

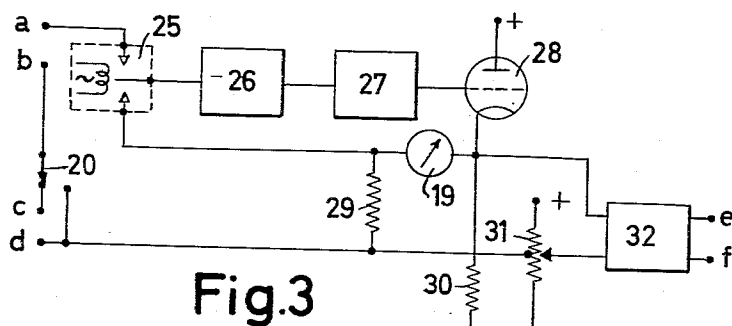
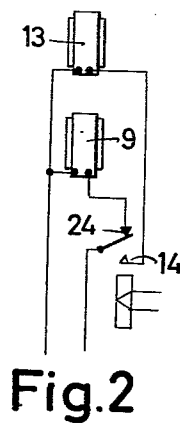
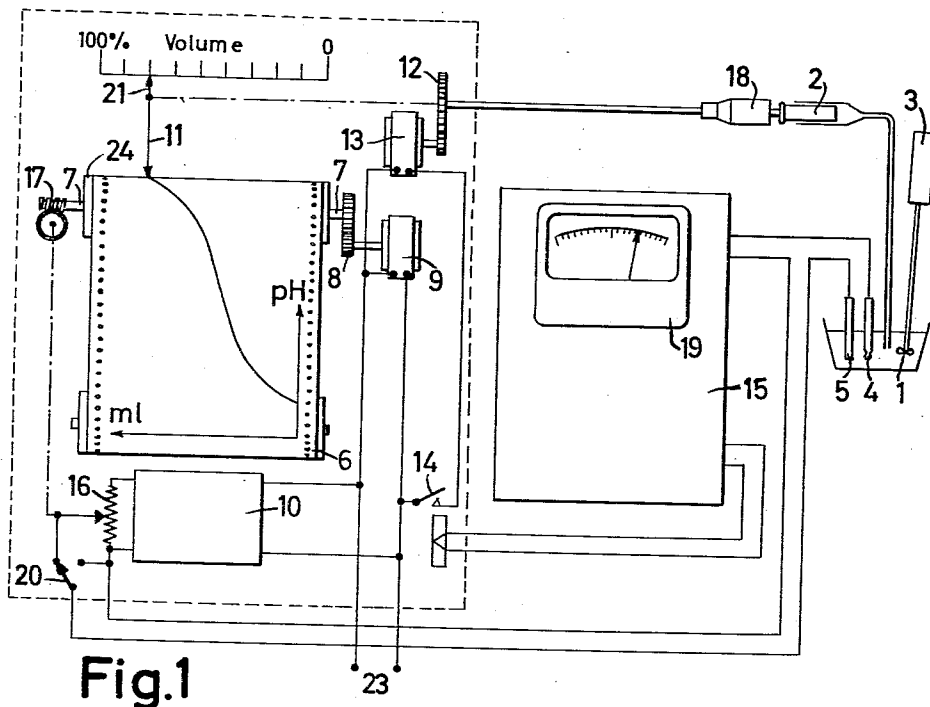
Aug. 1, 1961

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2,994,590

RECORDING TITRATION DEVICE FOR RECORDING TITRATION CURVES

Filed May 27, 1959



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2,994,590

RECORDING TITRATION DEVICE FOR RECORDING TITRATION CURVES

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Filed May 27, 1959, Ser. No. 816,285

Claims priority, application Denmark May 30, 1958

3 Claims. (Cl. 23—253)

The invention relates to a recording titration device for recording a curve representing the dependency of the pH-value of a solution on the volume of added titrating agent or the like, said device comprising two motors for producing a relative movement of a writing member and a curve sheet in two co-ordinate directions, one of which motors is connected with a titrating agent supply mechanism while the other motor is connected with a potentiometer, from which a voltage is derived which is proportional to the relative movement of the writing member and the sheet produced by said other motor, which voltage together with a measuring voltage from the solution serves to control the two motors.

The prior art devices of this type are, if they are intended to operate with a satisfactory accurateness, particularly complicated and, consequently, expensive to manufacture.

Recording devices are known in which the movement in one direction is effected at constant speed, so that said devices are of very simple construction. As a rule such devices are used for recording the variation of a quantity with time, i.e. as a function of the constant variation of an independently varying quantity and, consequently, only a controlling of the movement is required in the other co-ordinate direction in dependence on the variation of the quantity measured. In principle such devices could very well be used also for the recording of a titration curve, if the supply of titrating agent is effected at constant speed and the course of the process is permitted to influence the recording movement in the other coordinate direction.

In so doing, the result will certainly be a simple device, but it will not be possible to obtain both the accurateness and the speed that are required at the same time for the purposes of the above prior art devices, because the speed at which the processes take place as a function of the titrating agent, often varies highly from point to point on the curve.

The present invention has for its object to provide a device of the above prior art type construction but of a substantially simplified and, therefore, cheaper construction and which is less subject to operational disturbances simultaneously with the obtainable precision being retained at a level which is comparable with that obtainable with the most superior devices of the prior art type.

According to the invention this is attained by the voltage from the potentiometer being series-connected with the measuring voltage, and by the resulting voltage service to control the motor of the titrating agent supply mechanism, so that said motor is operative when the resulting voltage differs from a predetermined value, and the sign of the potentiometer voltage is such that an alteration of the potentiometer voltage caused by the other motor is compensated for by the alteration of the measuring voltage caused by the supply of titrating agent.

As a rule, the movement in one coordinate direction is performed as a movement of the curve sheet, which may either consist of an actual sheet secured to a movable carrier of some kind or other, or constitute part of a paper web which is moved from a supply roll across one or more guiding rollers.

In the following the invention is explained in detail with reference to the accompanying drawing where

FIG. 1 diagrammatically shows an embodiment of the device according to the invention,

FIG. 2 shows a modified embodiment of a detail of the device shown in FIG. 1, and

FIG. 3 shows a simplified diagram of a controlling stage for the device shown in FIGS. 1 and 2.

The device shown in FIG. 1 is intended for recording a titration curve where the pH-value of a sample solution is recorded as a function of added volume of a standard solution acting as titrating agent.

However, it should be noted that the devices may also in a corresponding or other embodiment be used in connection with processes, where it is an ion, other than the hydrogen ion, the concentration of which it is desired to measure, and further the recording device according to the invention may in itself find application for recording the course of processes other than titration processes.

In the embodiment shown, a certain amount of sample solution is poured into a vessel 1, while standard solution is supplied from a syringe 2. A stirring mechanism 3 is used in the usual manner for making a uniform concentration in the whole sample, and further, as is usual when performing this kind of measurements, provision is made for two electrodes 4 and 5 in the vessel 1, of which one is a reference electrode while the other is a measuring electrode of the type being ordinarily called an indicator electrode, most normally denoted a calomel electrode and a glass electrode.

The pH-value of the sample is to be recorded on a curve sheet as a function of supplied volume of standard solution. In the embodiment shown, the sheet constitutes part of a paper roll (not shown on the drawing) and is moved by means of a driving roller 24 having a shaft 7.

The shaft 7 and, consequently, the sheet 6 is through a gearing 8 driven by a motor 9, which is fed from a voltage source, e.g. a mains, indicated by 23.

A writing member 11 is in contact with the curve sheet 6 movable in a direction at right angles to the direction of movement of said sheet by means of an actuating mechanism (not shown) which through a gearing 12 is driven by a motor 13.

Like the motor 9 the motor 13 is fed from the voltage source 23. However, it is fed not directly, but through a relay 14 operated by a control voltage derived from the output of the controlling stage 15.

This controlling stage 15 is controlled by a control voltage which is equal to the sum of the voltage difference between the electrodes 4 and 5 or a voltage proportional thereto and a voltage which is proportional to the movement of the curve sheet, which voltage is derived from a potentiometer 16, across which a constant voltage is connected which is derived from the voltage source 23 via a voltage stabilizer 10, and the movable contacts of which is interconnected with the shaft 7 through a gearing 17.

The piston of the syringe 2 is actuated by means of an actuating mechanism 18 which is interconnected with the writing member 11 so that the amount of standard solution supplied to the sample is proportional to the movement of the writing member in a direction at right angles to the movement of the curve sheet.

In that the sheet moves at a constant speed the voltage derived from the potentiometer 16 will also vary at a constant speed. The sum of this voltage and the measuring voltage is to be kept constant, and for this purpose the controlling stage 15 is so arranged that, as soon as a deviation from the predetermined constant voltage occurs at its input, a voltage occurs, preferably a pulse-shaped voltage, on its output, which serves for making

the contact of the relay 14 for starting the motor 13, whereby standard solution from the syringe 2 is supplied in such an amount that the predetermined voltage is restored. The size and sign of the potentiometer voltage should, as will directly be understood, be chosen in dependence on the measuring voltage produced by the said titration process and on the variation direction of said measuring voltage.

As the sum of the two said voltages is constant, and one of said voltages, namely the one derived from the potentiometer 16, is proportional to the movement of the sheet, this will involve that the measuring voltage, i.e. the voltage between the electrodes 4 and 5 of the pH-value dependent thereon, will be recorded on the axis parallel to the direction of movement of the sheet, and in that the writing member 11 is moved in accordance with the supply of standard solution from the syringe 2, the volume of standard solution will be recorded on the axis at right angles to the direction of movement whereby the desired curve occurs.

In the embodiment shown, the controlling stage 15 is further provided with a measuring instrument 19 for directly reading the potential between the electrodes 4 and 5 or the pH-value of the sample.

Further, there is in the connection between the potentiometer 16 and the input of the controlling stage 15 inserted a switch 20, whereby this connection can be interrupted from the slide contact of the potentiometer and moreover be short-circuited so that only the voltage between the electrodes 4 and 5 is supplied to the input of the controlling stage 15. This involves that it is possible to use the device shown directly for keeping the pH-value of the sample solution constant at a predetermined desired size, in that in case of initiating alteration of the voltage difference between the electrodes 4 and 5, a control voltage on the output of the control stage 15 will be incurred whereby the relay 14 causes the motor 13 to be started for supplying further standard solution from the syringe 2 for settling the deviation of the voltage from the predetermined value.

FIG. 2 shows a modified detail of the embodiment shown in FIG. 1, where a switch 24 is also interposed in the supply circuit of the motor 9. This switch belongs to the same relay as the switch 14 and is made when the latter switch is broken, and broken when the latter is made, so that the two motors are not operative simultaneously. Otherwise the principle of the function is quite the same as in FIG. 1, but the motor 9, becoming only operative when the state of balance is obtained, gives the result that an improved accurateness of the curve parts having a flat course is obtained, i.e. where a great supply of titrating agent only involves a small alteration of the pH-value.

In the embodiment shown, the writing member 11 is connected with a hand 21 whereby at any time it is possible to read the supplied volume of standard liquid on a dial 22.

The said dial 22 as well as the instrument 19 may in principle be dispensed with which by the way also applies to the switch 20.

In both embodiments the two motors may be of a particularly simple construction, in that no control of their speeds is required.

The device may expediently be composed of three separate units, namely, a recording unit consisting of the part of the device which in FIG. 1 is framed by dotted lines, a titration unit consisting of the syringe 2 with the actuating mechanism 18, provided with a flexible shaft for connecting the first unit and the electrodes 4 and 5 and, if required, the stirrer 3, and finally the third unit consisting of the controlling stage 15.

Sometimes the last-mentioned two units will be available as a device for keeping a pH-value constant, the actuating mechanism 18 being connected to a motor

which is controlled by the controlling stage 15. To this available equipment it is only required to provide the first-mentioned unit and connect it instead of the said motor in order to obtain the described recording titration device.

Instead of the curve sheet being supplied from a paper roll and guided by a driving roller, the apparatus may comprise a movable carrier for separate plane sheets which by suitable driving means can be moved in parallel to their own planes. Eventually, the writing member may be designed for movement in both co-ordinate directions across a stationary sheet so that the movement in one direction is effected by one motor and in the other direction by the other motor.

FIG. 3 shows an embodiment of the controlling stage 19 in FIG. 1, wherein *abcd* are input terminals. The terminals *b* and *c* are mutually connected through the switch 20 of FIG. 1. The terminals *a* and *b* are to be connected with the electrodes 4 and 5 and the terminals *c* and *d* are to be connected with the potentiometer 16 of FIG. 1.

In the embodiment shown the controlling stage comprises a D.C.-A.C. converter diagrammatically shown at 25 as an electromagnetical vibrator unit. Said converter 25 is connected with an amplifier 26, the output of which is supplied to a detector stage 27. The output from the detector 27 is supplied to the grid of a cathode follower 28. In the cathode circuit of said cathode follower 28 the meter 19 is inserted in series with a resistance 29 whereas the output from the cathode follower is taken out across a cathode resistance 30.

This output is through part of a potentiometer 31 supplied to the input of an output stage 32 having output terminals *e* and *f*, which are to be connected to the relay 14 in FIG. 1.

The output stage 32 is of the well-known type in which an input voltage above a certain limit value gives rise to a certain output voltage, whereas an input voltage beneath said limit causes a zero output voltage. The limit may be a limit interval in that the limit at decreasing input voltage may be a little lower than the limit at increasing input voltage.

A feedback from the resistance 29 to the converter 25 is provided for stabilization purposes.

I claim:

1. In a recording titration device provided with a chemical cell adapted to contain a quantity of test specimen having electrodes between which the E.M.F. of the cell is produced, supply means for introducing a titrating agent into said cell, and recording means comprising a chart and a writing member in cooperation therewith, a first driving means for mutually relative movement of said chart and said writing member in a first co-ordinate direction, a second driving means for simultaneously feeding of titrating agent from said supply means for introducing titrating agent into said cell, and for mutually relative movement of said chart and said writing member in a second co-ordinate direction, said first driving means comprising an electric motor connected with a supply circuit, a potentiometer having two end terminals and a sliding contact, said end terminals being connected with a voltage supply means, said sliding contact being in driving connection with said first driving means, an electric control device comprising an input circuit and an output circuit and means rendering said output circuit operative upon the application upon said input circuit of a voltage different from a pre-determined voltage, said E.M.F. from said cell being connected to said input circuit in series with the voltage between said sliding contact and one of said end terminals of said potentiometer, said output circuit being connected with said second driving means for reestablishing said pre-determined voltage on said input circuit.

2. In a recording titration device provided with a chemical cell adapted to contain a quantity of test specimen having electrodes between which the E.M.F. of the cell is

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produced, supply means for introducing a titrating agent into said cell, and recording means comprising a chart and a writing member in cooperation therewith, a first driving means for mutually relative movement of said chart and said writing member in a first co-ordinate direction, a second driving means for simultaneously feeding of titrating agent from said supply means for introducing titrating agent into said cell, and for mutually relative movement of said chart and said writing member in a second co-ordinate direction, said first driving means comprising an electric motor connected with a supply circuit, a potentiometer having two end terminals and a sliding contact, said end terminals being connected with a voltage supply means, said sliding contact being in driving connection with said first driving means, an electric control device comprising an input circuit and an output circuit and means rendering said output circuit operative upon the application upon said input circuit of a voltage different from a pre-determined voltage, said E.M.F. from said cell being connected to said input circuit in series with the voltage between said sliding contact and one of said end terminals of said potentiometer, a relay being connected to said output circuit and having a contact being open in the rest position of said relay, said contact being inserted in said supply circuit of said motor of said second driving means.

3. In a recording titration device provided with a chemical cell adapted to contain a quantity of test specimen having electrodes between which the E.M.F. of the cell is produced, supply means for introducing a titrating agent into said cell, and recording means comprising a chart and a writing member in cooperation therewith, a first driving means for mutually relative movement of said

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chart and said writing member in a first co-ordinate direction, a second driving means for simultaneously feeding of titrating agent from said supply means for introducing titrating agent into said cell, and for mutually relative movement of said chart and said writing member in a second co-ordinate direction, said first driving means comprising an electric motor connected with a supply circuit, a potentiometer having two end terminals and a sliding contact, said end terminals being connected with a voltage supply means, said sliding contact being in driving connection with said first driving means, an electric control device comprising an input circuit and an output circuit and means rendering said output circuit operative upon the application upon said input circuit of a voltage different from a pre-determined voltage, said E.M.F. from said cell being connected to said input circuit in series with the voltage between said sliding contact and one of said end terminals of said potentiometer, a relay being connected to said output circuit and having a first contact being closed in the rest position of said relay, said first contact being inserted in said supply circuit of said motor of said first driving means, said relay having a second contact being open in the position of rest of said relay, said second contact being inserted in said supply circuit of said motor of said second driving means.

References Cited in the file of this patent

UNITED STATES PATENTS

2,650,256	Lingane	Aug. 25, 1953
2,666,691	Robinson	Jan. 19, 1954
2,668,097	Hallikainer	Feb. 2, 1954
2,878,106	Malmstadt	Mar. 17, 1959