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A PRECISION ELECTRONIC pH CONTROL

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Abstract—A complete precision pH control system suitable for laboratory use is described briefly. The mechanism of operation and a detailed circuit description are given for the electronic control portion of the whole system. The instrument described makes possible pH control of biological reactions to an accuracy of 0.01 pH intervals and pH measurement or comparison to an accuracy of 0.002 pH intervals.

I. INTRODUCTION

THE development of this instrument began several years ago when the Division of Applied Biology of the National Research Council of Canada was studying various fermentations. They were interested in studying these biological reactions under variations of the numerous parameters involved, namely temperature, different specific organisms, different compositions of the media in which the growth takes place, and variations of the acidity or pH of this solution. The control of these various parameters was of course accomplished differently in each case but for one of the most important of them, pH, no satisfactory control was available. True, there were available a number of industrial type pH controllers but those which were investigated proved to have such limitations as to make them unsatisfactory for this work.

Variations in the pH of a fermentation is a result of the growth of the organisms themselves rather than a failure to adjust the solution to the correct value in the first place. In the case of bacteria which consume sugar, acid is produced and an alkaline solution must be added in small quantities from time to time as growth proceeds to maintain the pH of the reaction within specified limits. This instrument was designed therefore to provide this control.

Essentially, pH control is achieved by the measurement of voltages produced by a pair of electrodes immersed in the solution which is being controlled. A change of the hydrogen ion concentration results in a corresponding change of voltage at the electrodes and this change is used to actuate the control mechanism which adds to the reaction an acidic or alkaline correcting reagent in order to restore the pH, and therefore the electrode voltage, to their former values.

II. GENERAL DESCRIPTION OF THE CONTROL SYSTEM

Industrial control of pH to 0.1 of a pH interval may be considered to be fairly accurate. For research purposes it is desirable to exceed this accuracy and therefore control to 0.01 pH intervals was set as a target, with the stability of the instrument such that this accuracy could be maintained without recalibration over a period of several days.

A further requirement was that the instrument should be able to control simultaneously several fermentations. The procedure desired by the biologists was to set up, say, three reactions at slightly different values of pH and upon completion of the fermentations, to analyze the by-products of the fermentations and thus be able to relate quantitatively the production of specific by-products with pH value. This quantitative analysis procedure was in fact one reason for attempting to control pH to one per cent of a pH interval for with such close control fermentations and quantitative analysis may be repeated with reasonable consistency. This requirement for multiple channel pH control was one facility not readily available on those industrial controllers which were considered.

These, then, are the principal requirements of the instrument to be described. It is a precision laboratory instrument and in its present form it is not intended to be directly applicable to industrial control, although this would be a logical direction for further development. The instrument is essentially a millivoltmeter, having output circuits for the control of valves to permit the correction of pH.

The complete electronic portion of the pH control system is illustrated in Fig. 1. This shows the instrument rack with the power supply on the bottom shelf and the electronic control unit or pH Monitor on the top shelf. The middle shelf is used in practice to support recording milliammeters.

Of secondary importance, but quite necessary for precision pH control, since the voltage appearing at the electrodes for a given pH is somewhat dependent on temperature, is the requirement for temperature control of the reaction. Also of secondary importance, but highly important, is the requirement that the reaction be thoroughly agitated in order that increments of correcting solutions will be rapidly mixed in.

These two requirements are provided for as illustrated in Fig. 2. The steel-tubing table supports a temperature-controlled cabinet; and located just below this is an agitator mechanism, part of which extends up through openings in the bottom of the cabinet to a frame on which the three flasks are supported.

A framework mounted outside and above the temperature-controlled cabinet is used to support burettes, containing the correcting reagent, and the valves which control the flow of the pH correcting reagent from the burettes.

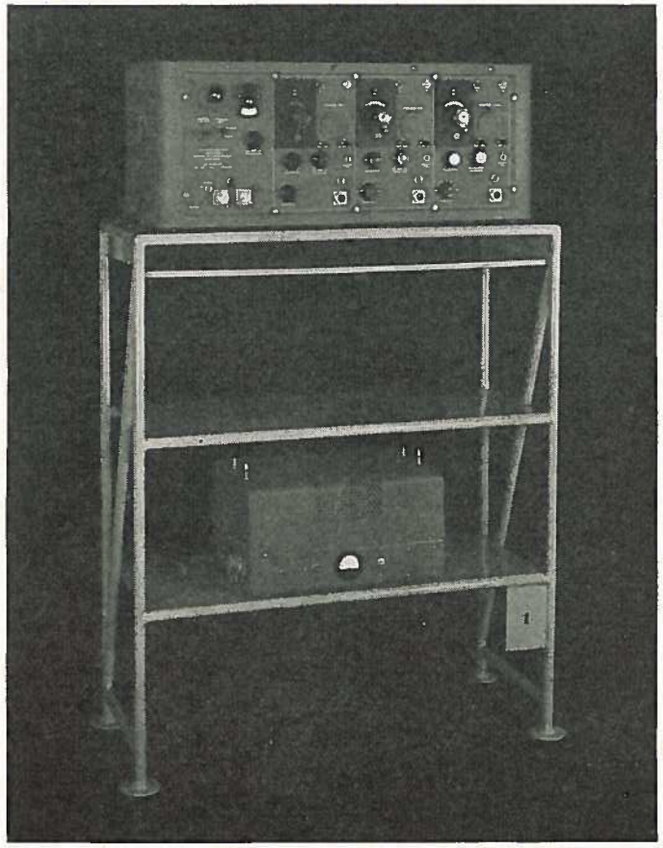

FIG. 1—The pH monitor instrument rack.

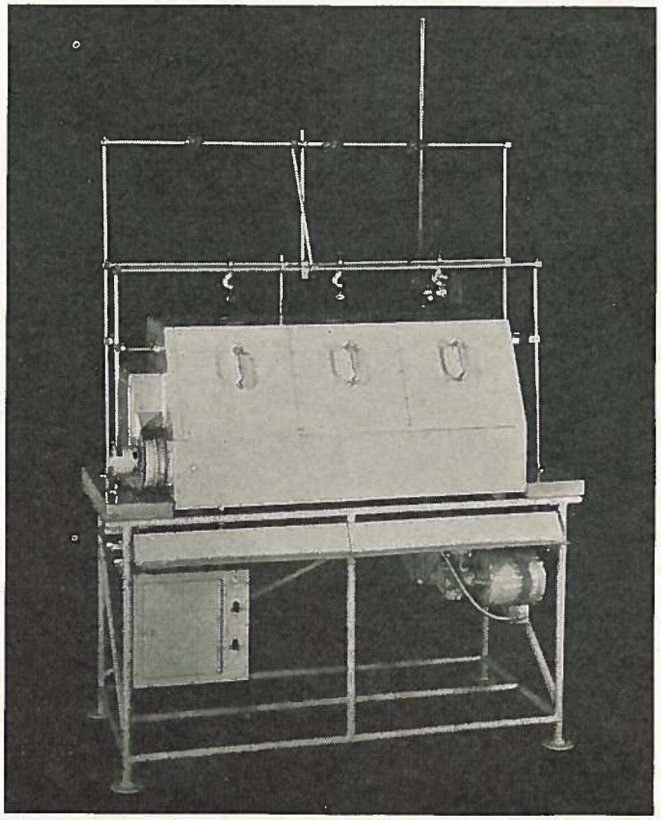

FIG. 2—Agitator table and temperature-controlled cabinet.

A functional block diagram of the pH control system is shown in Fig. 3. The electronic control or pH monitor comprises only those blocks identified as "input circuits", "amplifier" and "relay output circuits." Below the first two named are listed items of special significance to those particular functions.

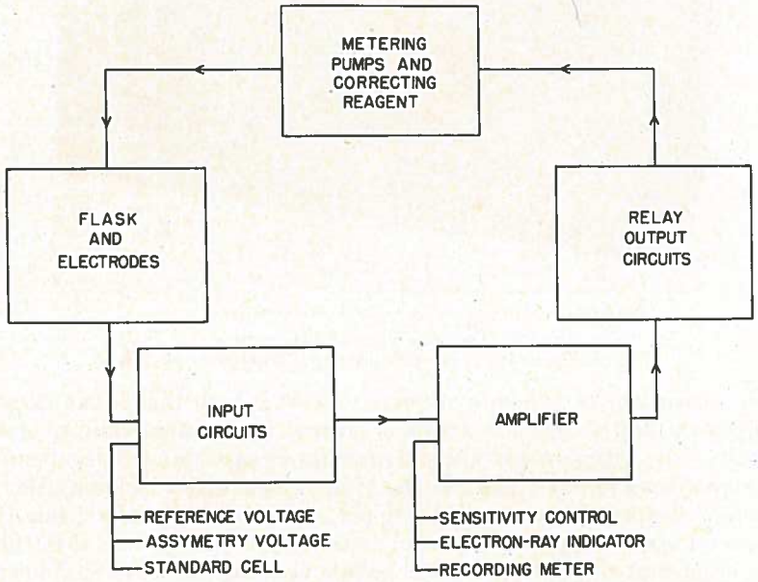

FIG. 3—Block diagram of pH control system.

III. THE THREE-CHANNEL pH MONITOR

The instrument which was designed to fulfil the above requirements and provide for the simultaneous control of three fermentations, is shown in Fig. 4. It is basically a three-channel pulsed millivoltmeter with suitable provision for calibration and adjustment as required by the specific demands of pH control.

The electrode system across which is developed the voltage to be measured comprises a "Glass" and a "Calomel" electrode having together an internal resistance of approximately 150 megohms. In order that the millivoltmeter will not appreciably load the electrode system, it is therefore necessary that the millivoltmeter input resistance be considerably higher than 150 megohms, and an input resistance in excess of 10,000 megohms has been achieved.

The instrument has a range of approximately zero to plus or minus 500 millivolts. Since a change of one pH interval results in a change of electrode voltage of approximately 60 millivolts the pH Monitor is therefore useful over the full range of pH from 1 to 12.

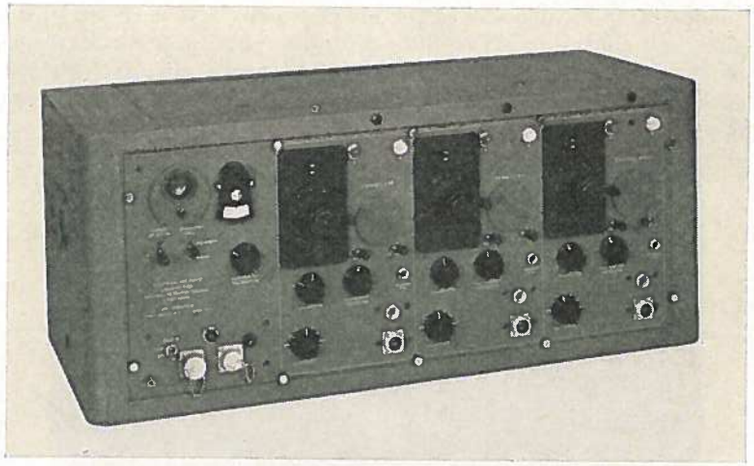

FIG. 4—The three-channel pH monitor.

The sensitivity of the millivoltmeter circuit is such that it can detect a change of 0.0001 volt, or in terms of current in the input circuit, of 10^{-12} amperes. In terms of pH the pH monitor is capable of pH indications or comparisons to 0.002 pH and the system as a whole including the pH monitor, temperature-controlled cabinet, agitator, and valves, has been designed to permit an overall control accuracy of fermentations to 0.01 pH.

In order that the instrument will have a very high order of stability, all precautions have been taken to provide line voltage regulation, d-c voltage stabilization, filtering, circuit isolation and shielding where necessary. As a result, over a period of several days, drift is only a fraction of a millivolt and accuracy of calibration is maintained throughout the duration of prolonged fermentations.

IV. PRINCIPLE OF OPERATION OF THE pH MONITOR

A simplified schematic diagram of one channel of the pH Monitor is shown in Fig. 5. The potential developed between the electrodes immersed in the solution is compared with a predetermined reference voltage by a single-pole double-throw snap action "Micro-Switch" in the grid circuit of the first amplifier tube V_1. This switch is caused to operate from the lower to upper position by an electric-motor-operated cam mechanism. The moving arm of the switch is connected to the grid of V_1 and it is normally in the lower position which is at reference voltage potential. On each switching operation it connects for about one hundredth of a second with the upper contact which is at electrode voltage potential. The electrode voltage is therefore connected to the amplifier proper at the rate of 30 times

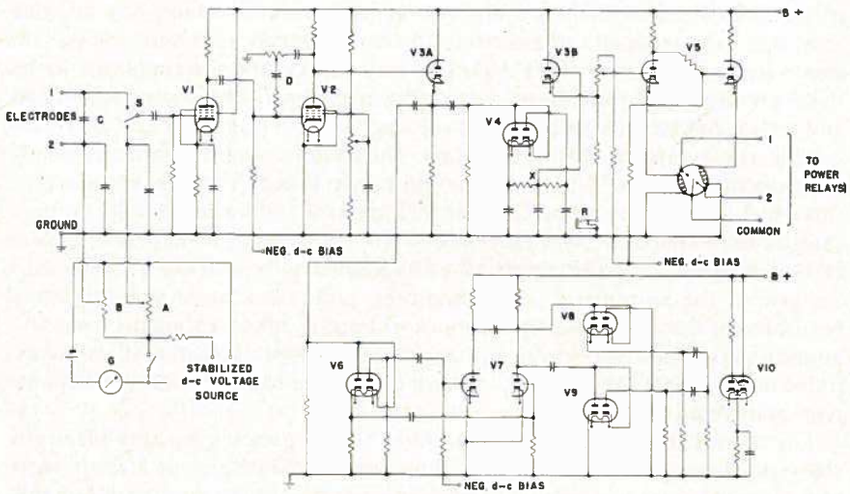

FIG. 5—Simplified schematic diagram of pH monitor.

a minute for this short interval only. It is this mechanism which contributes largely to the very high input resistance of the circuit because with respect to the electrode terminals the actual input resistance of the first amplifier is multiplied by the time ratio of the switching interval of the "Micro-Switch".

When the electrode voltage differs from the reference voltage, a momentary change of voltage occurs at the grid of the amplifier V_1 during the brief switching interval. The amplitude of this pulse is determined by the magnitude of the difference between the electrode and reference voltages and the polarity of the pulse (i.e. positive or negative) is determined by the sign of the difference between the two voltages. The amplitude of this pulse is used to indicate when a correction of pH is required and the polarity of the pulse is used to indicate the sense of the required correction. Successive stages of amplification and rectification produce from this pulse a d-c voltage having a polarity and amplitude proportional to the pulse and this voltage actuates relays which control the valves which add the pH correcting reagent to the solution being monitored.

V. A DETAILED DESCRIPTION OF THE CIRCUIT

Referring again to Fig. 5, the electrode voltage is connected to the input amplifier circuit V_1 at terminals 1 and 2. A standardized reference voltage is provided by the precision potentiometer A which may be fitted with a calibrated dial to read in pH units either directly or from a calibration chart. Precision potentiometer B provides the asymmetry

correction voltage which compensates for differences in electrodes so that although different pairs of electrodes produce slightly different voltages in solutions of the same pH a balance may always be obtained with the same setting of the reference voltage potentiometer. G is a standard cell and galvanometer circuit for standardizing these voltages.

This whole amplifier stage is very thoroughly shielded and all leads entering the amplifier compartment are carefully filtered. Fig. 6 illustrates this shielding in the three-channel pH monitor. The electrode voltage charges the capacitor C which is selected for very high leakage resistance. Pulses developed by the switch S as explained previously are coupled to the grid of the amplifier V_1. Cathode bias, plate- and screen voltages have been chosen for low-noise operation and care is taken to ensure that the amplification of both positive and negative pulses is the same. This condition however need only hold for small pulse amplitudes near the balance point, say from zero to 5 or 10 millivolts.

The second stage V_2 is a pulse amplifier having gain variable by means of the sensitivity control network D. Since these pulses occur at a fairly slow rate, low-frequency response of the amplifier is important and for this reason fixed grid bias and fixed screen voltage are used. The screen voltage is variable over a small range to compensate for tube differences so that the amplification for both positive and negative pulses will be the same.

V_{3A} is a pulse cathode follower directly coupled to the plate of V_2. Its cathode is coupled to V_4, a double diode rectifier so arranged that at point X a d-c voltage is developed whose sign and amplitude correspond to the sign and peak amplitude of the input pulse.

This d-c voltage is connected to the grid of V_{3B}, a cathode follower whose cathode is connected by a resistor network to V_5. A recording milliammeter

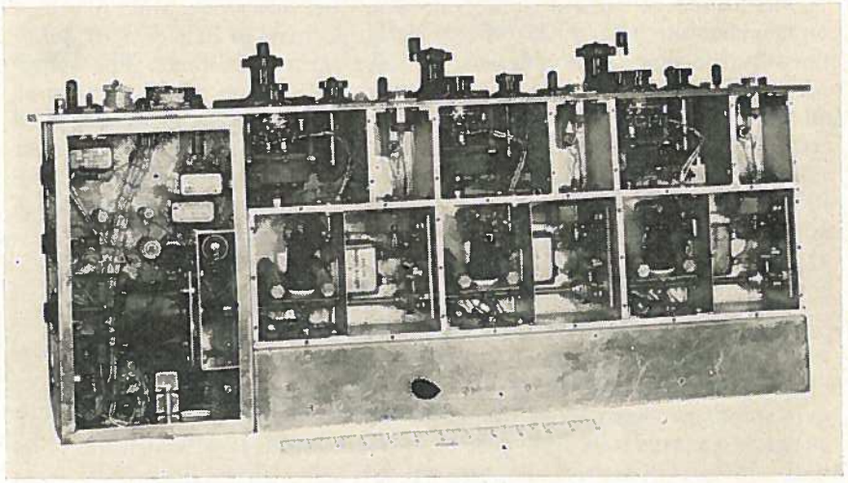

FIG. 6—Bottom view pH monitor chassis, with cover plates removed.

may be connected into the circuit at R to record current variations in this network; these variations are proportional to variations of the electrode voltage. Such a recorder provides a constant and most useful check on the operation of the instrument, on the electrodes, and on the progress of the reaction. Experience has shown that much can be learned about the operation of the complete system by observation of these records. Common faults such as faulty electrodes produce quite characteristic traces and these difficulties are thus easily identified. In addition to this, however, it is of considerable value to be able to observe the progress of the fermentation, to note the deviation in pH, the rate of growth and particularly the termination of the reaction.

V_5 is a differential d-c amplifier in whose cathode circuits is placed a sensitive differential relay. In order to compensate for differences between individual tubes used as V_5, the potentiometer in the coupling network between V_{3B} and V_5 is provided to bring V_5 to an initial balance condition when the input pulse amplitude is zero. The sensitive relay is connected as a single-pole double-throw relay which has a normally off position when the instrument is at balance, and which connects one way or the other when an off-balance condition occurs. This sensitive relay actuates two output circuit power relays which are used to control the operation of the valves so that pH correcting reagents may be added to the reaction as required.

An auxiliary circuit provides a means of observing off-balance conditions and so facilitates rapid balancing of the instrument. This circuit operates an electron-ray indicator tube and it is connected from the cathode of V_{3A}, the pulse cathode follower, to V_6, a limiter, which serves to separate positive and negative pulses into two channels.

The two outputs of V_6 are coupled each to one half of V_7, a double-triode amplifier, one half being biased to operate on positive pulses and the other on negative pulses.

In order that the pulses to be applied to the electron-ray tube be easily observed, it is necessary that they be of considerably longer duration than one-hundredth of a second, the approximate duration of the original pulse. The integrators V_8 and V_9 perform this function, one being connected for positive pulses and the other for negative pulses.

The outputs of these circuits are connected together to the grid of the electron-ray indicator tube V_{10}. This tube is biased so that the target is normally in the half-open position with the result that on the application of pulses of one polarity it winks open and on pulses of the opposite polarity it winks closed. The gain and sensitivity of the circuit are such that in this way a very precise balance may be obtained.

Standard receiving type tubes have been used throughout and referring to Fig. 5 the tubes used in each stage are as follows: V_1-1620 (6J7), V_2—6SJ7, V_3—6SN7, V_4—6AL5, V_5—6SN7, V_6—6AL5, V_7—6J6, V_8—6AL5, V_9—6AL5, V_{10}—6E5. Every effort has been made to make the circuits noncritical to tube replacements and this has been possible in every case

but V_2 and V_5 where adjustments for tube variations are provided.

The power supply for the pH monitor has been made as free from power-line variations as possible. The primary a-c supply is regulated by a line voltage regulating transformer and all d-c voltages are electronically stabilized. Separate voltage sources are provided for the "B" supply, bias supply, reference and asymmetry voltages and relay voltages.

VI. CONCLUSION

Two of these complete three-channel pH control systems have been built. One has recently been installed in the Prairie Regional Laboratory of the Division of Applied Biology of the National Research Council at Saskatoon, Saskatchewan and the other, which has been in operation for nearly a year, is installed in the Biology Division's Laboratories in Ottawa. The operation of this instrument has been satisfactory in every respect and it has provided the biologists with a powerful tool to aid them in their studies of biological reactions.

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