to determine and identify the specific mass of the ions to which each peak corresponds.

In accordance with the invention described and claimed in the copending application of Robert V. Langmuir Serial No. 494,807, filed July 15, 1943, the interpretation of a mass spectrogram is facilitated by indicating in a coordinated manner and preferably simultaneously with the indication of the peaks (ion currents), the specific masses of the ions to which the respective peaks (currents) correspond. Thus Langmuir contemplated marking on the mass spectrogram adjacent the respective peaks and during the recording thereof, the specific masses of the ions to which the peaks correspond.

In one form of the Langmuir apparatus, the specific mass indicator is operatively connected with the beam sweeper and is actuated by it. In such apparatus, the beam sweeper automatically and gradually alters the potential impressed upon the ions passing through the analyzer and thus changes the path of the ions so that the beams are swept successively over the collector. A "specific mass" indicator is connected in a circuit with the beam sweeper and a change in the potential actuates the indicator. For example, the mass indicator may be a galvanometer calibrated in terms of ion masses or a vacuum tube circuit which is tripped at intervals at successive values of ion accelerating potential, means being provided to mark the spectrogram each time the circuit trips. In this way, the beam sweeper and the mass indicator are synchronized and the peaks on the spectrogram are correlated with the specific masses of the ions to which they correspond.

Apparatus described in the aforementioned Langmuir application includes a beam sweeper which automatically decreases the ion accelerating potentials applied to electrodes in the mass spectrometer, and is connected to these electrodes through a potential divider. This in turn is connected in series with a rotary stepping relay, the contact arm of which is connected to the slider of a potentiometer in a direct current amplifier circuit. The output of this D. C. amplifier is employed to mark the mass spectrogram at points corresponding to the peaks thereon.

As the result of my investigations, I have developed a mass marker which correlates a specific mass and the current of the beam to which the mass corresponds with great accuracy. In general, my invention contemplates in a mass indicator of a mass spectrometer having a resistance, means for impressing across the resistance a voltage which is a function of the specific mass being detected, and means for selecting successive fractions of this voltage during a period in which the voltage is changing, the combination which comprises means connected to the voltage selector for producing an alternating current corresponding in amplitude to the selected fraction of the voltage, and means responsive to a deviation in the amplitude of the alternating current from a threshold value for indicating the specific mass of ions detected when the threshold is reached and for causing the voltage selector to select the next fraction of voltage. In its preferred form, my invention contemplates, in combination with the voltage

selector, a balanced network, means for converting the output of the balanced network into alternating current, a high gain A. C. amplifier, and means for rectifying the amplifier output and applying this rectified output to a trip circuit which marks the spectrogram.

These and other features of my invention will be more thoroughly understood in the light of the following detailed description, taken in conjunction with the accompanying drawing, which is a wiring diagram of a preferred form of my mass marker.

Referring now to the drawing, it will be observed that a mass spectrometer 1 is provided with an ionization chamber 2, an analyzer tube 3, an ion collector 4, and an inlet conduit 5 for the material to be analyzed in the spectrometer. A high voltage from a direct current source is applied to the mass spectrometer through a beam sweeper 6. Thus the beam sweeper impresses a high but gradually decaying potential between electrodes in the mass spectrometer. Gas molecules that are ionized in the ionization chamber by bombardment with an electron beam 7 are propelled to a slit S_1 in an accelerating electrode 8 by a potential impressed between pusher electrodes P_1, P_2 and the electrode 8. A heterogeneous ion beam is thus formed and this is further accelerated into the analyzer tube by a potential impressed between the accelerating electrode 8 and a second accelerating electrode 9, which has a slit S_2 that matches the slit S_1 in the first accelerating electrode. The potential applied, respectively, to the pusher electrodes P_1, P_2 may be adjusted by means of a potential divider 11 which comprises two potentiometers in parallel and connected, respectively, to the two pusher electrodes. The potentiometers in parallel are followed by a large resistance 11A in series. The size of this resistance, which is connected to ground through a tapped resistor 12A of a rotary stepping relay 12, controls the proportion of the potential applied across the gap P_1, P_2—S_1 and the gap S_1—S_2. An ammeter 13 is connected in series with the resistor 12A of the rotary stepping relay and the potential divider and may be calibrated in terms of specific mass.

The major portions of the apparatus, in addition to those already described, comprise a balanced network, a high gain A. C. amplifier, an oscillator coupled to a vibrator, a trip circuit, and appropriate power supplies.

The rotary stepping relay conveniently is the type designated by Guardian Electric Manufacturing Company as "Series R stepping relay." It comprises a rotary contact arm 35 which upon rotation may touch any one of a series of equally spaced circumferentially positioned fixed taps T_1, T_2, T_3 . . . T_{25} on the resistor. A tap indicating disc or a cylinder 36 rigidly secured to the same shaft as the arm has numbers thereon which are moved beneath the pointer and become illuminated by a lamp 37 when the arm contacts the corresponding tap. Thus, as shown, the numeral 3 is illuminated on the tap indicator 36 when the rotary arm touches tap T_3. The indicator 36 may also carry specific mass numbers in addition to tap numbers.

The rotary stepping relay also includes a stepping coil 38 and a reset coil 39. When an electrical impulse is applied to the stepping coil, the rotary contact arm moves to the next tap in sequence. When current is applied to the reset coil, the rotary arm returns to the first tap position T_1.

The contact arm of the rotary stepping relay is connected to a balancing network 40 of conventional design. This balancing network balances the potential between the rotary arm and ground against a standard potential, i. e., the standard potential and that between ground and the rotary arm are opposed to produce a differential potential. The balancing network is connected to a vibrator 41 which is coupled to an oscillator 42 and these convert the difference between the standard potential and that impressed from the rotary arm to ground into an alternating current. This alternating current is amplified by a high gain A. C. amplifier 43. As described hereinafter, the output of the amplifier is rectified and the voltage proportional to the amplitude of the alternating current is applied to a trip circuit 44, which controls the operation of a control relay 45 which in turn actuates a mass marker lamp 46 that marks a mass spectrogram produced on a photographic film 47 of a recorder 48.

Currents generated through discharge of ion beams at the ion collector are amplified and recorded as a spectrogram on the moving photographic film 47 by means of a galvanometer 50. The mass marker is synchronized with the galvanometer by the mass marker control just described.

The control relay, in addition to marking the spectrogram, steps up the rotary arm 35 to the next tap, say T_4 of the rotary stepping relay.

The oscillator and vibrator are coupled together because a vibrator coil 55 is connected in the output of the oscillator. A condenser 56 connected in parallel with this coil forms with the coil a parallel resonant network which may be electrically tuned to the same frequency as the resonant frequency of the mechanical elements of the vibrator. These elements include one normally closed pair 57 of contacts and another set of contacts comprising an armature contact 60, a signal contact 61 and a ground contact 62. The armature normally is in the neutral position and contacts the signal contact and the ground contact alternately when alternating current is applied to the vibrator coil.

The high gain A. C. amplifier has a signal grid 65 connected to the armature contact 60 through a shielded conductor 66. The signal contact 61 is connected through a second shielded conductor 67 to the slider 68 of a potentiometer 69 in the balancing network. The positive terminal of the potentiometer is connected, as indicated hereinbefore, to the rotary arm of the rotary stepping relay.

The amplifier 43 includes a resonant circuit tuned to the same frequency as the oscillator, so as to render the amplifier most sensitive to input signal components having this frequency. The output of the amplifier is applied through the normally closed contacts 57 of the vibrator to the signal grid 70 of a relay tube 71 included in the trip circuit 44. The output of the relay tube is applied to a coil 73 which actuates the control relay 45.

A pulse relay 75 is connected in the balancing network 40. It has a pair of normally open contacts 76 connected between the positive terminal of the potentiometer 69 and its slider 68.

A conventional regulated power supply 80 supplies power to a panel light 81, the marker light

46, the oscillator, the amplifier and the trip circuit.

A large capacity condenser 90 is connected between the potentiometer slider and ground. A condenser 92 of small capacity is included in the high gain amplifier and is connected between ground and the signal grid 66 of the first amplifier tube.

The operation of the mass marker control described hereinbefore is as follows:

The beam sweeper reduces the voltage across the potential dividing network in order to shift the separated ion beams across the collector at the end of the analyzer tube. As the voltage across the potential dividing network decreases, the voltage present at any time between the rotary arm and ground is balanced against a negative voltage supplied to the balancing network from the potentiometer 69. The difference between these two voltages is applied to the large condenser 90.

The armature contact of the vibrator alternately, and at the frequency of the oscillator, comes in contact with the signal contact 61 and the grounded contact 62, so that part of the charge on the large condenser is alternately applied to the small condenser and then discharged to ground. In consequence, a voltage equal to that appearing across the large condenser is periodically applied to the control or signal grid of the amplifier, producing on this grid pulsations having a substantially rectangular, unidirectional wave form. Thus, in effect, the vibrator functions as an inverter. The first amplifier tube has a plate circuit with a resonant LC network and this filters from the amplified signal all components other than the fundamental. The latter is thereupon applied to the second amplifier tube 100 and thence appears at the output of the amplifier.

The normally closed pair of contacts 57 of the vibrator are open when the amplifier output signal voltage is positive and are closed near the negative peak of the amplifier output voltage. Consequently, negative pulses are applied periodically to a parallel resistance condenser network 101 which constitutes the grid circuit of the relay tube 71. The time constant of this grid circuit is long compared to the period of the vibrator, so that there is applied to the relay tube a negative bias having an amplitude corresponding to the excess of the rotary arm voltage over the potentiometer voltage, i. e., corresponding to the differential-potential.

When the bias on the relay tube grid 70 falls below a threshold value inherent to the tube, the tube passes current and closes the normally open contacts 110 of the control relay 45. When this occurs the panel light is illuminated and the marker light 46 marks the spectrogram. At the same time the rotary arm is stepped up to the next tap and the normally open contacts of the pulse relay are closed momentarily, thereby connecting the positive terminal of the potentiometer 69 to its sliding contact and impressing on the signal grid of the first amplifier tube a large positive potential. This in turn causes a large negative bias to be applied to the grid of the relay tube, thereby opening the contact of the control relay and the pulse relay. In this condition, the apparatus is ready to make another mark on the mass spectrogram when the trip circuit again closes the control relay.

By maintaining a proper relationship of resistances between the taps of the rotary stepping relay, as described in detail in the aforementioned copending application of Langmuir, the action of the mass marker is synchronized perfectly with the recording galvanometer. In consequence, as each peak is recorded on the photographic paper a beam of light marks the paper adjacent that peak.

The mass marker described and claimed herein fires more accurately than one provided with a direct current amplifier. This advantage is achieved through the use of the high gain alternating current amplifier in conjunction with the means for converting the output of the balance network into alternating curret which is applied to the amplifier, and the means for rectifying the output of the amplifier and applying the rectified output to the trip circuit. The use of the alternating current amplifier obviates fluctuations in the firing threshold voltage due to drift, as occurs in certain direct current amplifiers. Moreover, since the alternating current amplifier has high gain any fluctuations in trip-circuit relay tube characteristics become relatively unimportant. All in all, the apparatus described is an extremely accurate one for correlating specific mass of ions to ion abundance.

The mass marker illustrated includes a plurality of coupled three-positioned switches 120, 121, 122. Position 1 on each switch is "off" position. Switch 120 is connected in the power line when on positions 2 and 3. Switch 121 is off in both positions 1 and 2, but in position 3 completes the circuit of the lower contacts of the control relay. In positions 2 and 3 the switch 122 connects the battery to the resistance of the potentiometer 69.

The three coupled switches may be thrown simultaneously from a common control lever, respectively, to positions 1, 2 or 3. When the switches are in position 1, the circuits, including the switches are open. In position 2, power is supplied to the potentiometer 69 and to the regulated power supply. In position 3, all three circuits controlled by the switches are completed.

I claim:

1. In a mass indicator of a mass spectrometer adapted to indicate the specific masses of ions being detected by the spectrometer and having a resistance, means for impressing across the resistance a voltage which is a function of the specific mass being detected and changes in accordance therewith, and means for selecting successive fractions of said voltage during a period in which the voltage is changing, the combination which comprises means connected to the voltage selector for producing an alternating current corresponding in amplitude to the selected fraction of the voltage, and means responsive to a deviation in the amplitude of the alternating current above a threshold value for indicating the specific mass of ions detected when that threshold is reached and for causing the voltage selector to select the next fraction of voltage.

2. In a mass indicator of a mass spectrometer adapted to indicate the specific masses of ions being detected by the spectrometer and having a resistance, means for impressing across the resistance a voltage which is a function of the specific mass being detected and changes in accordance therewith, and means for selecting successive fractions of said voltage during a period in which the voltage is changing, the combination which comprises means connected to the voltage selector for producing an alternating current corresponding in amplitude to the selected fraction of the

voltage, said means including a balancing network, an oscillator and a vibrator coupled to the oscillator, and means responsive to a deviation in the amplitude of the alternating current above a threshold value for indicating the specific mass of ions detected when that threshold is reached and for causing the voltage selector to select the next fraction of voltage.

3. In a mass indicator of a mass spectrometer adapted to indicate the specific masses of ions being detected by the spectrometer and having a potential dividing network, means for impressing across the network a voltage which is a function of the specific mass being detected and changes in accordance therewith, and means for selecting successive fractions of said voltage during a period in which the voltage in changing, the combination which comprises means connected to the voltage selector for producing an alternating current corresponding in amplitude to the selected fraction of the voltage, a high gain AC amplifier for amplifying current, and means responsive to a deviation in the amplitude of the alternating current above a threshold value for indicating the specific mass of ions detected when that threshold is reached and for causing the voltage selector to select the next fraction of voltage.

4. In a specific mass indicator for a mass spectrometer provided with a circuit and means for impressing across the circuit a voltage which is a function of the specific mass of the ions being detected at a given instant, the combination which comprises a stepping relay connected in said circuit and provided with a movable arm making contact with successive points in said circuit and a lead through which the arm is connected to a terminal, means for opposing the potential between the lead and an end of said circuit against a standard potential, means for converting the resulting differential potential into an alternating current, means for rectifying the alternating current, a mass marker, a control relay which actuates the mass marker and the stepping relay, a trip circuit connected to the control relay, and means for applying to the trip circuit a voltage proportional to the amplitude of the rectified alternating current.

5. In a mass marker for a mass spectrometer having a potential dividing network the voltage across which is a function of the specific mass of ions being detected and means for selecting progressively different fractions of the voltage across the network as the voltage across it decreases, the combination which comprises means for converting the selected fraction into alternating current corresponding in amplitude to the selected fraction, and means responsive to a deviation of the amplitude of the alternating current from a threshold value for indicating the specific mass of ions which may be detected when that threshold is reached and for selecting a new fraction of the voltage across the network.

6. In a mass marker for a mass spectrometer having a conductor, means for impressing across the conductor a voltage which is a function of the specific mass of ions being detected in the spectrometer, and means for successively selecting different fractions of the voltage applied across the conductor as that voltage changes, the combination which comprises a balancing network adapted to oppose the selected fraction of the voltage with a standard potential to produce a differential potential, an A. C. amplifier, circuit means for applying the differential potential to the amplifier as a series of pulses, a relay tube having a grid and an anode, means for applying rectified pulses from the A. C. amplifier output to the grid of the relay tube, means connected to the anode of the relay tube for altering the selected fraction of the voltage, said means being operative only when the grid voltage of the relay tube is greater than a threshold value, and a vibrator having one set of contacts for alternately connecting the A. C. amplifier to the balancing network and to ground and another pair of contacts operating to apply half cycles of the A. C. amplifier output voltages to the grid of the relay tube.

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CERTIFICATE OF CORRECTION.

Patent No. 2,370,631. March 6, 1945.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 14, for "curret" read --current--; page 4, first column, line 17, claim 3, for "in" second occurrence, read --is--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of November, A. D. 1945.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

voltage, said means including a balancing network, an oscillator and a vibrator coupled to the oscillator, and means responsive to a deviation in the amplitude of the alternating current above a threshold value for indicating the specific mass of ions detected when that threshold is reached and for causing the voltage selector to select the next fraction of voltage.

3. In a mass indicator of a mass spectrometer adapted to indicate the specific masses of ions being detected by the spectrometer and having a potential dividing network, means for impressing across the network a voltage which is a function of the specific mass being detected and changes in accordance therewith, and means for selecting successive fractions of said voltage during a period in which the voltage in changing, the combination which comprises means connected to the voltage selector for producing an alternating current corresponding in amplitude to the selected fraction of the voltage, a high gain AC amplifier for amplifying current, and means responsive to a deviation in the amplitude of the alternating current above a threshold value for indicating the specific mass of ions detected when that threshold is reached and for causing the voltage selector to select the next fraction of voltage.

4. In a specific mass indicator for a mass spectrometer provided with a circuit and means for impressing across the circuit a voltage which is a function of the specific mass of the ions being detected at a given instant, the combination which comprises a stepping relay connected in said circuit and provided with a movable arm making contact with successive points in said circuit and a lead through which the arm is connected to a terminal, means for opposing the potential between the lead and an end of said circuit against a standard potential, means for converting the resulting differential potential into an alternating current, means for rectifying the alternating current, a mass marker, a control relay which actuates the mass marker and the stepping relay, a trip circuit connected to the control relay, and means for applying to the trip circuit a voltage proportional to the amplitude of the rectified alternating current.

5. In a mass marker for a mass spectrometer having a potential dividing network the voltage across which is a function of the specific mass of ions being detected and means for selecting progressively different fractions of the voltage across the network as the voltage across it decreases, the combination which comprises means for converting the selected fraction into alternating current corresponding in amplitude to the selected fraction, and means responsive to a deviation of the amplitude of the alternating current from a threshold value for indicating the specific mass of ions which may be detected when that threshold is reached and for selecting a new fraction of the voltage across the network.

6. In a mass marker for a mass spectrometer having a conductor, means for impressing across the conductor a voltage which is a function of the specific mass of ions being detected in the spectrometer, and means for successively selecting different fractions of the voltage applied across the conductor as that voltage changes, the combination which comprises a balancing network adapted to oppose the selected fraction of the voltage with a standard potential to produce a differential potential, an A. C. amplifier, circuit means for applying the differential potential to the amplifier as a series of pulses, a relay tube having a grid and an anode, means for applying rectified pulses from the A. C. amplifier output to the grid of the relay tube, means connected to the anode of the relay tube for altering the selected fraction of the voltage, said means being operative only when the grid voltage of the relay tube is greater than a threshold value, and a vibrator having one set of contacts for alternately connecting the A. C. amplifier to the balancing network and to ground and another pair of contacts operating to apply half cycles of the A. C. amplifier output voltages to the grid of the relay tube.

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