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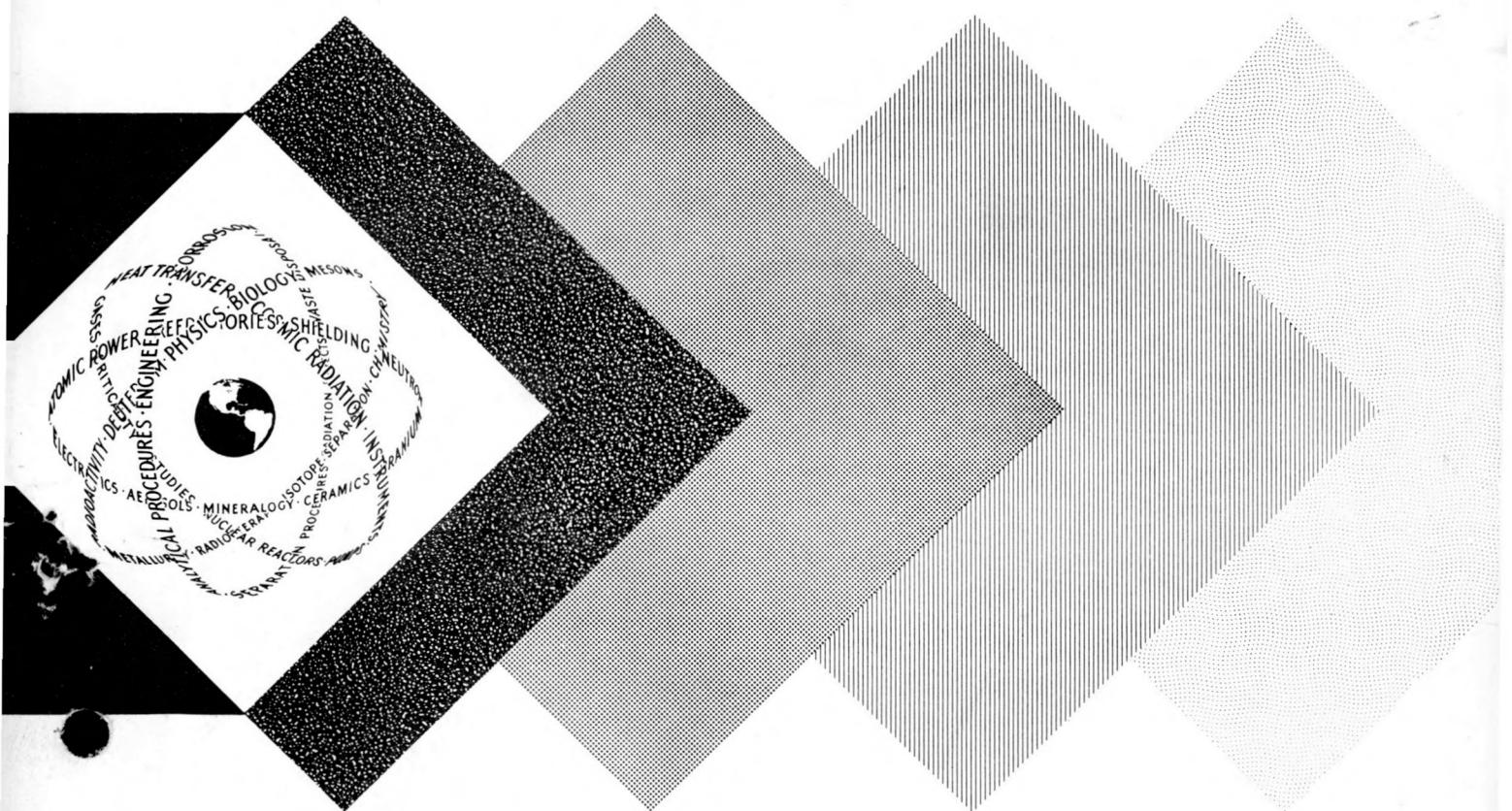
CHEMISTRY — GENERAL

AN AUTOMATIC RECORDING TITRATOR

By
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December 1957

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An Automatic Recording Titrator*

Gerald Ross Umbreit and J. S. Fritz

Abstract

An automatic recording titrator is described which is applicable to all types of potentiometric titrations. Particular attention has been paid to the maintenance of accurate potential recording of the entire titration curve as well as accurate recording of the volume of titrant used. As a result the instrument is well-suited for analytical research where the complete curve, rather than just the equivalence point of the titration is of interest.

Simplicity of the instrument is maintained by use of commercially available components for the major functions of amplifying and recording. Each of the major components retains its separate identity, and thus may be used for other applications without alterations. Acceptable substitutes for each of the major components are suggested, and the relative merits of each are discussed. Suggestions for improving the instrument are also discussed.

* This report is based on a Ph.D. thesis by Gerald Ross Umbreit submitted December 1957, to Iowa State College, Ames, Iowa. This work was done under contract with the U. S. Atomic Energy Commission.

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INTRODUCTION

The increasing need of modern industry for rapid, accurate and dependable methods for quality control, along with the increasing pace of research in recent times, has made the instrumentation of analytical procedures a subject of prime interest. In-line instruments that not only record, but also are capable of controlling the composition of a plant stream are being used in ever increasing numbers. Of the standard analytical methods in use, potentiometric measurements are among the most readily adaptable to this type of instrumentation.

The amount of information obtainable from a complete potentiometric titration curve, and the speed with which an automatic titrator can perform the titration make these instruments extremely valuable as analytical tools.

Robinson (38, p.447) says of potentiometric titrations:

When performed manually so as to give a detailed plot versus reagent volume, the potentiometric titration is a tedious and time-consuming operation having two distinct disadvantages. For exploratory work involving unknown samples, the human tendency to accelerate the operation often results in plots lacking needed detail, whereas, for routine analytical operations, the method does not have the speed and simplicity of comparable procedures employing visual indicators. Accordingly, many of the modifications and improvements in potentiometric technic have been directed toward the development of electrode systems or end-point detection devices which reduce or eliminate the need for plotting, enhance the ease and precision of end-point detection, and generally increase the speed with which the titration can be performed.

In general, there are two types of automatic titrators that are described in the literature or are available from commercial sources. These can be classified as recording instruments or end-point sensing devices. The designation as a recording instrument is restricted for purposes of this discussion to the type of instrument that records the entire titration curve as it would normally be determined by manual methods. End-point sensing devices are instruments that control a valve or stopcock on a titrant reservoir either by reacting when a pre-set end-point potential is reached, or by reacting to the sharp change in potential which is encountered at the end-point.

For general applications, the recording type of instrument requires automatic performance of several functions. It must incorporate a potentiometric recorder which may also be equipped with certain warning or controlling devices, and is generally equipped with a motor-driven strip chart on which the titration curve is recorded. An amplifier must be included, in addition to that which is normally a part of the recorder, to prevent loading of the electrode circuit by the recorder. Means must also be provided to deliver the titrant and to correlate the titrant delivery with chart spacing. A commercial instrument that fulfills these requirements is manufactured by the Precision Scientific Company (34, 35). This instrument is based primarily on the specifications of a similar

titrator described by Robinson (38) and patented by Robinson and Briggs (39). Other instruments of this type for general applications are described by Duggan and Stevens (8), by Kordatzki and Wulff (22) and Neilands and Cannon (32). Lingane (24, 25) described an instrument which is applicable to all types of potentiometric titrations except where the use of the glass electrode is involved. Eades et al. (10) described an instrument that records the results of up to 225 samples consecutively by means of an automatic sample changer.

Several instruments of this type are reported that have been designed for specialized applications (1, 9, 46-48). In general, these instruments have been designed for remote operations with radioactive systems, or for analytical control applications where only one component of the system is analyzed.

Some of the earlier attempts at instrumentation of this type are rather interesting. Kordatzki and Wulff (22) described such an instrument in 1932. In principle, its operation was as follows: Titrant is forced into the sample slowly but continuously by means of a falling steel cylinder which successively displaces mercury, paraffin oil and titrant. The potential change is continuously recorded on a chart, the travel of the chart is proportioned to the volume of titrant delivered since the falling cylinder drives the chart drum. Several excellent titration curves plotted by

this instrument were reproduced in the paper. Still earlier, in 1922, Keeler (19) described an instrument that was designed to control the composition of a plant stream. The functions of the instrument were the same as the titrators described above, but the instrument was so regulated that when the potential of the system being measured drifted beyond preset limits, a valve on a reservoir of acid was opened. The instrument functioned well as a titrator when a suitable method of titrant delivery was used. Here also, several very good titration curves were reproduced in the paper. Hydrogen electrodes were used for measurements of acidity in both cases cited above, and elaborate amplifying systems such as are needed with the glass electrode, were not required.

The end-point sensing device is not generally designed to transmit a voltage signal which will permit the recording of the normal titration curve. This type of instrument is more specifically adapted to the routine type of work generally encountered in a control laboratory. Here the equivalence of titrant with sample is of prime importance, rather than the shape of the titrant curve itself. Many of these instruments are equipped to drive recorders, but these are mainly for industrial purposes where the recorder also acts as a controller and operates other equipment whenever the potential of the system being measured drifts beyond pre-set limits. The principal requirement in this

type of instrument is a method of stopping delivery of titrant from a reservoir at the exact end-point of the titration. There are two methods of accomplishing this which are inherently based on the electronic circuitry of the instrument.

The circuit can be designed to trigger a relay when the input signal from the electrodes reaches a certain pre-determined value. This requires a pre-setting of the instrument to respond to the end-point potential before the titration is attempted. Among commercially available instruments, the Beckman titrator is an example of this type. Others are described in the literature by several authors (7, 14, 31, 33, 41, 43, 45). Several of these authors describe instruments for highly-specialized applications, but all instruments require this pre-setting of the end-point potential. Lingane (24, 25) described the alteration of a recording titrator to permit its use as an end-point sensing device of this type.

The circuitry may also be designed to react to the rapid change in potential produced at the end-point of the titration. The derivative circuit designed by Malmstadt (26) and adapted for several analytical applications (27-29) functions by computing the second-derivative voltage of the ordinary potentiometric curve. This triggers a relay system that stops delivery of titrant from the buret. An instrument adapted from Malmstadt's circuit is commer-

cially available as the Sargent-Malmstadt Titrator. This instrument is equipped to drive a recording potentiometer for the purpose of recording the derivative curve.

These two basic types of instrument can be adapted, with slight alterations, for several other analytical measurements. Automatic photometric titrations are reported by several authors (16, 30, 42). Linde et al. (23) describe an apparatus for automatic thermometric titrations. Juliard and Van Cakenberghe (17) described an instrument for automatically performing conductometric titrations. In all these cases the instrumentation required is the same as described for the recording titrator. The only difference being that the signal for operation of the instrument is obtained from sources other than the electrodes used for potentiometric titrations.

One of the most important components of any automatic titrator is a titrant delivery system. In conjunction with end-point sensing devices, this delivery system requires that the total volume used for the titration be measurable, and that the flow of titrant be accurately stopped at the end-point. The rate of titrant feed should be regulated sufficiently so that numerous false end-points are not obtained before the true end-point is reached. In general, end-point sensing devices permit relatively rapid titrant flow for the major part of the titration. Titrant delivery systems suitable for these purposes are

described by Audran and Dighton (3) and by Blaedel and Malmstadt (6) in addition to those described by some of the authors listed in the previous paragraphs.

The recording titrator requires rigid correlation of titrant delivery with chart spacing. In general, the chart is driven by a synchronous motor which moves the chart at a uniform rate. The simplest means of correlating chart spacing with titrant volume would then be the use of a constant-flow buret which is actuated by the same switch that controls the recorder chart motor. Of the several methods of accomplishing this uniform rate of delivery, two appear to be the most important.

The first of these is the constant-head buret. Burets of this type are described by Barredo and Taylor (4) and by Shapiro and Brannock (42). These burets are all based on variations of the familiar Marriotte bottle classically used in carbon-hydrogen determinations. The use of a calibrated orifice in conjunction with this constant-head titrant delivery system is described by Eades et al. (10). This type of titrant delivery system has not been too widely accepted because the accuracy of the system is generally inferior to that obtained by motor-driven syringe burets.

The most satisfactory method of obtaining constant titrant delivery is by means of a motor-driven syringe. The use of a well-made syringe driven by a synchronous motor virtually assures uniform delivery (17, 24, 38).

Allen (2) however, feels that imperfections in the barrel or piston of the syringe might introduce irregularities. He suggests a precision-ground glass rod driven through a gasket into an oversize barrel as an alternative.

The basic construction of a titrant delivery system of this type is quite simple. A threaded shaft is turned by a motor through a gear train or a belt and pulley system. The threaded shaft, in turn, drives a movable threaded block which pushes the piston of the syringe. A cam-driven syringe has also been described (30). The inclusion of a revolution counter on the motor or gear system adapts these systems ideally for use with an end-point sensing instrument (18, 24, 25).

One of the problems of automatic titrations is the finite rate of attainment of equilibrium near the end-point. With some end-point sensing devices this results in over-titrating the sample by 0.1 to 0.3 ml. (14, 43). If the titrant is standardized instrumentally rather than manually, this difficulty is avoided.

A method of slowing the rate of titrant delivery near the end-point while maintaining the titrant volume to chart spacing correlation is a desirable feature of some of the recording instruments. This is accomplished by two different approaches. Lingane (24) and Neilands and Cannon (32) used a clutch and gear shift system for changing the rate of titrant delivery. The gear train driving the chart

is shifted simultaneously, and the volume to spacing ratio is maintained. Duggan and Stevens (8) accomplished this change in rate similarly. They used two synchronous motors of different speeds incorporated in the syringe drive. The second method is described by Robinson (38) who used a Selsyn motor-generator combination on the buret drive, and a Selsyn motor actuated by the generator for the chart drive. The recorder is equipped with an unbalance detector that stops delivery of titrant whenever the balancing potentiometer is more than 5 mv. behind the input signal. A brake is provided on the buret driving motor-generator combination to prevent motion when the power is turned off by the unbalance detector. This method is more complicated mechanically and electrically, but appears to be superior in operation.

The instrument to be described in this report is of the recording type as defined earlier. It represents an attempt to provide this type of instrumentation with maximum flexibility in application at minimum cost. It is also designed to exemplify simplicity of construction such that it could be reconstructed by the average analytical chemist who has only a brief acquaintance with electronic circuitry.

DESCRIPTION OF THE INSTRUMENT

The instrument that has been constructed incorporates several component parts. These are an amplifier, a strip-chart recording potentiometer, a constant-flow syringe-type buret, a range and zero adjusting circuit which is self-contained, and a self-contained control circuit which contains all the operating switches. For the amplifying and recording functions, commercially available instruments are used. The complete instrument is pictured in Figure 1.

The amplifier is a Kay Lab model 202B microvoltmeter and amplifier. The manufacturer of this instrument has been succeeded by Kintel Laboratories, Inc. (21). This instrument was chosen primarily for its excellent adaptability for the purposes of the titrator, and secondarily for its flexibility for other uses. It has 14 voltage ranges from 300 microvolts to 1000 volts. The meter registers positive or negative values for any range so that the input signal leads do not need to be reversed. The amplifier output is 1 volt for full-scale deflection of the meter on any range. The stability and accuracy exceed the specifications of other instruments of the same type that were investigated (12, 13, 20). The input impedance for all ranges from 300 mv. to 1000 volts is 100 megohms. This is satisfactory for all electrode systems in common use except

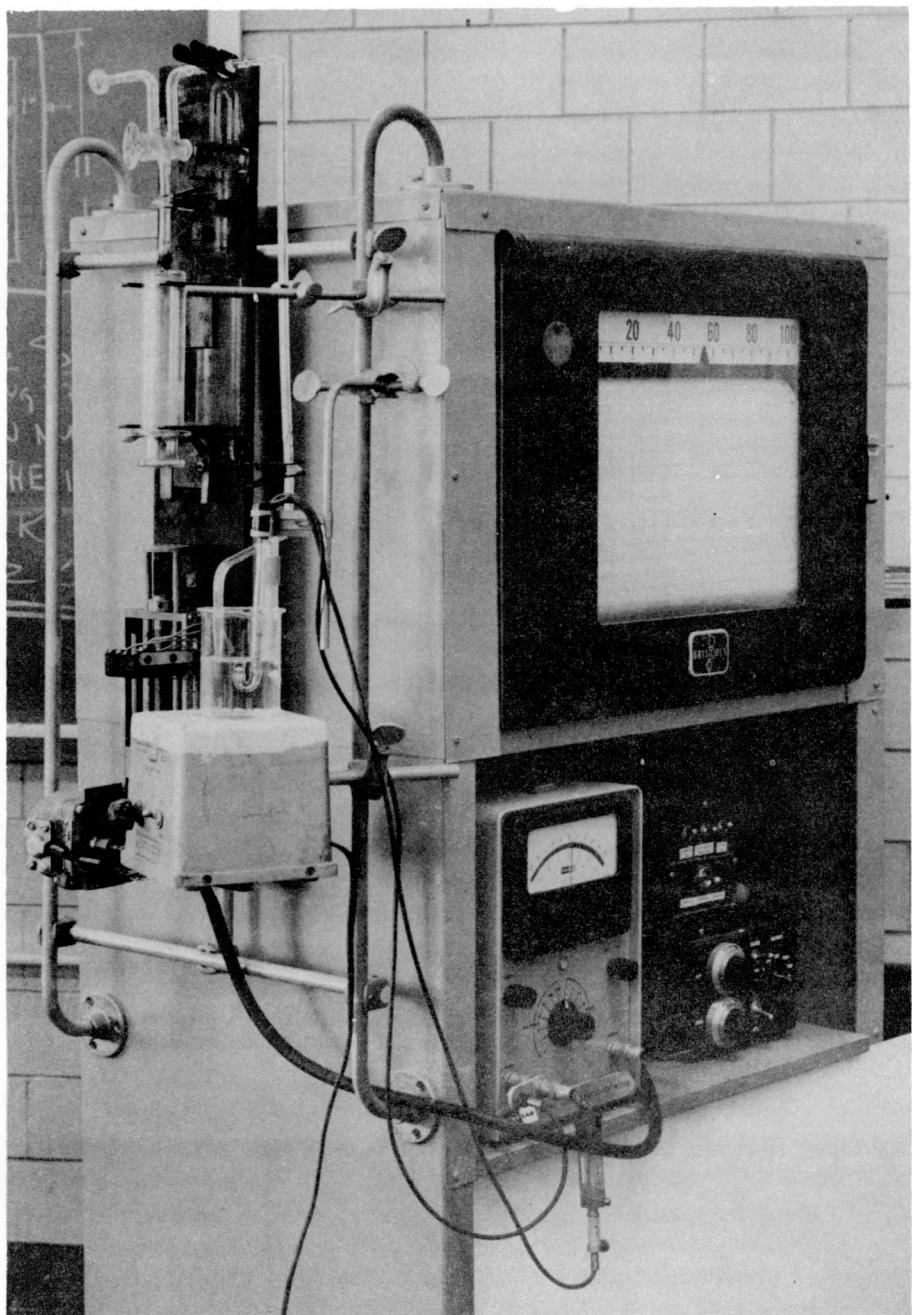


Figure 1. Complete instrument

the glass electrode. The impedance of the glass electrode varies from 18 to 200 megohns (5, p.251) depending on the type used. It is felt that the glass electrode system is not overloaded by using this meter, but the voltage values registered are only proportional to the actual voltage of the electrode system. The use of electrode systems requiring the glass electrode is permitted by proper compensation of this proportionality in the range-and zero-adjusting circuits.

The recorder is a Bristol Model 560 wide-strip Dyna-master D-C potentiometer and D-C bridge. The choice of this recorder is somewhat arbitrary because there are several other commercially available instruments of this type that can meet the required specifications. The recorder has a 12-inch chart width of which 11 inches are calibrated from 0 to 100. The chart speed can be changed by interchange of gears to any of 7 speeds from 3/8 to 4 1/2 inches per minute. Full-scale deflection of the pen requires 1 second. The recorder has a fixed range of 10 mv. These specifications provide a recorder with great flexibility in application.

Some alterations have been made on the recorder to adapt it for these purposes without limiting its possible adaptations for other purposes. These alterations are noted in Figures 2 and 4. The internally-supplied power for the chart motor has been disconnected and power supplied to this unit from the control circuit. This is required

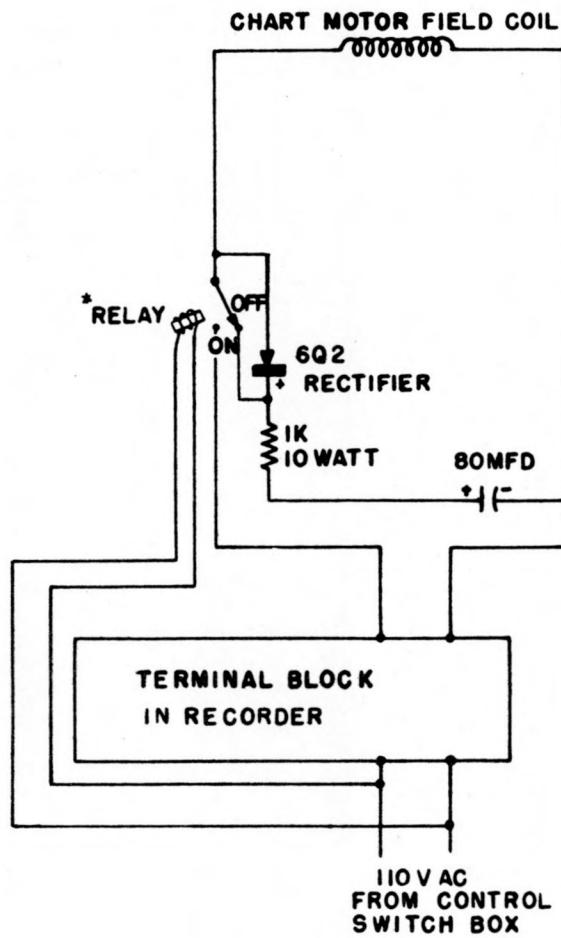


Figure 2. Electronic Brake

*POTTER+BRUMFIELD DPDT RELAY

to permit the synchronization of chart spacing with titrant delivery. An electronic braking circuit has also been added to the chart motor. The connections for this system are taken at the same terminal block in the instrument as that which altered for the chart motor power supply. This circuit is easily placed inside most recorders. In this case it is inside the recorder door mounted on a plate behind the chart motor. This brake serves to stop the chart instantaneously whenever the power is turned off. It prevents backlash in the motor and gear train driving the chart, and maintains the volume to spacing ratio when the buret is turned off during the course of the titration. This break functions by charging the large condenser while the instrument is in operation, and discharging this condenser through one of the field coils of the motor when the power is turned off. The D-C current produced momentarily stops the rotating armature within a quarter-turn or less.

The range and zero adjusting circuits provide for proper placement of the titration curve on the chart, and permit the recorded curve to cover the major portion of the chart width. The details of this circuit are illustrated in Figure 3. The range selecting portion of this circuit is essentially a voltage-dividing system that uses the amplifier output. The resistors are of the 0.1% precision wire-wound type. The actual values are chosen to correspond to

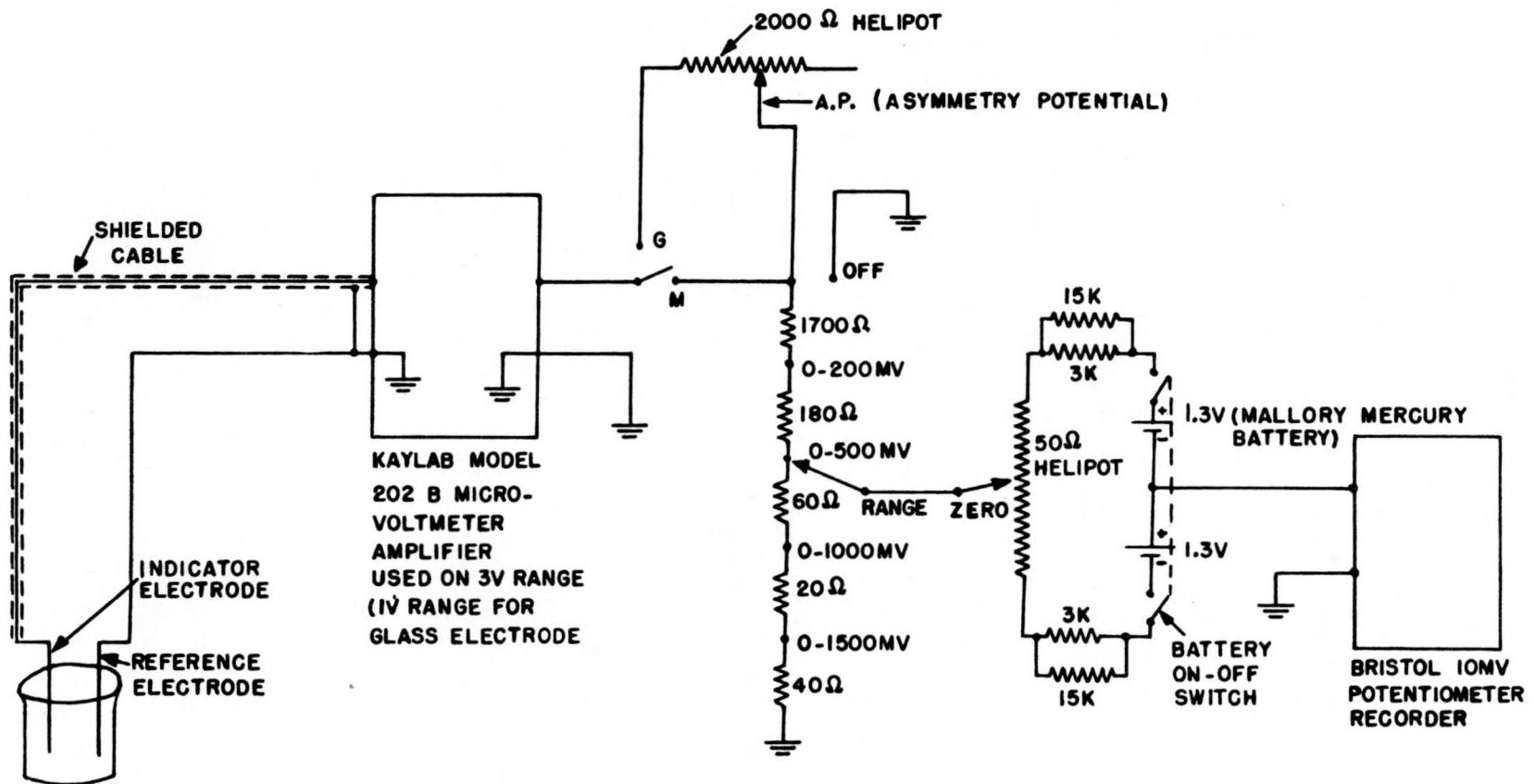
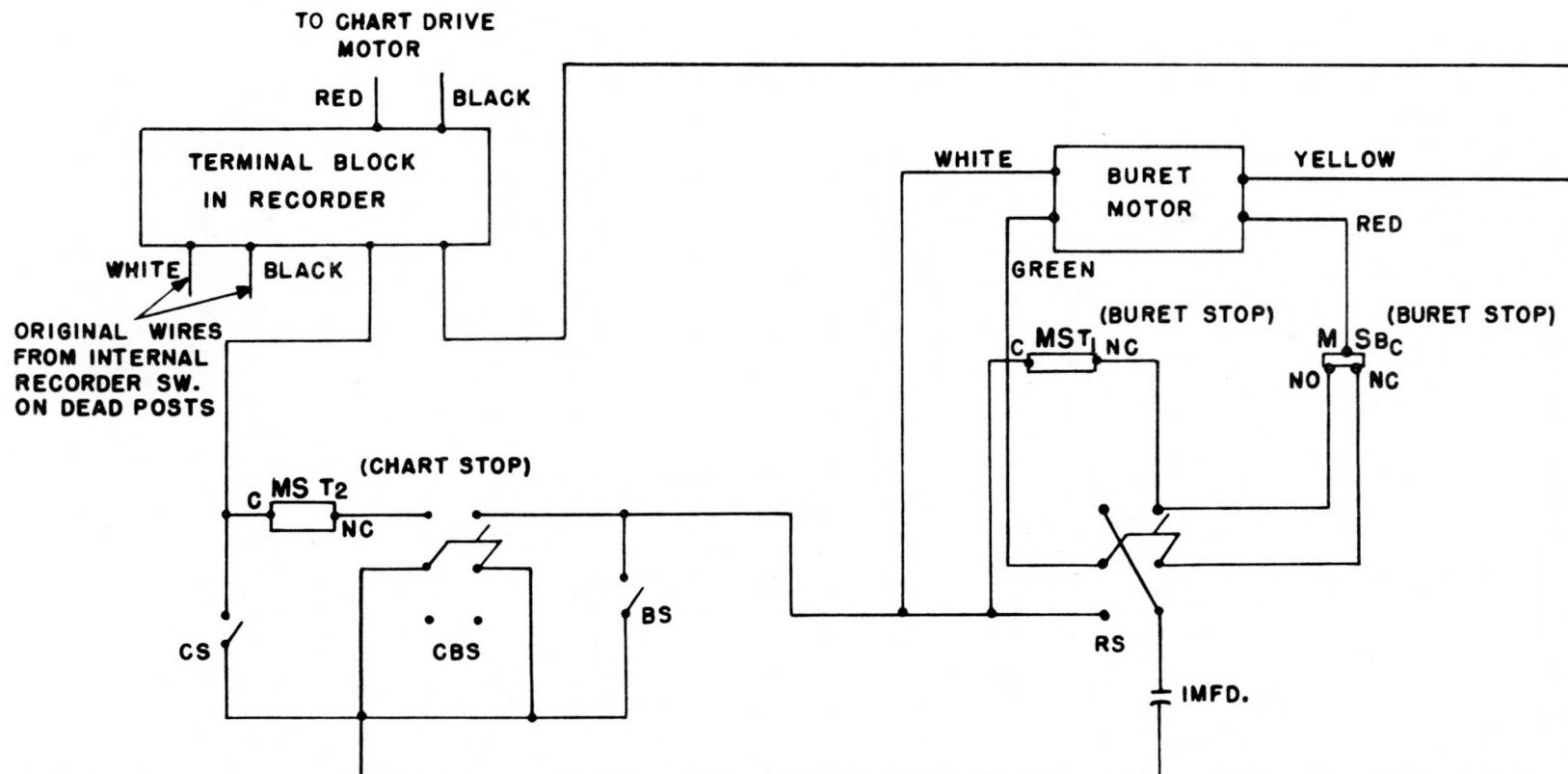


Figure 3. Range and zero adjusting circuit with complete signal circuit

the known amplifier output. The switch designated as G-M is used in the M position in all cases where the glass electrode is not required. The G position permits use of electrode systems requiring the glass electrode. The zero and asymmetry potential adjustments are used to standardize the instrument with standard buffer solutions in the same manner as with an ordinary pH meter. The details of standardizing will be discussed in a later section. The zero adjusting circuit is designed to permit the placement of the zero potential of the titration anywhere on the full chart width, or in the case of a titration in which the total range of the curve is above or below zero, the zero position can be set up to an equivalent of 1.25 chart widths beyond either limit of the calibrated portion of the chart.

The control circuit provides switching arrangements for independent or simultaneous operation of the chart and buret, and for reversing the buret for re-filling with titrant. The control circuit also contains provisions for limiting the forward and reverse travel of the buret to prevent breakage and to stop the chart at the upper limit of travel. These provisions are accomplished by the placement of microswitches at the top and bottom of the channel through which the threaded block moves. These switches are placed as shown in Figure 5, and included in the circuit shown in Figure 4. The upper microswitches are on a movable mount so that they can be pre-set to stop the instrument,



C - common terminal

NC - normally closed

NO - normally open

TO 110VAC LINE

CS, CBS, BS and RS in box; 8 conductor cable using only 7 from box to buret, 2 wires from box to chart motor

MS_t and MS_b - microswitches top and bottom of buret frame

CS - chart only on-off

BS - buret only on-off

RS - buret motor reversing switch

CBS - chart and buret on-off

Figure 4. Control circuit

when a desired volume of titrant has been delivered, without wasting chart or titrant. The microswitch that controls the chart is set to trigger shortly before the buret-controlling microswitch, because the buret movement operates both switches.

Figure 5 shows the syringe drive mechanism. The buret is a 50 ml. Luer syringe which is available from all laboratory suppliers. It is fitted with a ground-glass ball joint which is secured to the tip of the syringe with a small ground-glass joint and sealed with Dekhotinsky cement. A 3-way stopcock fitted with ground-glass sockets at all 3 positions fits the ball joint on the syringe. This permits filling the buret or delivery of titrant by turning the stopcock to the proper position. To direct titrant into the sample beaker, 1 mm. glass tubing is used. To keep the parts required for this purpose small enough for structural rigidity, 12/1 standard ground-glass ball and socket joints are used. The syringe piston is driven into the barrel in the following manner: A Brown 60 rpm. reversible synchronous motor fitted with a worm gear drives a shaft with 40 threads per inch by means of a 100-tooth spiral gear fixed to the bottom of the shaft. The worm gear passes 4 teeth of the spiral gear with every revolution of the motor. The shaft, in turn, drives a threaded block through the guiding channels. A disc fixed to this block by two rods pushes on the syringe piston. This arrangement provides a titrant

delivery rate of approximately 1 ml. per minute.

The description of this instrument is intended to be a guide for construction of a similar instrument. Any number of variations may be adopted to suit the needs of a particular application. This instrument is designed primarily to carry out titrations requiring 5 to 20 ml. of titrant. The recorder chart speeds are chosen to provide a titration curve which uses about 10 inches of the chart length as compared to the 11 inch chart width. For these purposes the 1/2 or 1 inch per minute chart speeds are normally used. If other titrant delivery rates are desired, the specifications of the chart speed ranges on the recorder should be chosen to correspond to the titrant delivery rate so that the recorded curves are not greatly distorted in either dimension.

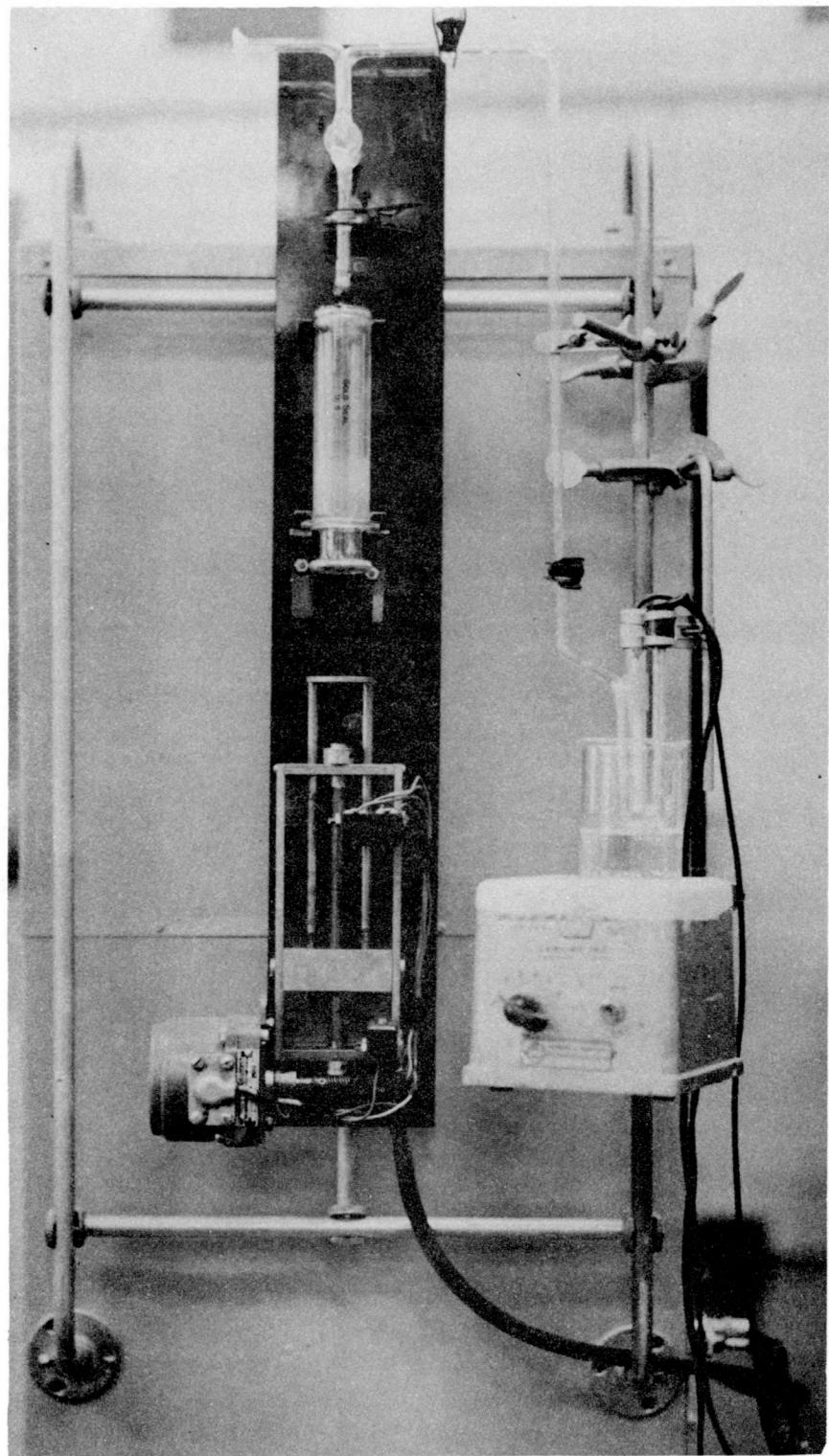


Figure 5. Buret drive mechanism

OPERATION

Operations preliminary to the actual titration require filling of the buret, and removal of air bubbles from the tubing which directs titrant into the sample beaker. The titrant reservoir is connected to one side of the 3-way stopcock by means of a ground-glass ball joint. The syringe piston is pushed the maximum distance into the barrel, with the stopcock opened to the titrant delivery side, to permit the expulsion of air. The stopcock is then turned to permit solution from the titrant reservoir to be drawn into the syringe by pulling the piston down toward the lower limit of travel. The stopcock is then turned back to the titrant delivery side, the piston is pushed into the barrel until air bubbles have been expelled, and the titrant delivery tubing is completely filled with titrant. The stopcock is again turned, and the syringe filled with titrant by pulling the piston to its lower limit of travel.

When these procedures have been completed, the range switch is turned to zero, and the amplifier, battery switch and recorder are turned on. The recorder on-off switch is inside the door of the recorder. It is important that the battery switch be turned on before the recorder. For titrations employing electrodes other than the glass electrode, the G-M switch is turned to M (metal electrodes). The potential range to be covered must be determined. This

is done by placing the electrodes first in the sample solution, and noting the potential of the starting point of the titration on the voltmeter, using the approximate range. The final potential to be encountered is then determined by placing the electrodes in an equivalent blank solution containing a small amount of the titrant, and noting the potential on the voltmeter as before. This fixes the potential range to be covered, and the position of the zero-potential point of the titration. The ranges available for use on the machine are 200, 500, 1000 and 1500 mv. The next larger range to the actual range of the titration must be chosen for the total curve to be recorded on the chart. If the potential range of the titration encompasses the point of zero potential, the pen is moved to the appropriate position on the scale by use of the zero adjusting potentiometer, noting that the 0 to 100 calibration on the front of the recorder will represent the range to be chosen (e.g. If the range to be used is 1000 mv., each major division on the scale will represent 100 mv.). The stop-cock above the syringe is turned to the delivery side; slack in the buret driving mechanism is taken up by running it for a moment and then wiping the delivery tip dry. The sample is then placed so that the electrodes and the buret delivery tip project below the surface of the sample solution. The recorder pen is released so that it rests on the chart, and the chart is turned manually until one

of the calibration lines is directly under the point of the pen. The range switch is then turned to the desired range designation, and the buret and chart are started simultaneously by turning the chart and buret on-off switch (CBS) to the on position. When the titration is complete, the switch is turned off.

When the potential range of the titration is all above or below the point of zero potential, the zero adjustment is not made until after the range switch is turned to the appropriate position. At this point, the recorder pen will move rapidly to the upper or lower limit of its travel. It is brought back on scale as quickly as possible with the zero adjustment. The position to which the pen is brought will then represent the potential of the starting point. The pen should be positioned so that the remainder of the titration curve will fall on the calibrated portion of the chart. The titration then proceeds as before. In a few cases it will be necessary to reverse the electrode leads into the voltmeter in order for the pen to be positioned on the calibrated portion of the chart, as described above. No titrations have been encountered where one or another of the procedures described does not permit recording of the total titration curve.

When the glass electrode is used, the voltmeter must be turned to the 1 volt range for the titration. If direct pH measurements are not required, the beginning and ending

points of the titration are determined by use of the range switch and zero adjustment, and noting the pen position for the two points on each range. The range switch position that gives the greatest pen travel within the calibrated limits will be chosen, and the titration carried out as before. This will give an arbitrary potential range which is only proportional to the actual potential of the electrode system.

To record the titration curve in accurate pH terms, pH buffers must be used as with all pH meters. For this purpose, the voltmeter is used on the 1 volt range, and the G-M switch is turned to the G (glass electrode) position. Two buffer solutions are required, usually pH 4 and 7 or pH 7 and 9. If the total pH range of 0 to 14 is desired, the 1000 mv. range will be used. The asymmetry potential adjustment is turned to the limit so that the total resistance represented by the asymmetry potential potentiometer is in the circuit. The electrodes are immersed in the pH 7 buffer solution, and the range switch is turned to the 1000 mv. position. The pen is moved to give the desired placement of pH 7 with the zero adjustment. The range switch is then turned to the off position, and pH 4 or 9 buffer is substituted for the pH 7 buffer. The range switch is again turned to the 1000 mv. position, and the pen is moved to the desired placement of pH 4 or 9 with the asymmetry potential adjustment. When this has been accomplished, the

sample can be titrated in the usual manner, and the pH of any point on the titration curve is accurately recorded. If lesser pH ranges are to be covered, the 500 or 200 mv. ranges can be used to permit the recorded curve to utilize most of the available chart width.

The electrodes should not be handled unless the range switch is in the off position. The extra procedures required for use of the glass electrode and the problem of the proportionality of actual to recorded voltages are easily eliminated by use of an electrometer-input voltmeter-amplifier in place of the Kay Lab voltmeter used here. This will be discussed in a later section. A Beckman 1190-80 blue label glass electrode has been used with this instrument, but a Leeds and Northrup electrode would be more satisfactory because the impedance is lower than that of the Beckman electrode. The ranges specified in the procedures for use of the glass electrode are correct when the Beckman electrode is used, but will change if the Leeds and Northrup electrode is substituted, and must be independently determined in that case.

APPLICATIONS

Figures 6 through 17 are reproductions of titration curves recorded on the titrator. A few points should be noted about these curves. It should be pointed out that some of the detail is lost in the reproduction process. The high-speed pen travel of the recorder results in the tracing of some of the extraneous signal that is inevitably present in all electronic systems. The level portions of the curves have varying degrees of waviness that are not reproduced. A rough comparison can be made to the appearance of a recorded polarogram before the half-wave potential is reached. This degree of waviness decreases as the range used is increased. The 1000 and 1500 mv. ranges give nearly smooth curves. As the range is decreased, the signal to noise ratio also decreases so that the greatest irregularity occurs with the 200 mv. range. No difficulty is encountered, however, in identifying a uniform curve. The break of the curve is always very neatly and smoothly defined. These irregularities in the tracing of the curve can be eliminated by using a recorder with a very slow pen speed, and incorporating the unbalance detector described by Robinson (38). This slow-speed pen does not respond to extraneous noise present in the signal, but a recorder of this type is very limited in other applications. The Precision Scientific Company instrument which incorporates this unbalance

detecting system uses a recorder that requires 24 seconds for full-scale deflection of the pen.

Figure 6 illustrates standardization of the instrument so that the pH scale corresponds to the reduction potential scale when the glass electrode is used. The titrator was standardized using pH 4 and 7 buffers as described above, and checked with pH 9 buffer. The pen position with the pH 9 buffer was within 3 mv. of the theoretical -531 mv. that would be calculated on the basis of 59 mv. per pH unit. The correspondence of the inflections of the curve with pH for the titration of sodium carbonate with hydrochloric acid illustrates the reliability of pH measurements made in this manner.

Figure 7 shows an ordinary aqueous acid-base titration with an arbitrary potential scale. Methyl orange indicator was added to the sample, and the range of color change noted to show that the automatic titration gives essentially the same end-point as would be obtained by manual titration with the use of an indicator. The non-symmetry of the curve indicates a slight over-sensing of the end-point. This illustrates still another point of interest in automatic titrations.

The factors involved in obtaining a normal potentiometric titration curve are the placement of the buret delivery tip in relation to the indicator electrode, the rate and direction of stirring, the rate of attainment of chemical equilibrium in the sample, and the rate at which

the electrode detects the changes in the sample solution. The determination of whether the recording system is under-sensing or over-sensing the end-point can be accomplished by stopping titrant delivery abruptly in the end-point region of the titration. If the pen drifts back toward the starting potential, the end-point is being over-sensed, and the sample determination will be low. If the pen drifts in the other direction, the end-point is being under-sensed by the instrument, and results will be high. Slight drifting may be ignored, but drifting of an inch or more must be compensated. Three corrective measures are available. The buret delivery tip can be moved away from, or closer to the indicator electrode in terms of the direction of stirring, to correct over-sensing or under-sensing, respectively. Stirring is generally maintained at a rate as fast as is permissible without loss of sample by spattering. Similar correction measures are obtained by interchanging the positions of the reference and indicator electrodes. A second method of compensating for these conditions is to slow titrant delivery in the region of the end-point. In the instrument described this is accomplished by stopping the buret drive and chart mechanism once or twice in this region. This is the primary purpose for installing the electronic brake on the chart motor. The third method of correcting these conditions is the use of a more, or less, sensitive indicator electrode to compensate

for under-sensing or over-sensing, respectively. This last method is illustrated in Figure 8 where the same acid-base titration has been carried out by using an antimony electrode as the indicator electrode.

Figure 9 shows the titration of hydroxylamine in the presence of hydroxylamine hydrochloride and triethanolamine hydrochloride with hydrochloric acid. The solvent for both sample and titrant is isopropanol. The potential scale is arbitrary. This titration curve is included to illustrate the use of the instrument for non-aqueous acid-base titrations. This particular titration is one of the steps in the analysis of carbonyl compounds described by Yamamura (49).

One of the more familiar of oxidation-reduction titrations is reproduced in Figure 10, that of the titration of iron (II) with cerium (IV). The potential scale in this titration compares within 2 mv., at all points, with the same titration performed manually.

Figures 11 through 17 illustrate the application of the titrator to potentiometric complex-forming titrations. The use of various electrodes for this purpose is described by Siggia et al. (44). The theory and use of the mercury electrode for this purpose is described by Reilley et al. in a series of papers (15, 36, 37, 40). The mercury electrode has been employed in all the titrations illustrated in Figures 11 through 17.

Figures 11 and 12 demonstrate the proper use of the range switch to attain maximum use of the chart width. When mercury (II) is titrated with EDTA at pH 6 (Figure 11) the potential range of the titration is about 300 mv. Using the 500 mv. range, this titration utilizes approximately three-fifths of the chart width. If the titration is carried out at pH 4.6 (Figure 12), the range is slightly under 200 mv., but using the 200 mv. position of the range switch permits the recorded curve to utilize nearly the full width of the chart. It should be noted that the available ranges on the titrator have been very carefully chosen, and have proven very satisfactory in use.

Figure 13, showing the titration of zinc and, Figures 14 through 17, showing titrations of thorium, illustrate some of the many EDTA titrations that may be carried out automatically by using the mercury electrode. The series of thorium titrations were carried out in conjunction with an investigation of the practical limits of dilution that could be attained while still providing a titration curve with an easily determined end-point. In the series illustrated, the intersection of the extrapolation of the steepest portion of the break of the curve to the extension of the level portion of the curve before the end-point gives the same point of intersection for all of the titrations.

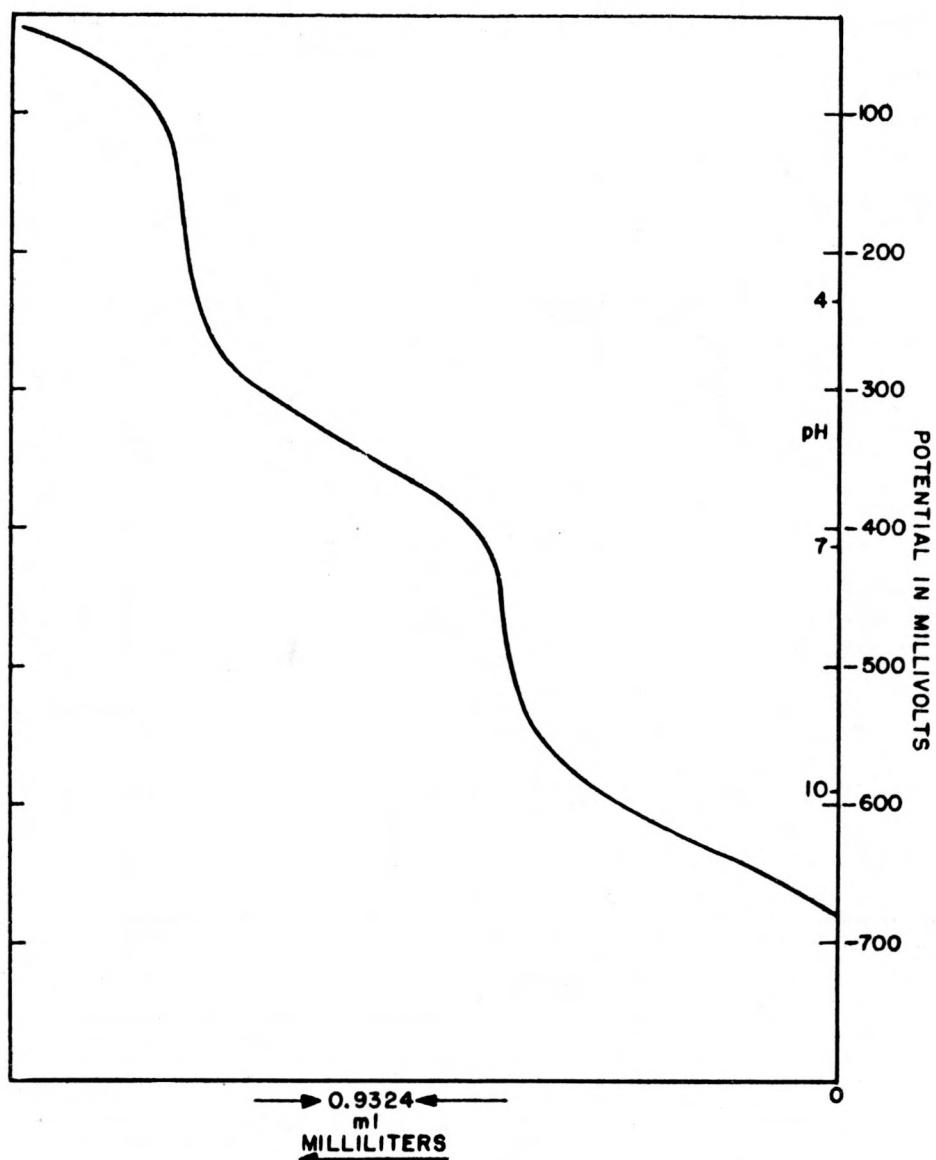


Figure 6. Titration of 0.05 M Na_2CO_3 with 0.1 M HCl
Glass-calomel electrode system
1000 mv. range correlated with pH scale

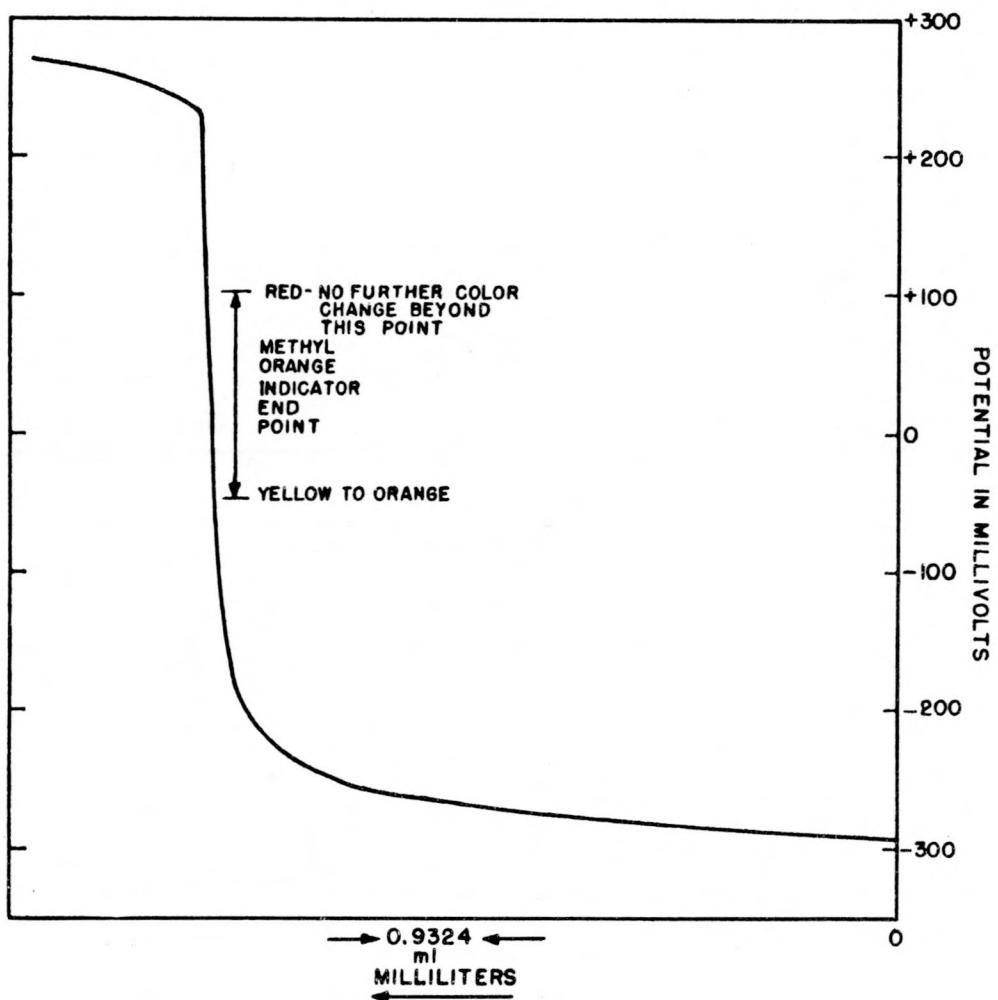


Figure 7. Titration of 0.1 M NaOH with 0.1 M HCl
Glass-calomel electrode system
1000 mv. range showing indicator end-point

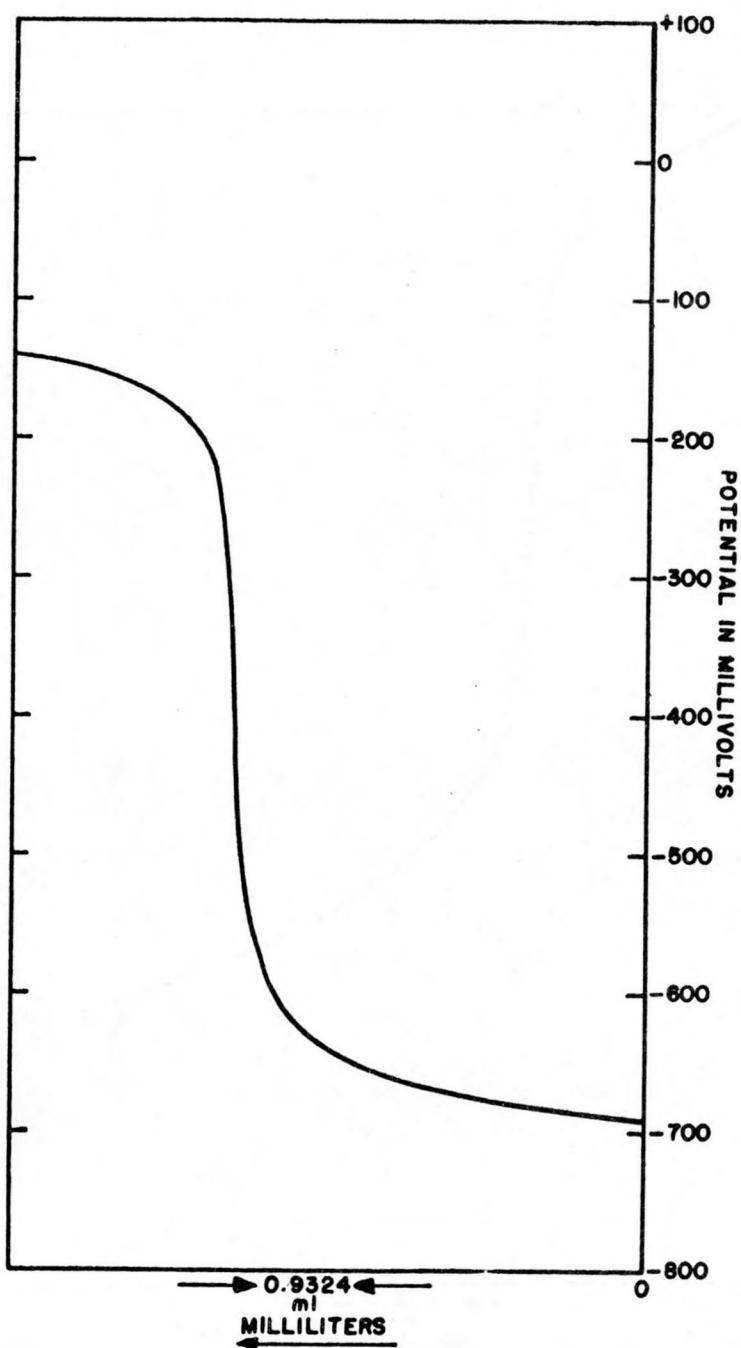


Figure 8. Titration of 0.1 M NaOH with 0.1 M HCl
Antimony-calomel electrode system
1000 mv. range

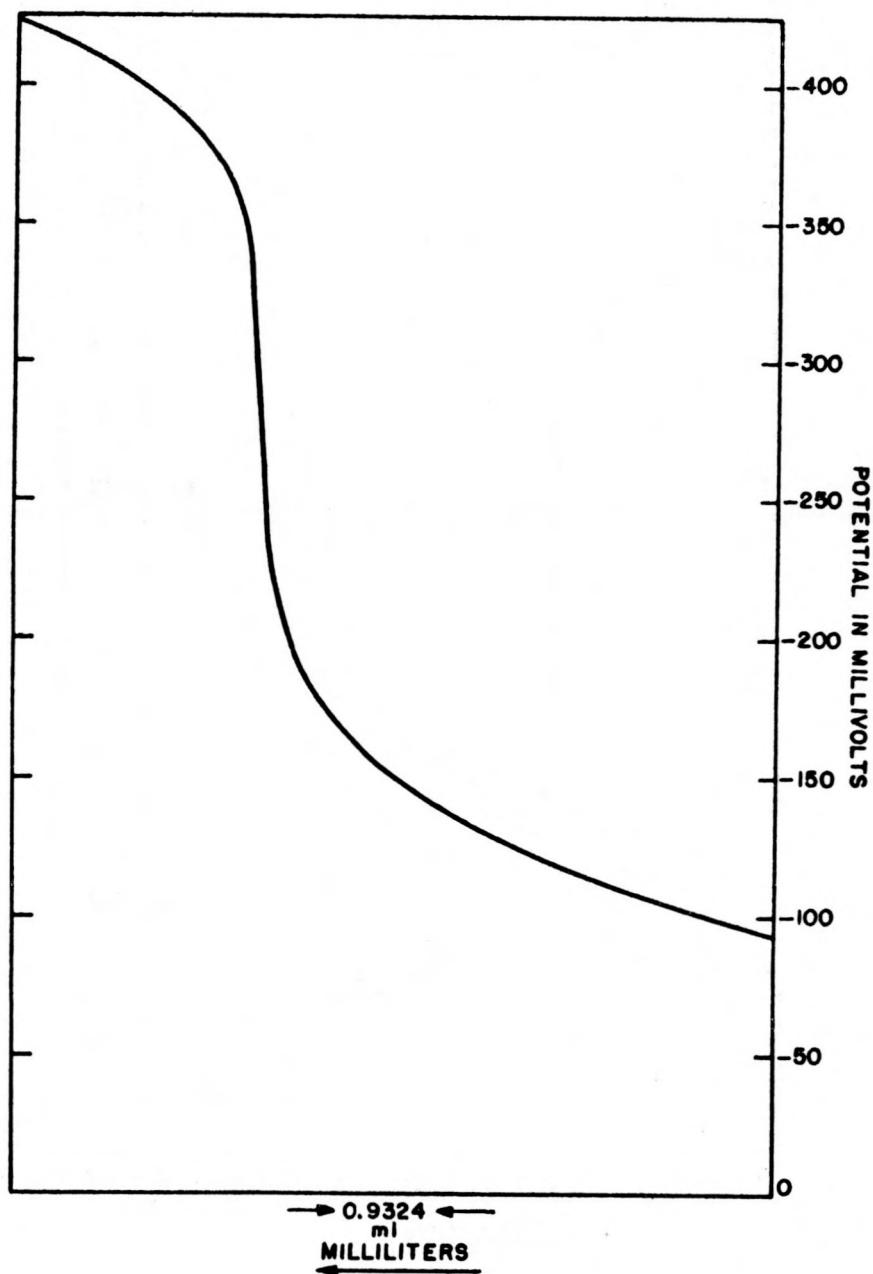


Figure 9. Titration of H_2NOH with HCl in isopropanol
Glass-calomel electrode system
500 mv. range.

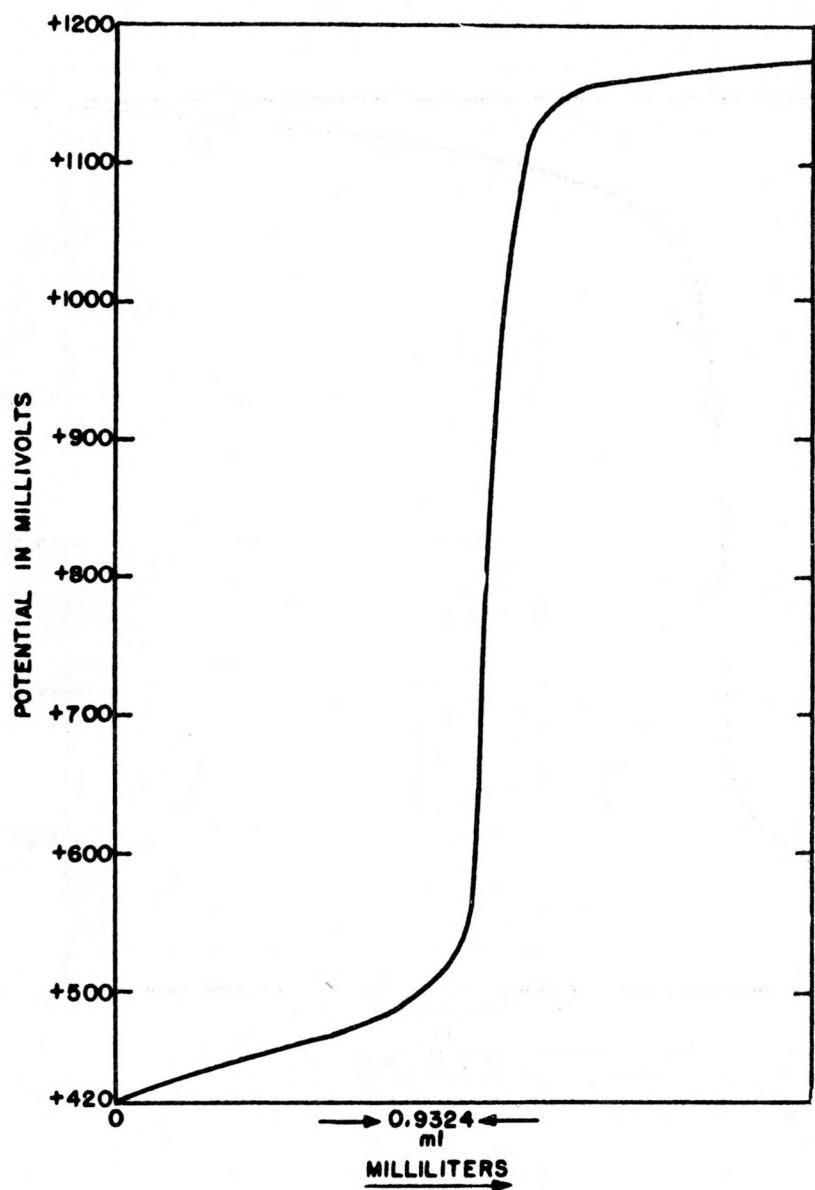


Figure 10. Titration of iron (II) with cerium (IV)
Platinum-calomel electrode system with leads
reversed
1000 mv. range with zero potential off scale

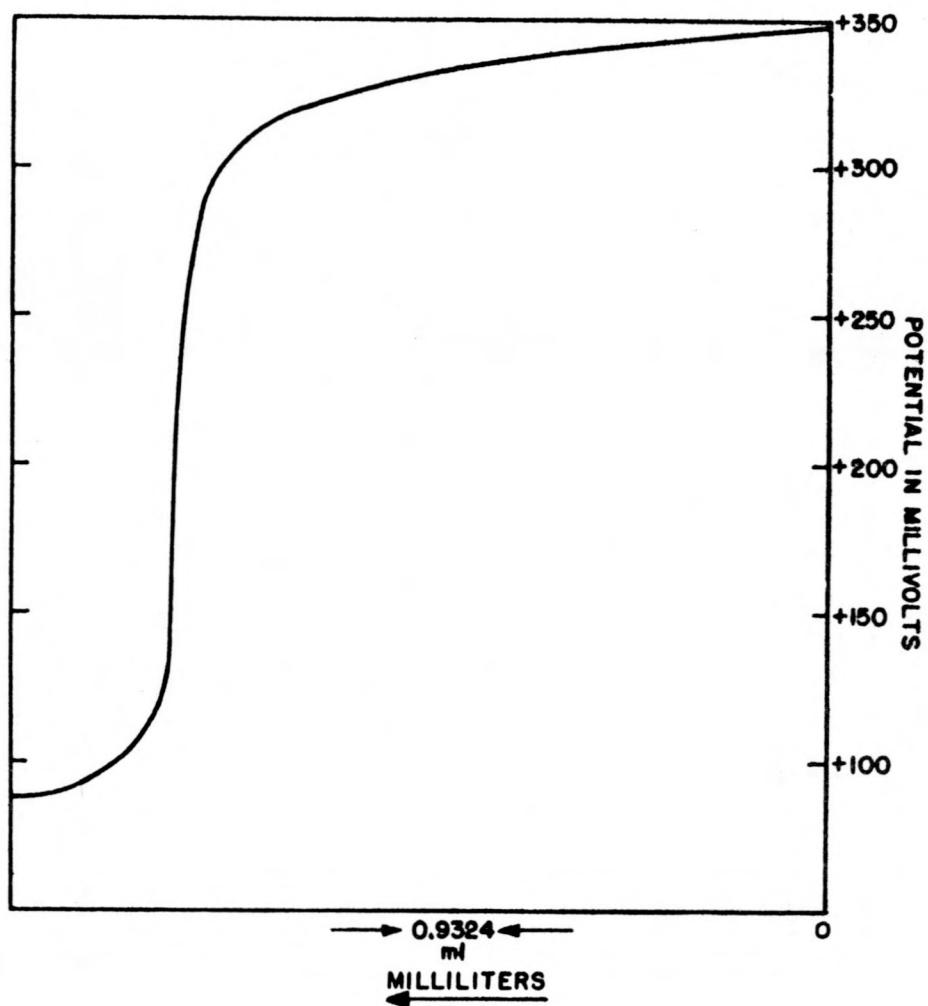


Figure 11. Titration of 0.05 M Hg (II) with 0.05 M EDTA
at pH 6
Mercury-calomel electrode system
500 mv. range.

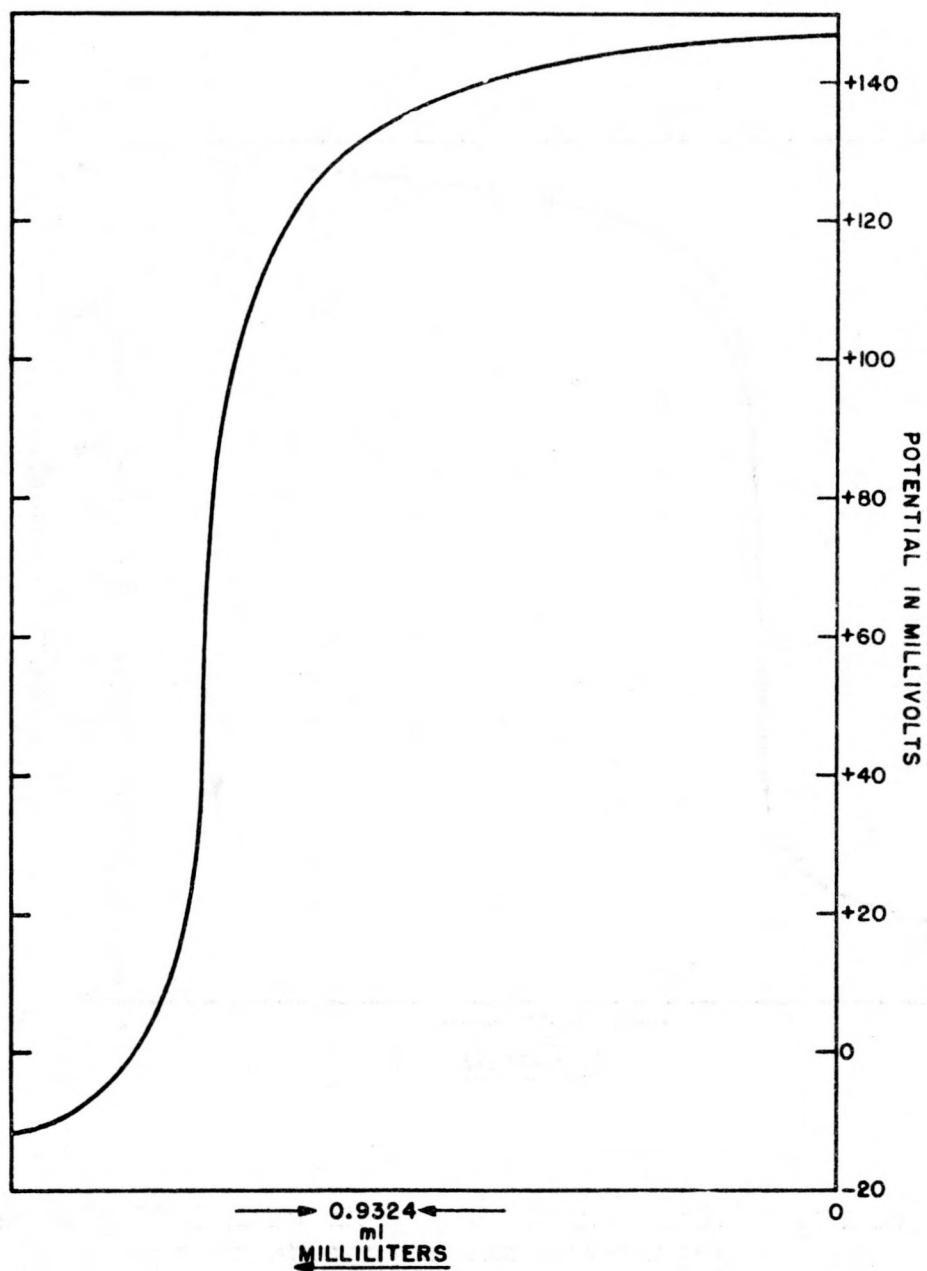


Figure 12. Titration of 0.05 M Hg (II) with 0.05 M EDTA
at pH 4.6
Mercury-calomel electrode system
200 mv. range.

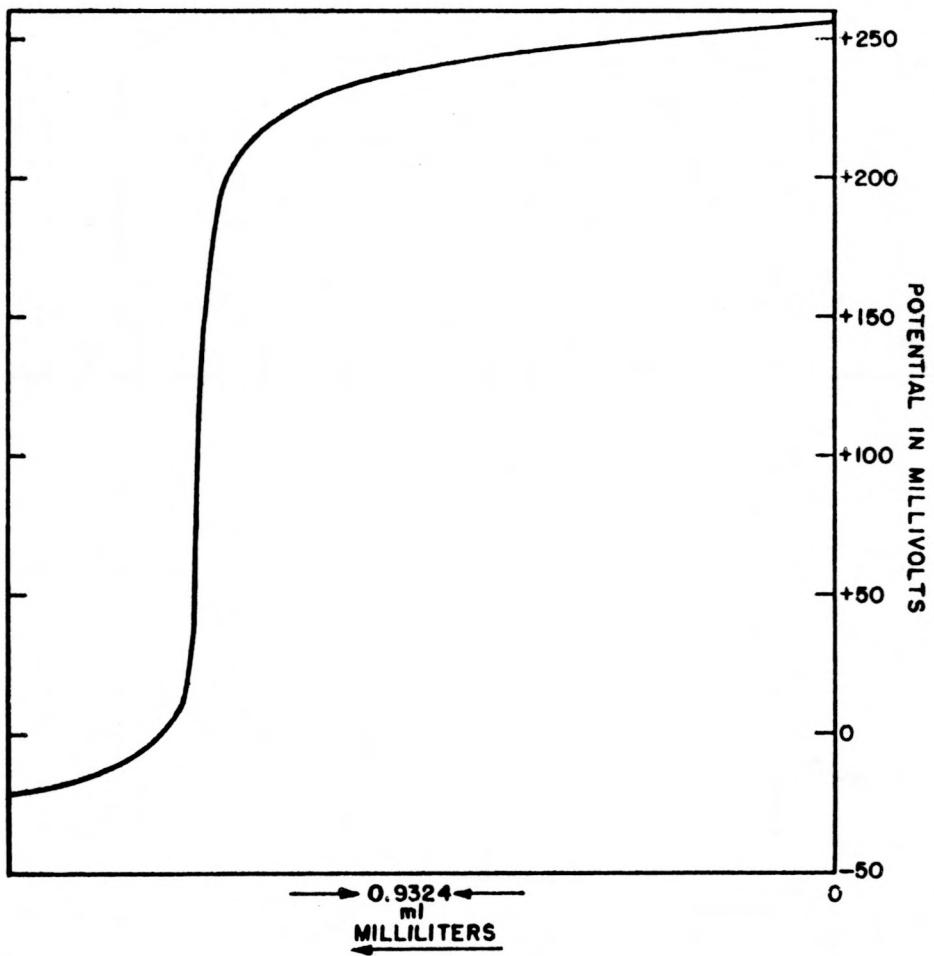


Figure 13. Titration of 0.05 M Zn with 0.05 M EDTA
Mercury-calomel electrode system
500 mv. range

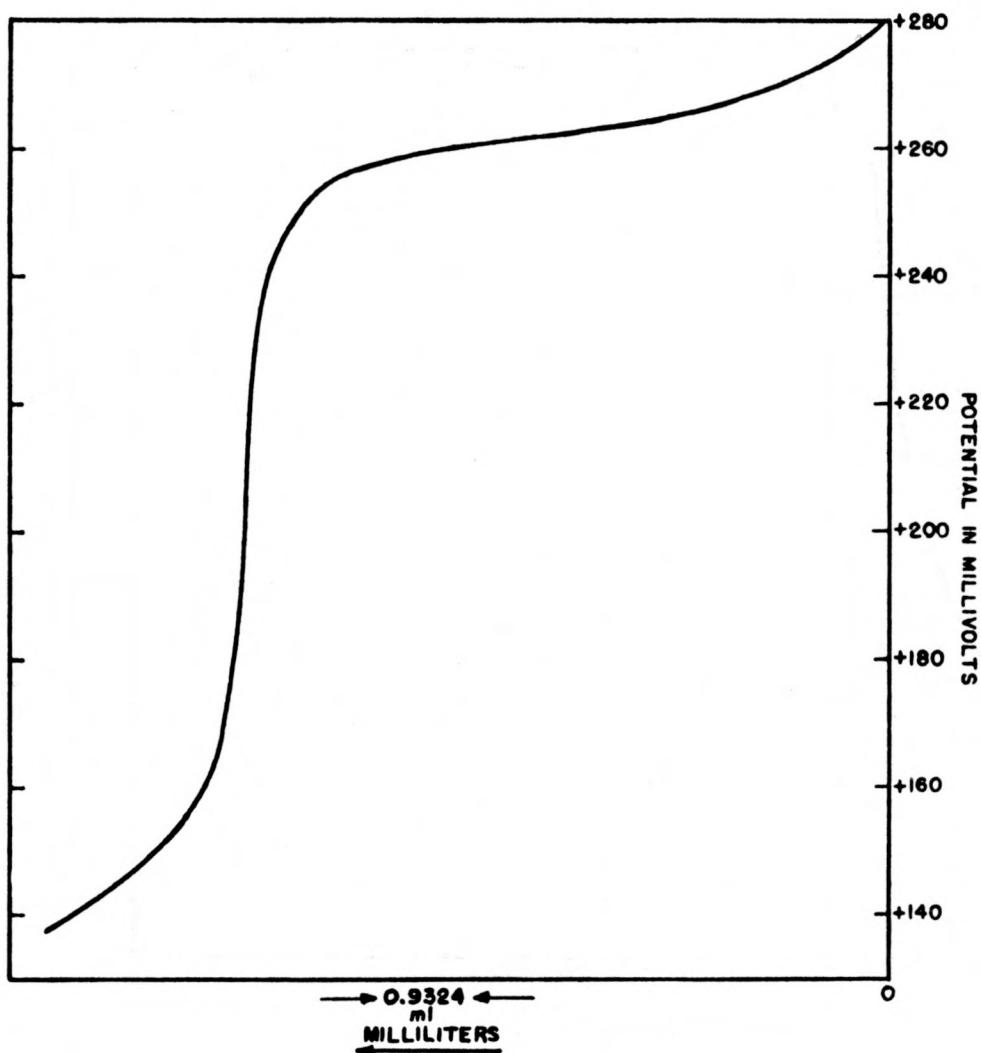


Figure 14. Titration of 0.05 M Th with 0.05 M EDTA
Mercury-calomel electrode system
200 mv. range

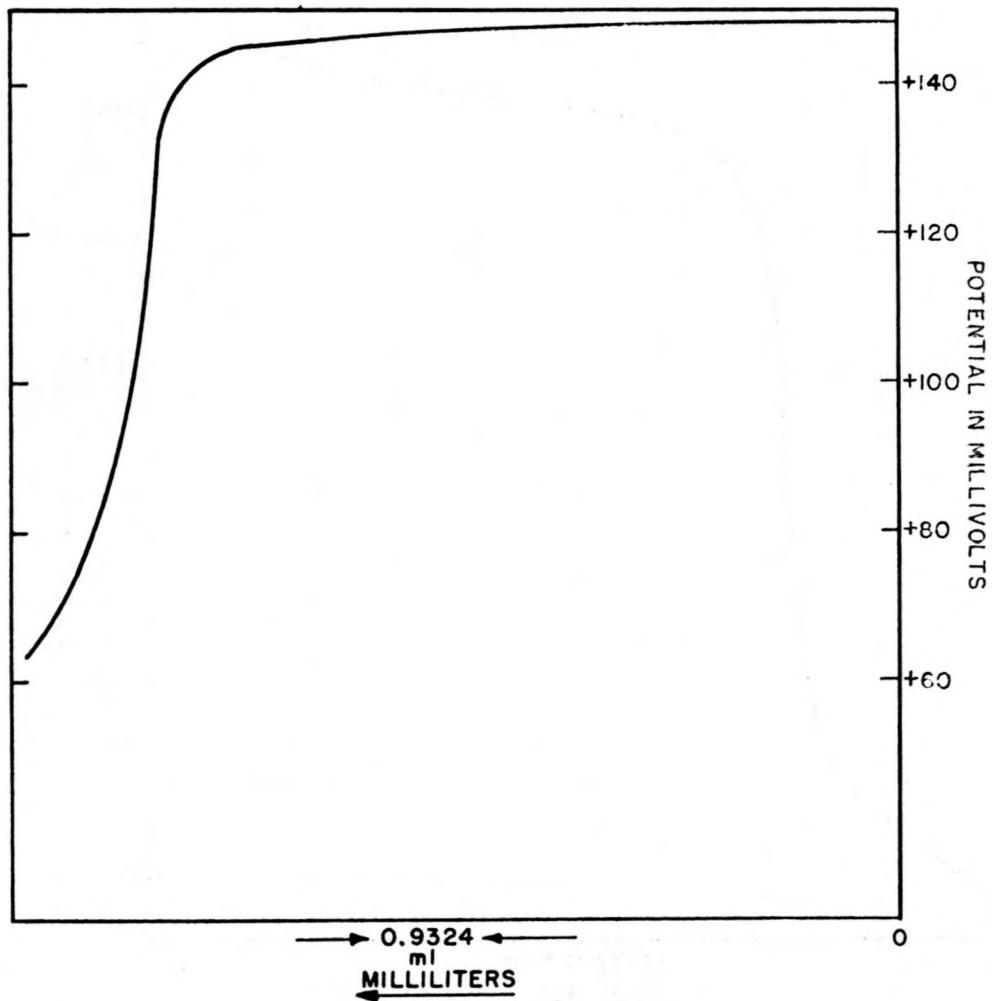


Figure 15. Titration of 0.005 M Th with 0.005 M EDTA
Mercury-calomel electrode system
200 mv. range.

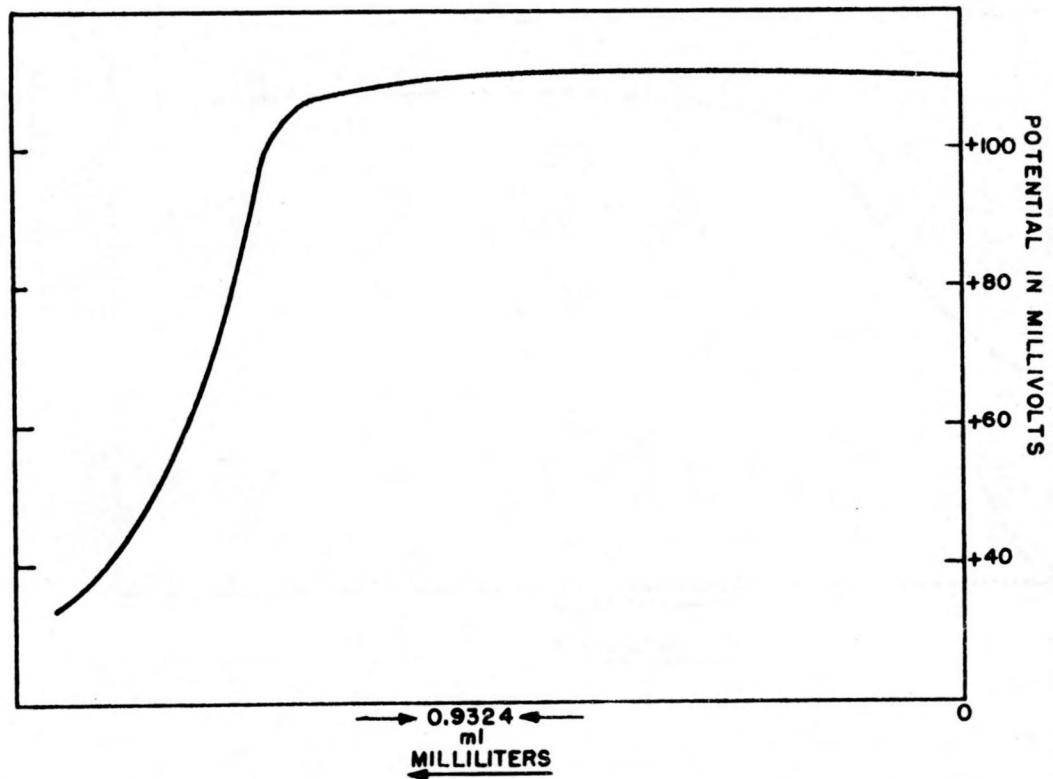


Figure 16. Titration of 5×10^{-4} M Th with 5×10^{-4} M EDTA
Mercury-calomel electrode system
200 mv. range

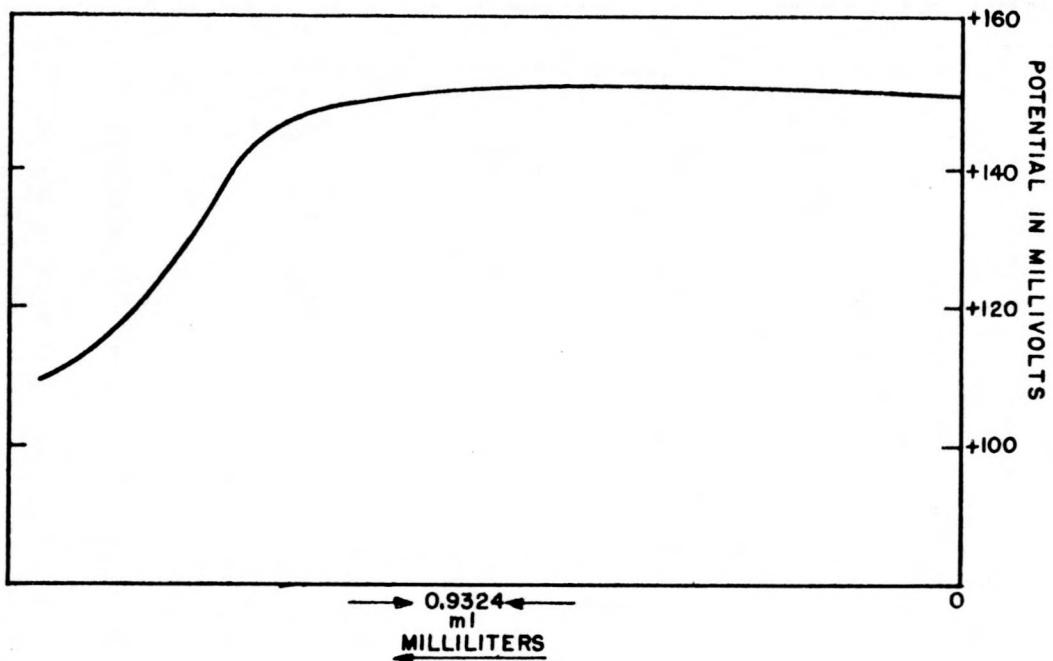


Figure 17. Titration of 1×10^{-4} M Th with 1×10^{-4} M EDTA
Mercury-calomel electrode system
200 mv. range

DISCUSSION

Recommendations for Improvements

The instrument that has been described is designed to give an accuracy of $\pm 0.3\%$ both in potential scale reading and in end-point determination as interpreted from the recorded titration curve. This has been demonstrated both in the determination of rate of titrant delivery and in actual titrations of known samples. As in any titration procedure, the titrant should be standardized by the method to be used for sample determinations. When this is done, the factors limiting the accuracy of the automatic titration are the limits of accuracy of the amplifier and recorder, and the accuracy of calibration of the resistors in the range selecting circuit.

In the instrument described, the recorder is the component of least accuracy. The actual electrical accuracy of the recorder is $\pm 0.25\%$ of full scale. This is further conditioned by the finite thickness of the line drawn by the recorder pen. The accuracy of locating the end-point is limited also by the finite thickness of the recorded curve, and the ability of the operator to start the titration with the pen exactly on one of the calibrated lines of the chart and thus accurately calculate the volume of titrant delivered. If the standardization of the titrant is carried

out by using the instrument, and the titrant is not to be used for any manual titrations, its concentration can be expressed in terms of equivalents per unit chart spacing, and the calculation of volume is not necessary.

This instrument can be easily converted to an end-point sensing device by inclusion of a mercury or contact switch attached to the shaft of the balancing potentiometer of the recorder, or on a movable mounting where the pen movement can be made to actuate the switch. Electrically, this switch is inserted in the power line to the control circuit.

Pre-setting the position of the switch to correspond to the end-point potential of the titration will result in stopping the titration automatically at the end-point. The details of this alteration are described by Lingane (24). Addition of a revolution counter to the buret drive would be desirable for this purpose.

The flexibility of the components has been emphasized. This flexibility will permit the use of the instrument for photometric, thermometric or conductometric titrations by suitable substitution of the required signal sources for the electrodes. Appropriate choice of the ranges available on the voltmeter and range circuit can be made for these purposes.

The recorder-amplifier-range circuit system is ideally suited for adaptation to gas chromatography. The additional components required for this purpose can be purchased sepa-

rately or assembled from commercial suppliers.

The inclusion of provisions other than the electronic brake for slowing the rate of delivery of titrant near the end-point would be desirable. Methods of accomplishing this have been described. The substitution of a nylon or teflon syringe for the glass syringe would be desirable for use with strongly basic titrant solutions. A teflon syringe has been constructed for this purpose, but has not yet been tested.

Acceptable Substitutes for Components

Several recorders are commercially available which can be supplied to fit the specifications described in previous sections. The Brown, Leeds and Northrup, Wheelco and Weston recorders are in this group. Recorders with narrower charts are manufactured by these organizations, and by Varian Associates. The narrower chart could be used in control applications where the exact potential values are of lesser importance. The end-points of titrations could still be determined with nearly the same accuracy as with the wide chart in most cases. Two recorders are available which would replace the range and zero adjusting circuit also. These are the Fisher Recordall (11) and the Sargent recorder. The Sargent recorder has been briefly tested by the authors and shown to be usable for this purpose. When use of the glass electrode is not

required, these two recorders can be used, without the additional amplifier, for most other electrode systems.

Most of the difficulties involved in the use of the glass electrode as described can be easily eliminated by substituting an electrometer-input voltmeter-amplifier for the Kay Lab instrument used in this titrator. This type of voltmeter will permit direct reading and recording of the actual voltage signal. Instruments of this type are made by the General Radio Company (12, 13) and by Keithley Instruments, Inc. (20). The substitution of either of these instruments for the Kay Lab voltmeter will result in a negligible reduction in the accuracy of the potential measurements. However, the advantages gained in operations with the glass electrode make this substitution desirable. The resistors used in the range circuit would have to be changed to conform to the voltmeter output unless the specification of 1 volt output for full-scale deflection is maintained.

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