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Title DESIGN OF A DIGITAL REPETITIVE TITRATOR

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An automatic digital titrator for use in potentiometric titrations is described. The automatic titrator described provides a permanent digital and analog record of all titrations. The modular units which combine to form the automatic titrator are described individually. Accuracy achieved by the titrator on successive acid-base titrations of ammonia in a borate system is 0.2%. The elapsed time from the start of a titration to the digital print-out was about three minutes.

DESIGN OF A DIGITAL REPETITIVE TITRATOR

by

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DESIGN OF A DIGITAL REPETITIVE TITRATOR

INTRODUCTION

Titrations are among the most common operations in the analytical laboratory, a fact which has prompted a number of investigators to devise instruments to perform these titrations more or less automatically. Lingane (4) lists a number of these investigators in his book "Electroanalytical Chemistry". More recently, potentiometric devices have been devised specifically for reactions dependent on the hydrogen ion concentration, such as hydrolysis reactions and certain kinetic studies (1, 3, 11, 16). These instruments hold the pH constant by the addition of an acid or an alkali and are therefore known as pH-stats (2, 3, 7, 8, 9, 13, 16). The instruments employ either photometric endpoint detection or potentiometric endpoint detection, with the latter being the most popular. The subject of pH-stats in biochemical investigations has been reviewed by Jacobsen, et al. (2), in which a variety of meter relays (photoelectric or capacity-operated types) useful for sensitive control is described. Josefsson, Rybert and Svensson (3) have used a pH stat which permits studies of both rapid reactions, as in enzymatic hydrolysis, and extremely slow reactions, with the reactants in small concentrations. Other investigators have used the pH-stat for the titration

of acidic or basic groups liberated in the reaction of hydrolytic enzymes (11), for the study of protein structures and amino acid sequences (8), for the determination of the kinetics of the reaction of chloracetamide with various mercaptans (16), and for the quantitative determination of urea and glucose (7).

The design of the apparatus is determined in part by the liquid feed mechanisms available. The instrument must sense the rate of change of signal as the balance point is approached and reduce the liquid feed accordingly. However, most of the early instruments of the pH-stat type were equipped with either a solenoid-operated burette or motor-driven syringes. These provided a "go, no-go" delivery, injecting a fixed quantity of reagent per signal. This principle of operation does not take into account the problem of overshooting the predetermined pH value upon delivery of the reagent into the reaction vessel. In general, liquid may be added in several ways to avoid overshooting the preset pH value: (a) continuously at a steady slow rate, (b) by fixed pulses with a variation of the repetition, (c) proportional to the rate of chemical reagent delivery in a continuous manner (8), or (d) by pulses with a variation of the pulse duration (12). The automatic titrator described employs yet another method for avoiding preset pH value overshoot. Titrant is added with the burette on full until the pen carriage makes contact with an "anticipator" switch. This diverts the power to the burette

through a pulsing switch operated by a cam (set at 1% on) which is driven by a 10 rpm motor. Thus, the endpoint is approached gradually during the last 2-4% of the titration.

In order that a pH titration apparatus work with reliability, a suitable impedance-matching device must be available when using a glass electrode. The very high input resistance requirement precludes the use of all but two types of amplifiers, the vibrating capacity input and an electrometer input (12). The electrometer input was employed for this work, specifically, the Heath Model EUW-301 pH Recording Electrometer. A definite advantage is the sensitivity obtainable with the EUW-301. With the electrometer switched to the pH 1 full-scale span, it is responsive to a pH change of 0.001 pH unit and accurate to 0.003 pH unit. Measurement of pH changes in this range is extremely difficult and more likely impossible with conventional or routine laboratory pH meters. A complete description of the EUW-301 is reported by Malmstadt (5). Malmstadt and Piepmeier (7) have used the EUW-301 as a part of a pH-stat for quantitative determinations. They used a photoconductive cell as the control sensor for the pen carriage movement. The Malmstadt-Piepmeier device also has a direct digital readout unit which is proportional to concentration.

The automatic titrator described in this thesis employs two microswitches for sensing, one as the anticipator and the other as

the endpoint sensor. The anticipator switch was mounted ahead of the endpoint switch so that the pen carriage makes contact with it first. The digital readout from the automatic titrator is in the form of a permanent record provided by the Hewlett-Packard Model 562A Digital Recorder.

A frequency divider is used to provide an input to the Hewlett-Packard Scalar, Model 521C. The frequency divider is composed of three discrete parts: an a. c. clipper section, a Schmitt trigger, and two flip-flops. Details concerning the operation of Schmitt triggers and bistable multivibrators (flip-flops) in general may be found in "Electronics for Scientists" by Malmstadt, Enke, and Toren (6).

INSTRUMENTATION

The complete titrator is shown in Figure 1. When a change in pH occurs, a subsequent change in the potential developed between the indicating and reference electrodes also occurs. This change in potential is applied to the electrometer input and amplified by a high-gain power amplifier. The output of the amplifier drives a servo-motor which is mechanically linked to the pen carriage of the recorder. When the automatic burette is full-on, titrant is delivered at the rate of 5 ml/min. A frequency divider is connected across the power supply leads to the burette. The output of the frequency divider is applied to the input of the Hewlett-Packard Scalar, Model 521C. Thus, when the burette is running, the scalar is counting line frequency or some fraction of line frequency which can be directly related to the volume of titrant delivered. As the pH changes during the titration, the pen carriage first makes contact with the continuous mode microswitch leverarm. This diverts the power to the burette through the pulsing switch, causing small increments of titrant to be delivered from the burette so that the endpoint is approached gradually. The pulsing circuit is connected between the neutral lead and the "normally closed" position of the cutoff microswitch. When the pen carriage reaches the cutoff microswitch, all power to the burette is off. The power to the d. c.

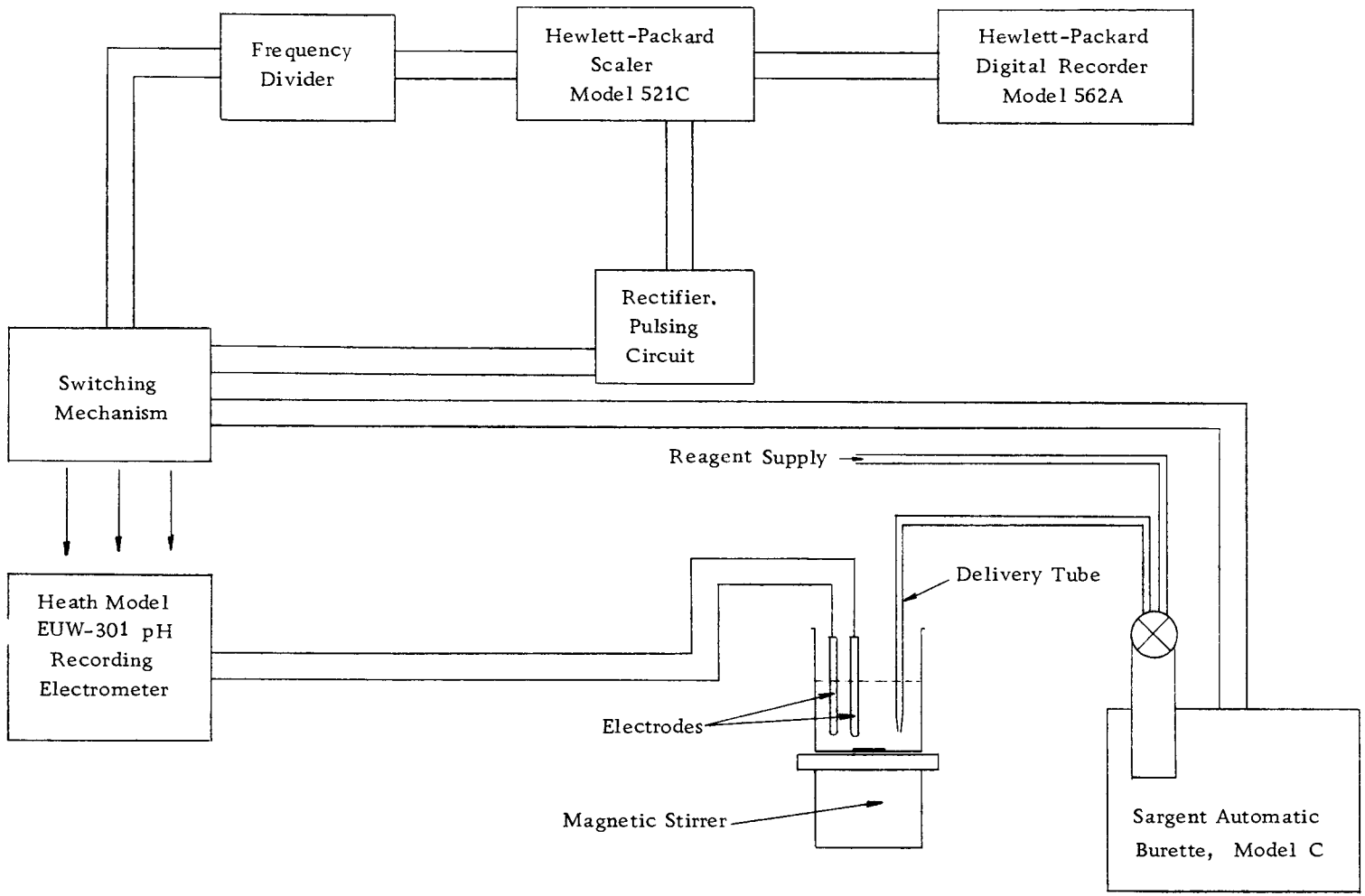


Figure 1. Block Diagram of Automatic Titrator.

relay in the pulsing circuit is also turned off by the cutoff microswitch. The "break" of the relay results in a negative pulse which triggers the scalar to stop counting and also causes the Hewlett-Packard, Model 562A, Digital Recorder to print out the scalar count. The addition of another sample to the titration cell causes the pen carriage to move upscale and the cutoff microswitch leverarm to drop. This action restores power to the burette and the d. c. relay of the pulsing circuit. The "make" of the relay results in a second negative pulse which returns the scalar count to zero and initiates the count on the new sample. The various components of the titrator will be discussed individually in the following sections.

Electrodes

A Beckman General Purpose (GP) Glass Electrode with a silver-silver chloride internal reference half cell was employed as the indicating electrode. The General Purpose Glass (Type 42) has a low electrical resistance (20-60 megohms) when compared with other glasses used in glass electrode construction (100-1000 megohms). This lower resistance permits the construction of thick bulbs which are nearly unbreakable and which have excellent chemical durability. The unbreakable feature is particularly desirable where magnetic stirring is employed since the stir-bar occasionally bumps against the electrodes. The reference electrode was a

Thomas Calomel Reference Electrode, No. 4857-F15. The sintered ceramic plug in the tip of the electrode provides a low electrical resistance contact with the bulk of the solution. This type of reference electrode is found to be better suited to the operation than a Beckman Fiber Junction Reference Electrode since the fiber has a much higher resistance and thus tends to pick up external noise. The pen response is excellent when using the Beckman Glass Electrode-Thomas Calomel Electrode setup.

Beckman Zeromatic pH Meter

Initial work performed in the construction of the titrator employed the Beckman pH meter to provide the amplified error signal to the servo-recorder. A series resistance between the servo-recorder and the pH meter was required to achieve the desired pH span on the servo-recorder. For a span of 5 with pH 8 at the top of the scale and pH 3 at the bottom, a resistance of 142 ohms was required. The pH meter was standardized with a pH 6.86 buffer containing 0.025 M KH_2PO_4 and 0.025 M Na_2HPO_4.

Heath Model EUW-301 pH Recording Electrometer

The pH meter and series resistance were replaced by the Heath Model EUW-301 pH Recording Electrometer. The pH recording electrometer actually consists of two discrete parts: (1) pH Adapter

Module (Model EUA-20-11) and (2) Servo-Recorder (Model EUW-20A). Full-scale pH spans of 1, 2, 5, 10 and 14 are available with the EUW-301. pH values are readable to 0.1% of the full-scale span (0.001 pH on span of 1 pH, 0.01 pH on span of 10 pH); therefore, the endpoint of a titration can be set quite accurately. The accuracy on a given titration is better than 0.5% on any of the calibrated full-scale spans. The pH recording electrometer was calibrated with two standard buffers: (1) 0.025M KH_2PO_4, 0.025M Na_2HPO_4 - pH 6.86 @ 25° C., (2) 0.05M potassium biphthalate - pH 4.01 @ 25° C.

Switching Mechanism

The switching mechanism (Figure 2) was mounted on a Bud Aluminum Panel Chassis, CB-1372, 17"W × 5 9/32"D × $5\frac{1}{4}$"H (Figure 3). An identical second chassis is secured to the bottom of the recording electrometer so that the legs of the top chassis are mounted on the legs of the bottom chassis (Figure 4). Microswitches S_1 (continuous mode) and S_3 (cutoff) are mounted side-by-side on a 3/8" threaded rod such that they can be placed at any position along the scale of the recording electrometer (Figure 4). These microswitches are operated by the pen carriage of the recorder. When the on-off toggle switch is "on" and S_1 is in its normally closed position, power is supplied to the automatic burette through S_3 and S_1. S_1 is mounted ahead of S_3 so that during a titration, the pen carriage

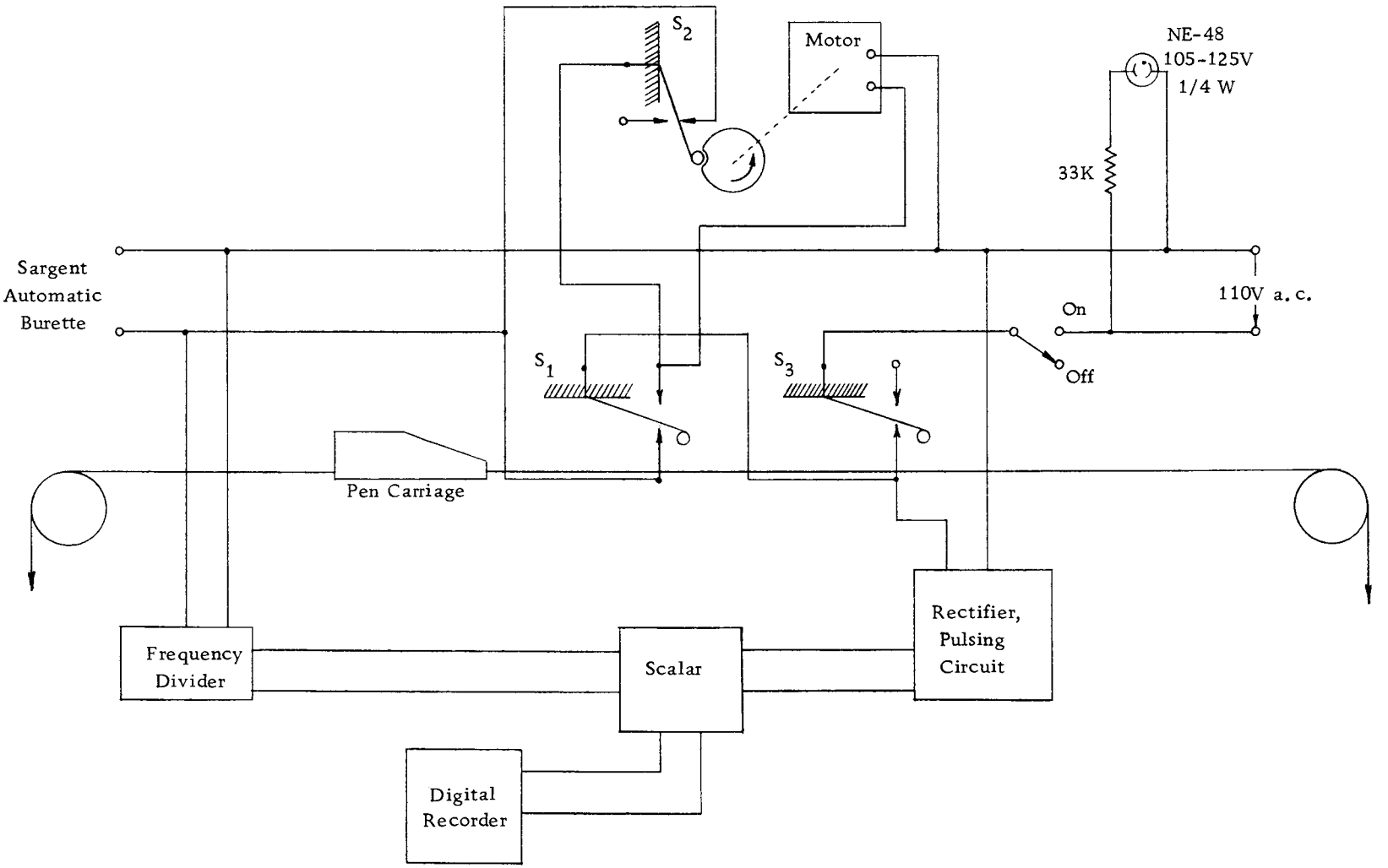


Figure 2. Switching Mechanism Circuit.

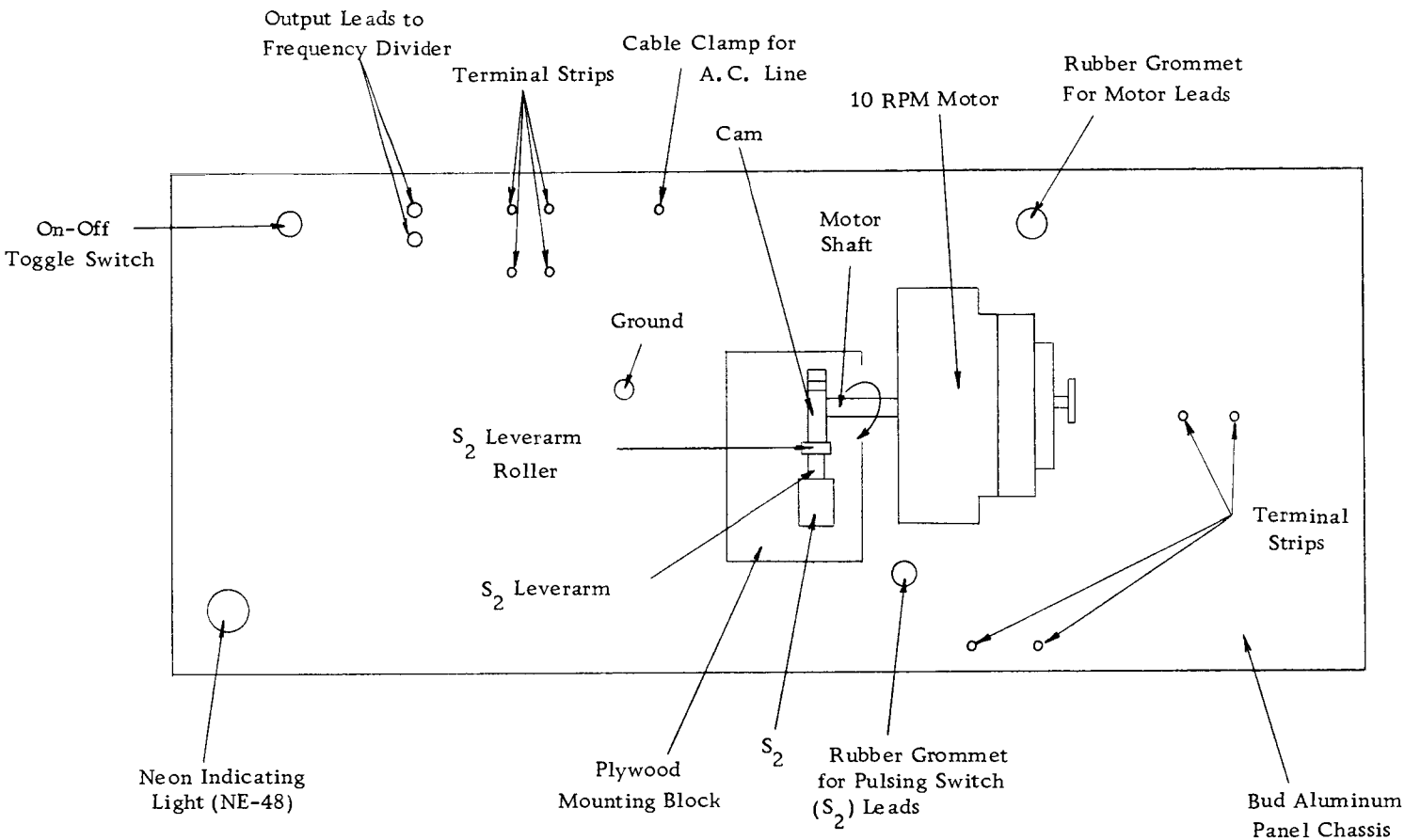


Figure 3. Top View, Switching Mechanism.

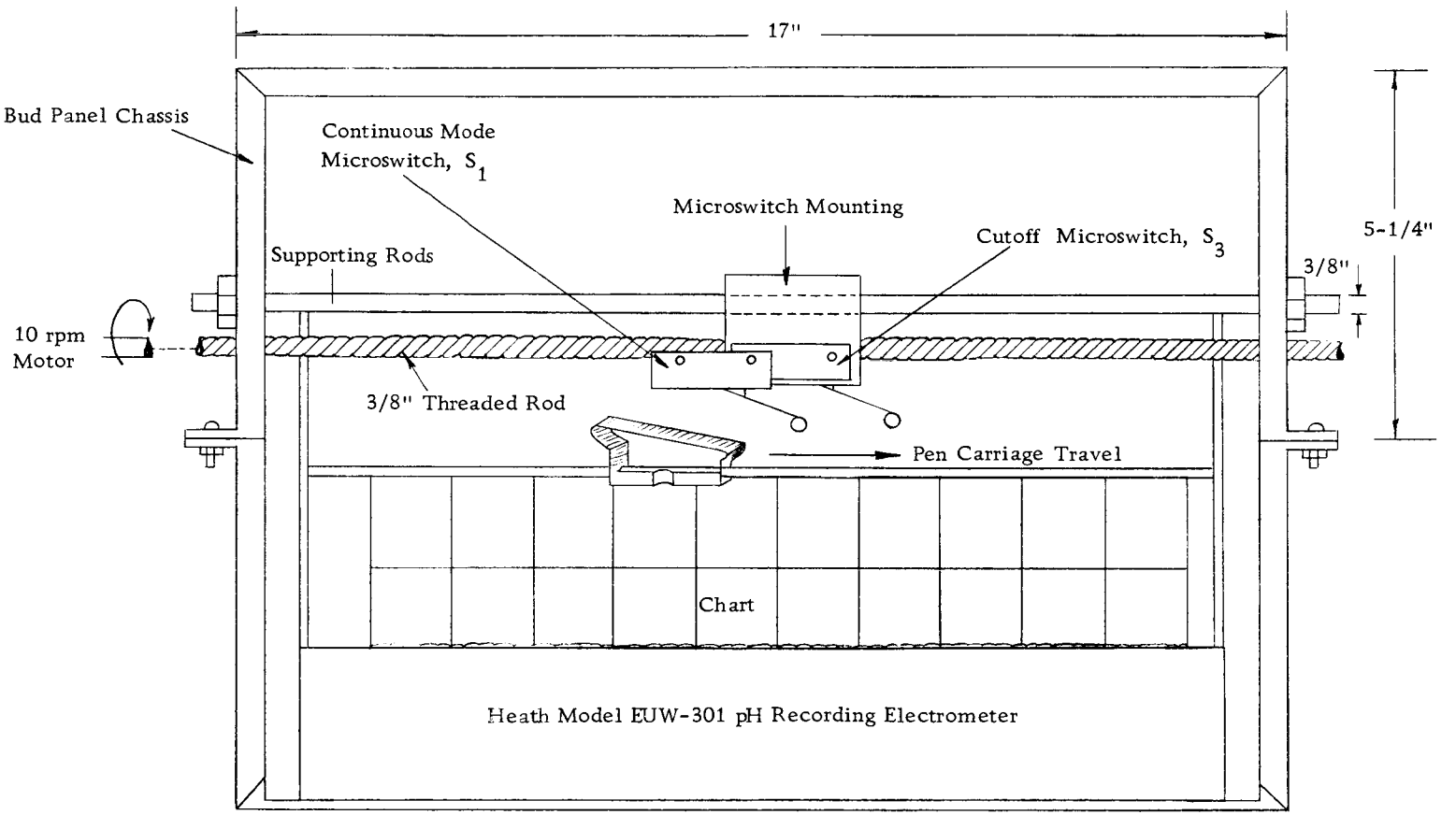


Figure 4. Front View of Recorder and Switching Mechanism.

makes contact with S_1 first. As the burette delivers titrant, the pH drops until the pen carriage makes contact with S_1. When S_1 is switched by the pen carriage, power can no longer be supplied directly to the burette through S_1; it must be supplied through the "pulsing" microswitch S_2. S_2 is operated by a cam, which is driven by a 10 rpm motor. The 10 rpm motor operates continuously during the period between the switching of S_1 and the switching of S_3 by the pen carriage. With the 10 rpm motor running, the burette delivers titrant in very short pulses since the burette is only on when the roller of S_2 is in the groove of the cam. Approximately 0.02 ml is delivered with each pulse. This step-wise addition of titrant continues until the pen carriage switches S_3, which turns off the burette completely. S_3 is positioned so that the burette is turned off at the endpoint of the titration. The switching of S_3 at the endpoint also results in a negative pulse from the pulsing circuit which triggers the digital recorder to print out the scalar count. A neon indicating light (NE-48) is connected across the input power leads, with a 33 kilohm current-limiting resistor between the hot lead and the neon light.

Motor-Driven Endpoint Setting

Prior to the motor-driven setup, the actual setting of the endpoint was performed by manually rotating the 3/8" threaded rod until

the desired point was reached. This mode of operation was replaced by a reversing motor manufactured by the Hurst Manufacturing Corporation. Figure 5 is a schematic of the motor circuit. When S_4 is off, power is supplied to the motor through S_5 but since the clutch is not engaged, no rotation of the motor shaft is observed. With S_4 on, the clutch is engaged, resulting in rotation of the motor shaft. The direction of rotation is a function of S_5. The black lead is common and power applied to the black and white leads gives right rotation. Switching the power to black and red leads gives left rotation. The change in direction of shaft rotation is produced by two oppositely-wound windings within the motor casing; the red lead supplies power to one and the white lead supplies power to the other. The output shaft rotates in either direction at a rate of six revolutions per minute. The shaft of the geared motor is connected to the 3/8" threaded rod with a short section of $\frac{1}{2}$" Tygon tubing. Endpoint settings are accurately achieved with a minimum of difficulty.

Sargent Automatic Burette, Model C

The Sargent Burette is connected to the switching mechanism as shown in Figure 2. It operates full-on during the early stages of a titration and then in a pulsing mode when the pen carriage switches the continuous mode switch, S_1. The cutoff switch turns the burette off completely at the endpoint of the titration. The automatic burette

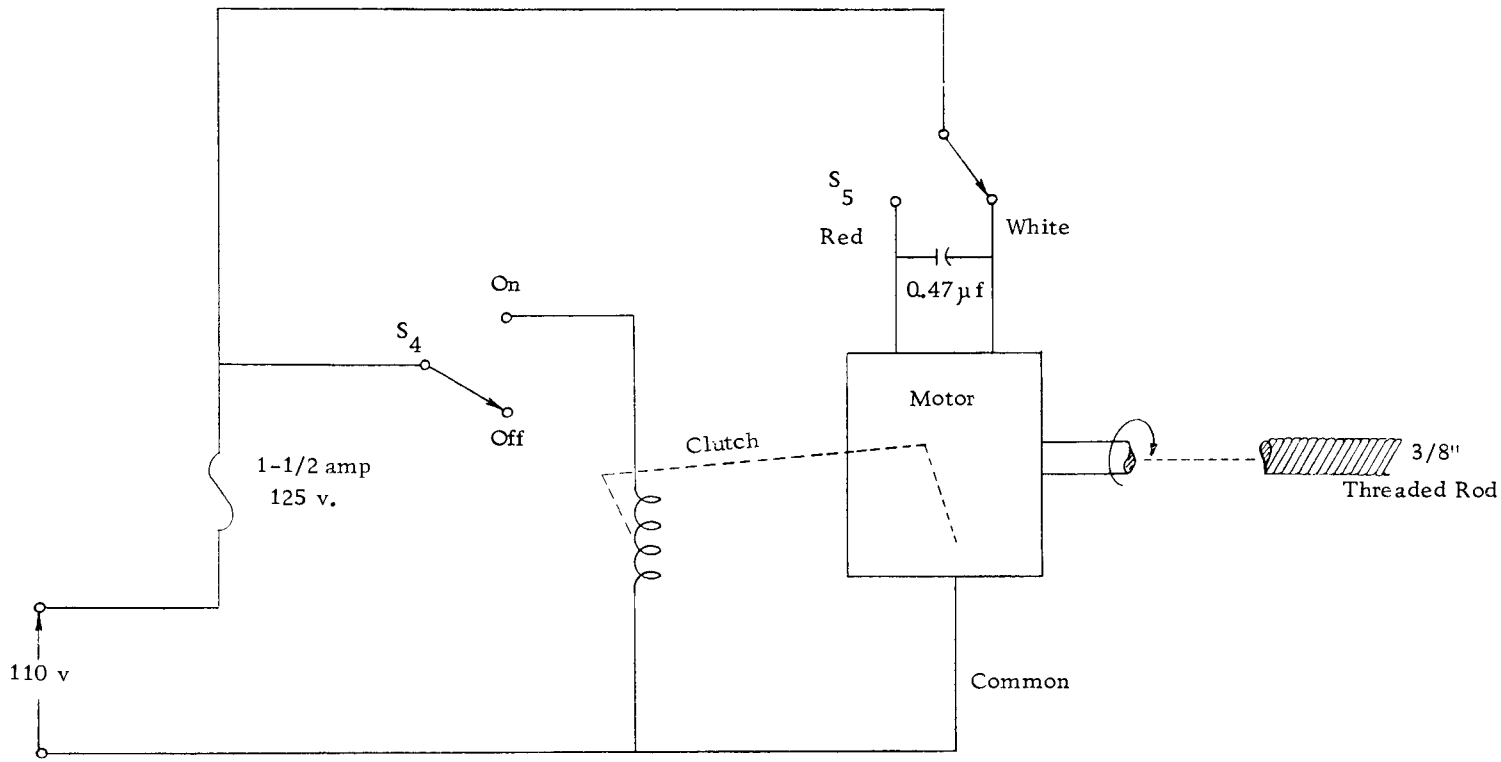


Figure 5. Motor-Driven Endpoint Setting.

is convenient in that the 50 ml burette permits the titration of many samples before refilling is necessary. The single rate of drive provided by a synchronous motor produces a delivery rate of 5 ml per minute with the 50 ml burette equipment. A direct reading digital counter is provided with the instrument which can be read as hundredths of a milliliter. Once the scalar counts and the number of milliliters required for a given titration have been related, the burette digital counter ceases to be of use. During a set of sample runs, the panel push button is locked in; the operation of the burette being controlled entirely by the switching mechanism.

Frequency Divider

Referring to Figure 6, the frequency divider is connected across the power supply leads to the automatic burette so that when the burette is operating the frequency divider is also operating. The 110 volt, 60 cps line voltage applied across the burette leads during operation is introduced into the input of the frequency divider. A clipper circuit composed of a 9.36 K power resistor (25 watt) and a 3-volt Zener diode, introduces a safe voltage level into the Schmitt trigger. The Schmitt trigger was required as a "squaring" circuit since the rise time of the clipped a. c. was too long and consequently the differentiated signal spike appearing at the input to the flip-flops was too small to trigger the flip-flops. The Schmitt trigger provides

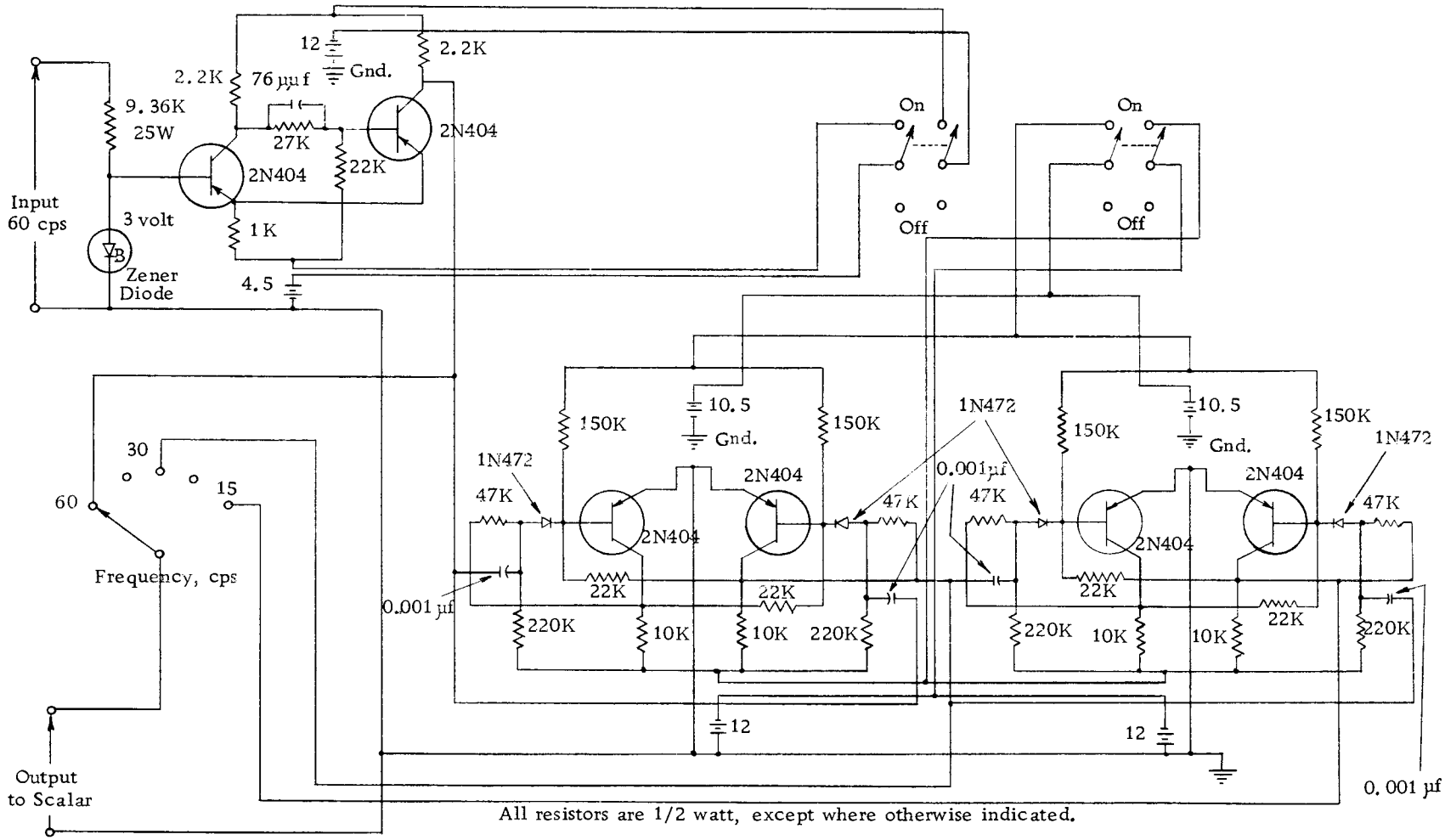


Figure 6. Frequency Divider.

a square wave output at the same frequency as the input signal. Differentiation of the square wave gives a sharp spike of sufficient magnitude to operate the flip-flops. The circuits for the flip-flops were obtained from the Geodyne Catalog on Miniature Logic Packages, published by the Geodyne Corporation, 151 Bear Hill Rd., Waltham, Massachusetts. At the output of the first flip-flop (the collector of the right-hand transistor) the frequency observed is 30 cycles per second. This frequency division occurs since positive-going spikes are necessary to switch the states of the two transistors. Thus, during the first positive-going spike the left-hand transistor is on and the right-hand transistor is off. The next positive-going spike reverses the states of each transistor: left-hand transistor--off, right-hand transistor--on. Therefore, only every other spike is seen by the right-hand transistor; or, in other words, the frequency at the output is exactly one-half of the frequency at the input. With two of these flip-flops in series the output frequency at the second flip-flop will be one-fourth of the input frequency. All three frequencies (60, 30, and 15 cps) are available at the output of the frequency divider, depending upon the position of the selector switch. The output of the frequency divider is applied directly to the input of scalar. Two double-pole double-throw toggle switches control the power to the Schmitt trigger and the two flip-flops.

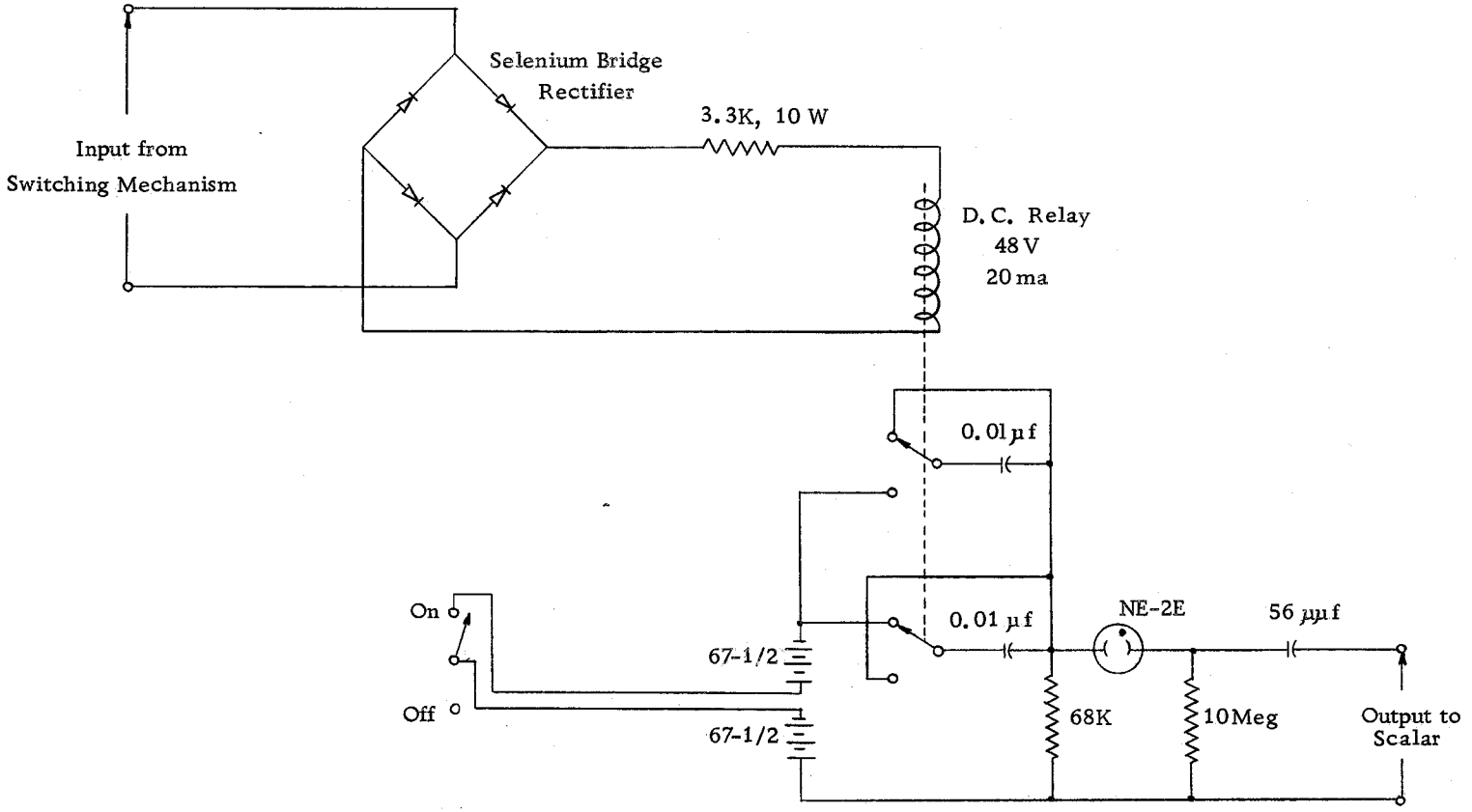
Pulsing Circuit

It was desired to have the results of each titration printed out by the digital recorder. Some external means of reporting to the scalar when the endpoint of a titration had been reached was therefore necessary. A pulsing circuit, which would introduce a pulse into the scalar precisely when the endpoint of a titration was achieved, received consideration. Prior to the construction of the pulsing circuit, the circuitry of the Hewlett-Packard Scalar, Model 521C, was examined. An oscilloscope revealed that the scalar in either the 1/10 sec, I sec, or 10 sec gate positions required two negative pulses to complete the gate cycle. The cycle consisted of two parts: (1) period of counting during which the scalar would be on, terminated by the first pulse after the length of time indicated by the gate selector switch position, and (2) the second pulse resulting in the count from the time period before reset to zero and initiating the new count. The negative pulses were very short (of the order of a microsecond) and quite sharp.

Several attempts were made to duplicate these pulses externally in a pulsing circuit. A small 15-volt a. c. relay proved inadequate due to the bouncing of the contacts. To eliminate some of the problems encountered with a. c., a d. c. relay (48 volt, 20 ma) was obtained. A selenium bridge rectifier provided the necessary

d. c. operation (Figure 7). A 3. 3 kilohm, 10 watt, current-limiting resistor was placed in series with the relay. Filtering of the rectified a. c. was not found to be necessary since the relay contacts did not chatter or buzz. The discharging of a capacitor produced a pulse which was much too broad to reliably trigger the scalar. A small neon bulb (NE-2E) provided the answer, producing a sharp pulse across the output of the pulsing circuit.

With the two $67\frac{1}{2}$ volt batteries connected, the pulsing circuit is operational. Considering the configuration of Figure 7, the lower 0. 01 μf capacitor is charged to the voltage of the two batteries in series. When the endpoint of a titration is reached, S_3 of the switching mechanism is switched by the pen carriage. This causes the relay to "break", resulting in the shorting out of the lower capacitor while the upper 0. 01 μf capacitor begins to charge. As the upper capacitor begins to charge, a voltage is developed across the 68 kilohm resistor. When this voltage reaches 90 volts (the starting voltage for the neon bulb) the neon bulb fires, resulting in a sharp pulse across the 10 megohm resistor. The 56 μμf capacitor, together with the COUNTER HOLDOFF ASSEMBLY in the scalar, differentiates the output pulse from the pulsing circuit to give a sharp spike. When S_3 is returned to its "normally closed" position at the start of another titration, the relay "makes". This produces a shorting out of the upper capacitor while the lower capacitor



All resistors are 1/2 watt. except where otherwise indicated.

Figure 7. Pulsing Circuit.

begins to charge. Again, a voltage develops across the 68 kilohm resistor which fires the neon bulb and another negative pulse is produced. Thus, when the endpoint of the titration is reached, the switching of S_3 results in a pulse, terminating the count. Upon the addition of a new sample to the titration cell, the pH changes, causing the pen carriage to travel up-scale. The leverarm of S_3 drops, resulting in a second negative pulse which resets the count to zero and starts the count on the new sample.

Scalar

To utilize line frequency or some fraction of line frequency as a reference, a suitable counter was required. The Hewlett-Packard Electronic Counter, Model 521C, was found to be quite satisfactory with an input frequency range of 1 cycle per second to 120 kilocycles per second. The 521C has an accuracy of ± 1 count and a 5-place columnar display count registration. It requires only 0.2 volt rms minimum input and is adjustable to 100 volts rms input with the sensitivity control. 1/10, 1, and 10 second gate times and a manual gate are available. For investigations with this titrator, the manual gate was used exclusively.

The scalar circuitry had to be modified in the "manual" position of the gate selector switch so that the external pulsing circuit would trigger the digital recorder to print. Referring to Sect. IV,

pp. 16-17, in the Hewlett-Packard Operating and Service Manual for the 521 Series Electronic Counters it will be noted that the Gate Selector Switch (S503, A&B) is double-decked. The upper deck, S503A, has the manual position connected to ground while the lower deck, S503B, in the manual position is connected to a voltage divider resulting in a fixed bias on the grid of the Gate Control Binary. To change both these functions in one operation required a phone jack which would make one connection and break another when a phone plug was inserted. The phone jack used was a "T-Jax" Switchboard type Jack (3 conductor type). Figure 8 shows a schematic of the phone jack and its incorporation into the scalar circuitry. It can be seen that when the phone plug is inserted into the phone jack, the manual lead to ground from the gate selector switch, S503A, is broken to allow a signal to be put in from the pulsing circuit. In order that the pulse from the pulsing circuit perform the desired function, the wiper of S503B must be disconnected from the 270 kilohm-1 megohm voltage divider; this function is also performed by inserting the phone plug into the phone jack. By disconnecting the wiper, the grid is essentially floating and an external pulse will "flip" the Gate Control Binary, causing the digital recorder to print.

The digital recorder was made to respond to the scalar pulses through a 50-pin connecting cable. To accommodate the cable connection, the scalar had to be modified--requiring the 521A-95D

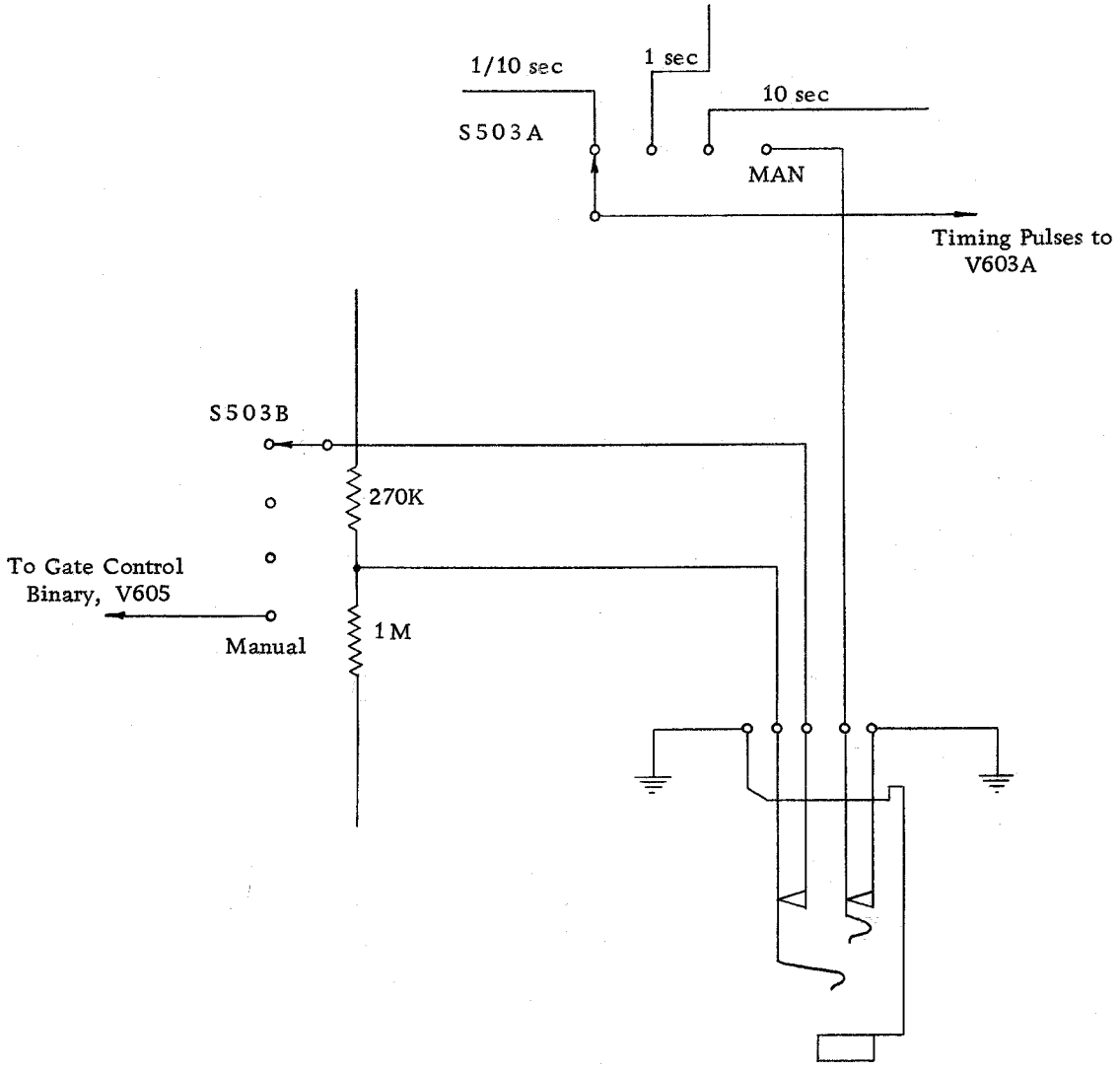


Figure 8. Phone Jack Modification of Scalar.

BCD + 1224 Modification Kit. This kit was acquired from the Hewlett-Packard Company.

Digital Recorder

Installation of the kit mentioned above in the Hewlett-Packard Model 521C Electronic Counter allows the counter to drive the Hewlett-Packard Model 562A Digital Recorder. The digital recorder provides a printed record of the counter display. The added circuit does not disturb normal operation of the counter. The accuracy of the digital recorder is identical to that of the scalar and has a maximum printing rate of 5 lines per second. The digital recorder operates on either a positive or negative pulse, 6 to 40 volts amplitude, 20 μsec or greater in width, a.c. coupled. The requirements are met by the BCD (+1224) kit; operation is with negative pulses.

RESULTS AND DISCUSSION

The work on this titrator was done in connection with the last step of the Kjeldahl determination of organic nitrogen. However, instead of absorbing the liberated gaseous ammonia in a standard acid as the Kjeldahl procedure specifies, the ammonia was added in the form of a 0.05 N solution. The Kjeldahl determination of nitrogen requires that two standard solutions be available. The first standard solution, either hydrochloric acid or sulfuric acid, is used to absorb and react with the ammonia. The second standard solution, usually sodium hydroxide, is employed in the back-titration of the excess acid. L. W. Winkler (14, 15) and Reith and Klazinga (10), found that a saturated solution of boric acid could be used as effectively as hydrochloric or sulfuric acid. The boric acid reduces the partial pressure of ammonia considerably by forming ammonium borate:

$$NH_3 + HBO_2 \longrightarrow NH_4^+ + BO_2^-$$

Borate ion is a slightly weaker base than ammonia, and the excess boric acid forces the reaction to the right. After absorption of ammonia, the solution is titrated back to the pH of the original solution of boric acid. The exact concentration and volume of the boric acid solution are not important, and only one standard solution is required.

The data in Tables 1, 2, 3 and 6 were obtained by adding successively

10 ml aliquots of approximately 0.05 N NH_3 to the same 40 ml of 4% boric acid (H_3BO_3) and the mixtures titrated with approximately 0.05 N HCl. A plot of pH versus meq HCl/meq BO_2^- similar to one of the individual curves in Figure 10 was obtained from the strip chart of the servo-recorder. Several titrations were performed in order to determine the proper endpoint setting. The average endpoint pH of 4.38 for these titrations does not agree with the theoretical value of the endpoint, 4.78. This discrepancy can probably best be explained by the assumption that some pyroboric acid, $H_2B_4O_7$, might be present and, because it is a stronger acid, would result in a lower pH than the expected value. All titrations were run with the endpoint setting at 4.40.

It was desired to know the number of samples that could be titrated with hydrochloric acid, using the same 40 ml of 4% boric acid as the ammonia absorbent, before the accuracy deteriorated. Table 1 reveals this number to be between 5 and 7. Depending upon the application and the accuracy desired, it is possible to titrate successively up to 15 samples, absorbed in the original 40 ml of 4% boric acid. Milliliter readings from the automatic burette, appearing in the table, were related to the scalar counts.

From a consideration of the standard deviations for the first, second and third sets of five samples in Table 1, it is evident that less accuracy is achieved as the number of titrations increase. It

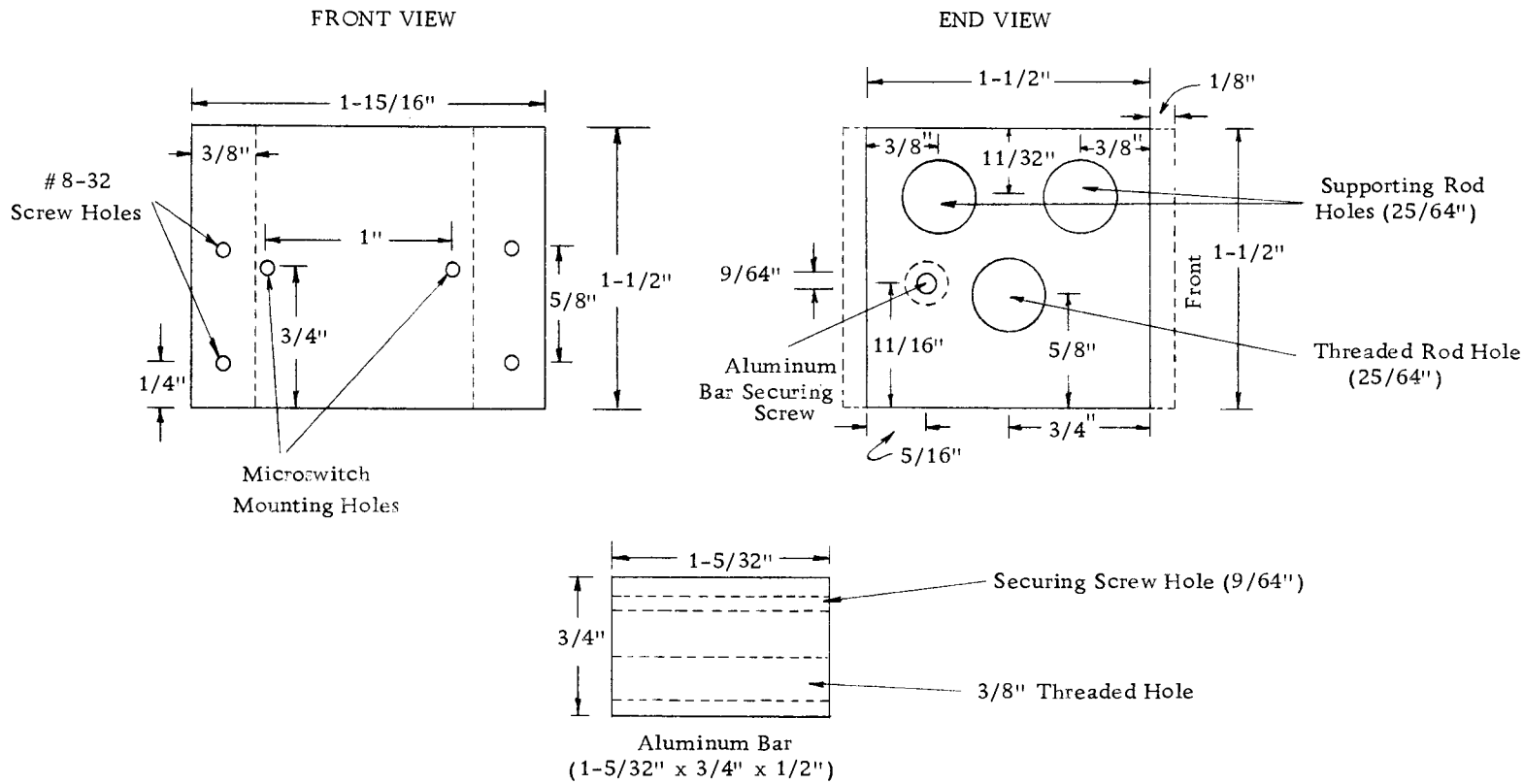


Figure 9. Microswitch Mounting.

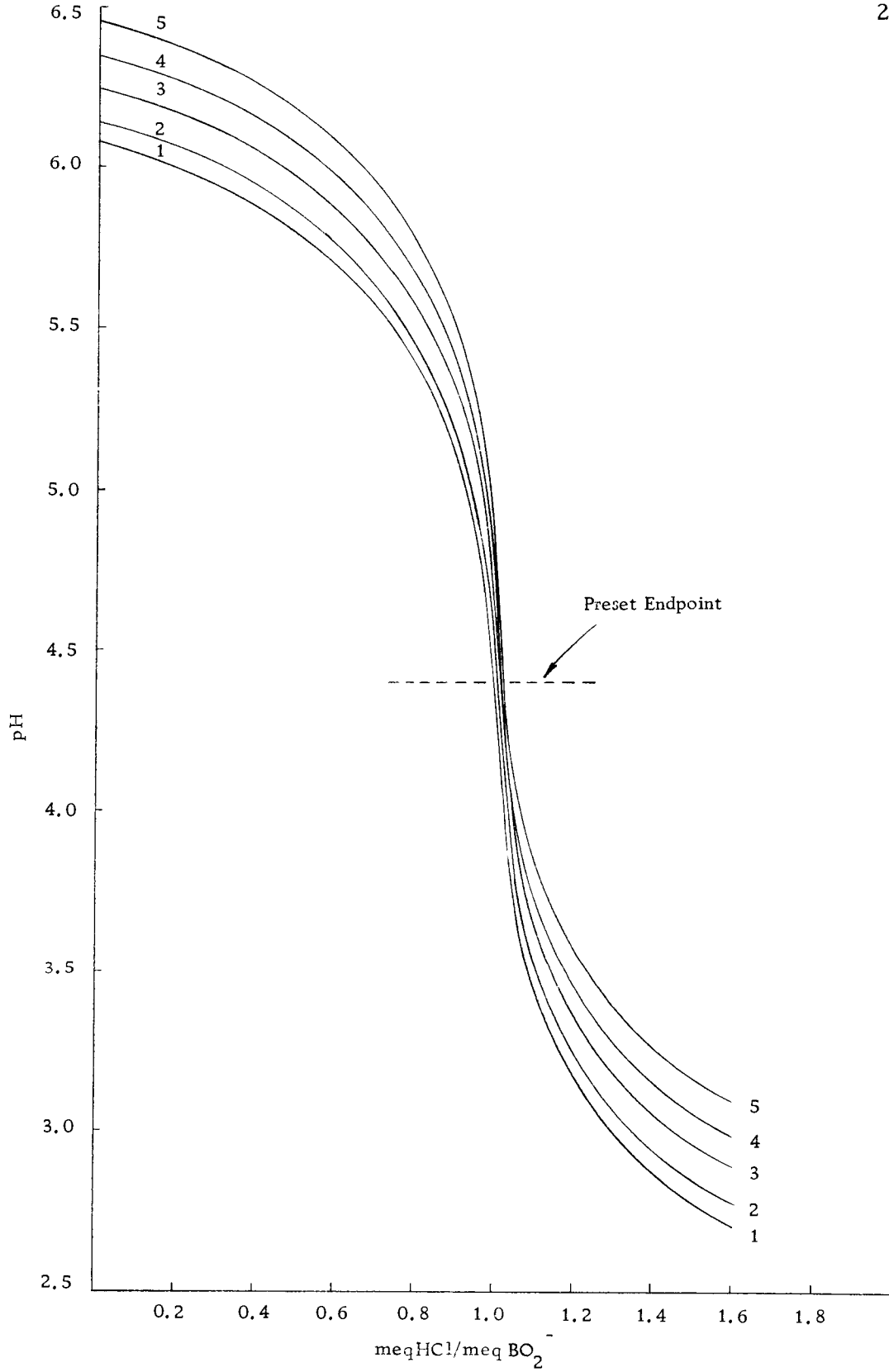


Figure 10. Effect of Dilution on Five Successive Titrations.

Table 1. A number of samples titrated using the same 40 ml 4% H_3BO_3

Run #	ml NH_3	taken meq NH_3	Ml HCl	found meq NH_3	Counts	Counts/ ml
1	10.00	0.488	9.67	0.487	6973	721
2	10.00	0.488	9.64	0.485	6999	725
3	10.00	0.488	9.69	0.488	7005	724
4	10.00	0.488	9.69	0.488	6993	722
5	10.00	0.488	9.66	0.487	6952	720
			Average value	0.487	6985	722
			Standard Deviation	0.0013 meq	21.8 Cts	2.07 Cts/ml
6	10.00	0.488	9.69	0.488	6995	722
7	10.00	0.488	9.72	0.490	7082	720
8	10.00	0.488	9.61	0.484	6958	724
9	10.00	0.488	9.74	0.491	7056	724
10	10.00	0.488	9.68	0.488	6895	712
			Average value	0.488	6997	721
			Standard Deviation	0.0027 meq	62.5 Cts	2.29 Cts/ml
11	10.00	0.488	9.61	0.484	6938	722
12	10.00	0.488	9.75	0.492	7061	725
13	10.00	0.488	9.86	0.497	7184	728
14	10.00	0.488	9.59	0.483	6922	722
15	10.00	0.488	9.52	0.480	6887	723
			Average value	0.487	6998	724
			Standard Deviation	0.0071 meq	122.7 Cts	2.55 Cts/ml

is interesting to note that the milliequivalents of ammonia found are not consistently higher or lower than the milliequivalents of ammonia taken, but are randomly interspersed. The reason for this behavior is not clear.

During a Kjeldahl determination, the ammonia from a given sample would be distilled into the boric acid. The ammonia would distill off rapidly at first and then in a decaying manner until a quantitative transfer was affected. Since distillation of ammonia was a little awkward, the ammonia was added incrementally in the form of a 0.05 N solution. It is far more difficult for a titrator to follow an incremental addition of sample than it is to follow a distillation of sample, since an increment results in a sudden change in pH and a distillation produces a gradual pH change. Table 2 shows the data obtained by the titrator as a result of adding the 0.05 N NH_3 incrementally. The milliliters of HCl in Table 2 were calculated from the scalar counts (722 counts/ml @ 60 cps).

Table 2. NH_3 solution added in increments--same 40 ml 4% H_3BO_3

Run #	ml NH_3	taken meq NH_3	ml HCl	found meq NH_3	Increments	Counts
1	10.00	0.468	9.28	0.467	3	6701
2	10.00	0.468	9.30	0.468	2	6712
3	10.00	0.468	9.38	0.473	5	6775
4	10.00	0.468	9.29	0.468	3	6707
5	10.00	0.468	9.30	0.468	3	6709
			Average value	0.469		6721
			Standard Deviation	0.0024 meq		30.6

The accuracy achieved by the titrator during the incremental additions of sample is excellent as evidenced by the standard deviation. The overall accuracy of Table 2 would have been much better if the results from run #3 had been closer to the meq of NH_3 taken. The results shown indicate that the titrator would follow an ammonia distillation quite well.

Table 3 illustrates the results obtained when the strength of the hydrochloric acid titrant is increased from 0.05 N to 0.1 N. The milliliters of HCl in Table 3 were calculated from the scalar counts.

Table 3. Set of samples titrated w/ 0.0988 N HCl in lieu of 0.0504 N HCl

Run #	ml NH_3	taken meq NH_3	ml HCl	found meq NH_3	Counts
1	10.00	0.468	4.75	0.469	3430
2	10.00	0.468	4.73	0.467	3446
3	10.00	0.468	4.70	0.464	3418
4	10.00	0.468	4.72	0.466	3436
5	10.00	0.468	4.73	0.467	3439
			Average value	0.467	3434
			Standard Deviation	0.0019 meq	10.5

No substantial improvement in accuracy over that achieved by the 0.05 N HCl was observed. The standard deviation is better than some and not as good as other 0.05 N HCl titration data. The scalar counts were essentially halved with 0.1 N HCl, although this can be accomplished with 0.05 N HCl by setting the frequency divider on

30 cps instead of 60 cps.

In theory, titrating the absorbed ammonia with a standard acid back to the pH of the original solution of boric acid should work quite well. However, since the addition of water causes a significant change in the pH of the boric acid solution (Table 4), the titration should proceed to that pH produced by the boric acid solution and the total volume of water from the ammonia solution and strong acid titrant. On the basis of the data in Table 4, one might conclude that successive titrations, using the same boric acid as absorbent, would yield results that would be far from accurate. Tables 1, 2, and 3 have shown this to be an incorrect conclusion, when indeed quite accurate results have been obtained.

Table 4. Dilution of H_3BO_3 solution with 10 ml aliquots of H_2O
pH of 40 ml 4% H_3BO_3 = 3.92

Solution	pH	Solution	pH
H_3BO_3 + 10 ml H_2O	4.12	H_3BO_3 + 110 ml H_2O	5.00
" + 20 ml "	4.29	" + 120 ml "	5.06
" + 30 ml "	4.43	" + 130 ml "	5.08
" + 40 ml "	4.54	" + 140 ml "	5.13
" + 50 ml "	4.63	" + 150 ml "	5.17
" + 60 ml "	4.70	" + 160 ml "	5.20
" + 70 ml "	4.78	" + 170 ml "	5.24
" + 80 ml "	4.85	" + 180 ml "	5.27
" + 90 ml "	4.89	" + 190 ml "	5.31
" +100 ml "	4.95	" + 200 ml "	5.34

Figure 10 shows how the dilution of the boric acid solution affects the pH at the start of each successive titration and to some degree, how the endpoint is affected. The dilution effect on accuracy is seen in Table 5.

Table 5. Aliquots of 10 ml and larger titrated with 0.0504 N HCl in the same 40 ml of 4% H_3BO_3

Run #	ml NH_3 taken	meq NH_3 taken	ml HCl	meq NH_3 found	Error,* meq	Counts
1	10.00	0.468	9.32	0.469	0.001	6725
2	15.00	0.702	14.11	0.711	0.006	10288
3	20.00	0.936	18.68	0.942	0.003	13596
4	30.00	1.404	28.14	1.416	0.005	20360
5	50.00	2.340	47.72	2.400	0.012	34610

* meq error/10 ml aliquot

With the exception of the 15 ml aliquot, Table 5 shows a tendency for the sample titration results to become less accurate as the boric acid solution becomes more dilute. This table also illustrates that it is possible for the automatic titrator to titrate samples larger than 10 ml of 0.05 N NH_3; however, less than 5 samples should be titrated if accuracy corresponding to the 10 ml aliquot titrations ($\sim$0.2%) is desired. The exact number of samples that may be titrated to within 0.2% accuracy depends on the concentration of the sample, the size of the sample, and the concentration of the titrant.

Data in preceding tables were obtained with the scalar counting

line frequency, 60 cps. Table 6 shows that the accuracy achieved with the scalar counting 60 cps, 30 cps, and 15 cps from the output of the frequency divider is comparable.

Table 6. NH_3 titrated with 0.0504 N HCl 60, 30, and 15 cps into scalar

	Run #	ml NH_3	taken meq NH_3	ml HCl	found meq NH_3	Counts	Counts / ml
60 cps							
	1	10.00	0.468	9.26	0.466	6629	716
	2	10.00	0.468	9.28	0.468	6713	723
	3	10.00	0.468	9.27	0.467	6690	721
	4	10.00	0.468	9.33	0.470	6726	721
	5	10.00	0.468	9.26	0.466	6648	729
				Average value	0.467	6681	722
				Standard Deviation	0.0017 meq	41.6 Cts	4.69 Cts/ml
30 cps							
	1	10.00	0.468	9.28	0.468	3325	358
	2	10.00	0.468	9.27	0.467	3318	357
	3	10.00	0.468	9.28	0.468	3329	359
	4	10.00	0.468	9.30	0.469	3341	359
	5	10.00	0.468	9.27	0.467	3314	358
				Average value	0.468	3325	358
				Standard Deviation	0.0009 meq	10.5 Cts	0.87 Cts/ml
15 cps							
	1	10.00	0.468	9.25	0.466	1646	178
	2	10.00	0.468	9.29	0.468	1668	179
	3	10.00	0.468	9.30	0.468	1672	180
	4	10.00	0.468	9.28	0.467	1657	178
	5	10.00	0.468	9.34	0.470	1676	179
				Average value	0.468	1664	179
				Standard Deviation	0.0015 meq	12.2 Cts	0.87 Cts/ml

The set of curves obtained in the 15 cps titrations is shown in Figure 11. The first sample titration is initiated by the on-off toggle switch of the switching mechanism and all others are initiated by the addition of a sample to the titration cell. The digital recorder makes a print-out whenever the pH reaches the value of the preset endpoint. It will also be noted that at the beginning of each successive titration, the pH reaches a higher value than the sample before. This clearly illustrates a point that was brought out in Table 4; the addition of water to the boric acid solution results in a solution of higher pH than the original boric acid solution. The accuracy obtained in Tables 1, 2, 3, and especially 6 show that successive titrations can be carried out to the same preset endpoint. Although it does not offer a full explanation for the continued accuracy, Figure 10 shows a sharp break in pH at the endpoint of a titration. In the region of the endpoint a large change on the pH scale corresponds to a very small HCl addition. The family of curves in Figure 10 represent 5 successive titrations in the same 40 ml of 4% boric acid.

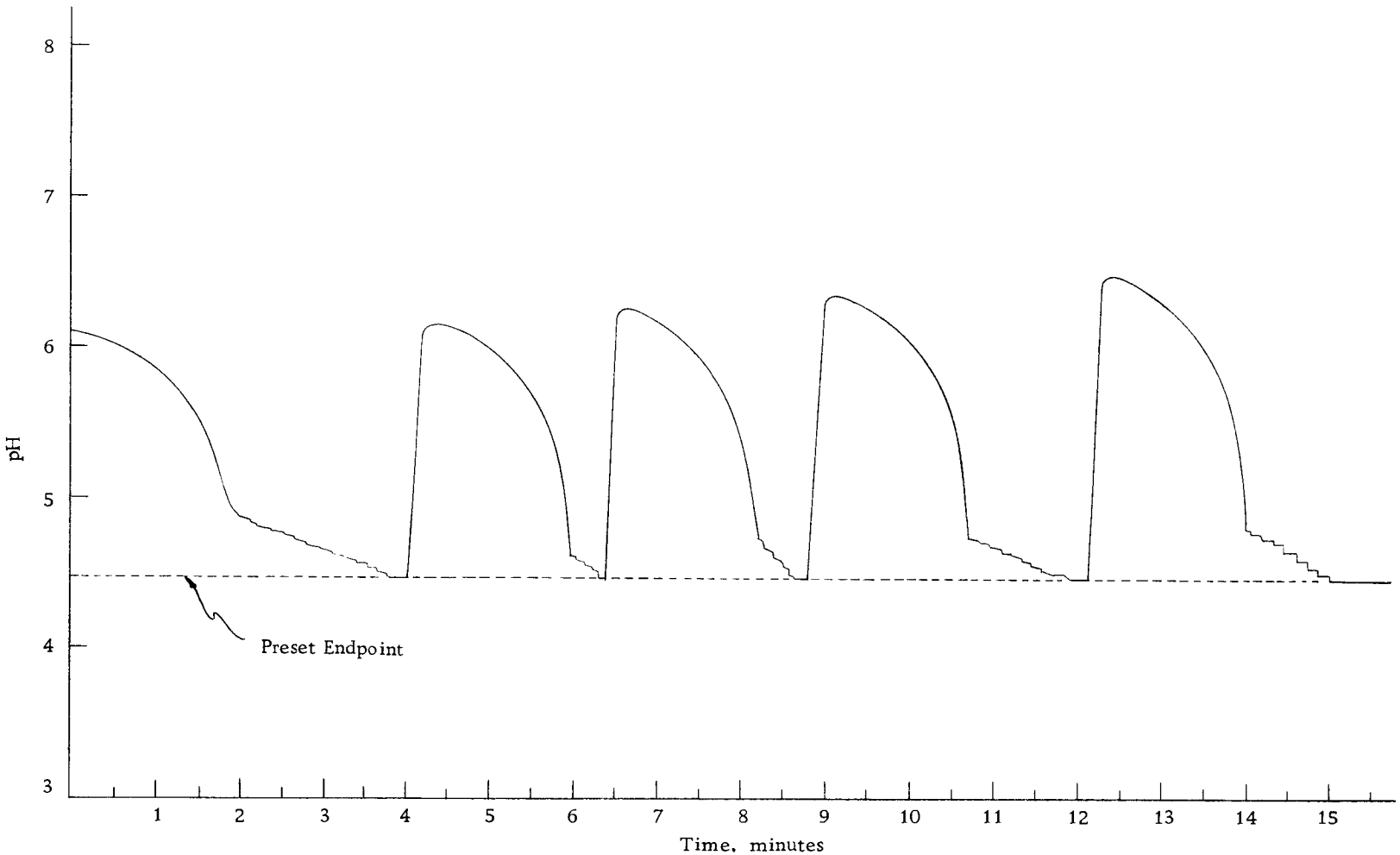


Figure 11. Continuous Analysis of Five Samples

CONCLUSIONS

The titration under study was unique in that more than one could be conducted with the same aliquot of boric acid as absorbent. The accuracy achieved by the automatic titrator on successive titrations was quite acceptable. Generally, the number of milliequivalents of ammonia found was within 0.2% of the number of milliequivalents of ammonia added to the titration cell. The delivery rate of the automatic burette is 5 ml/min with the 50 ml equipment. With 60 cps operation, the scalar has a counting rate of 722 counts/ml. This counting rate is particularly advantageous since it permits a high degree of accuracy even on small samples. If one desired to titrate 100 ml of 0.1 N NH_3, however, the high counting rate would be a disadvantage since the 5-place columnar display of the scalar would be exceeded and the count would be meaningless. Slower counting rates of 358 counts/ml with 30 cps and 179 counts/ml with 15 cps are offered by the frequency divider. This counting rate flexibility vastly increases the versatility of the titrator, including the expanded range of sample concentrations and the increased size of sample range that may be titrated. Another advantage of this titrator is the printed record of each titration supplied by the digital recorder. By suitable adjustment of the concentration of the titrant, the digital recorder can be made to print out the result of a titration

in milliequivalents, parts per thousand, percentage, etc. The titrator in its present form is not a truly automatic device, someone must be present to add samples to the titration cell. An automatic sampling device, such as a fraction collector, would make the titrator completely automatic.

The automatic titrator could be used in conjunction with the Technicon Continuous Digestor (Technicon Controls, Inc. Chauncey, New York) to provide a permanent record of the nitrogen content of various organic samples. The Technicon Continuous Digestor is now used with a colorimeter, which provides a measure of the nitrogen content spectrophotometrically (Technicon Bulletin No. 461A). The automatic titrator can be used not only for Kjeldahl-type titrations but also for strong acid-strong base, precipitation, oxidation-reduction, and perhaps complexometric titrations.

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APPENDICES

APPENDIX I

Microswitch Mounting

To permit an endpoint setting anywhere along the scale of the servo-recorder, it was necessary to construct a mounting which would either move upscale or downscale, depending on the direction of rotation of the 3/8" REDI-BOLT threaded rod. The threads on this rod are standard 60° running threads. Only left and right movements of the mounting are desired. This requirement is met by two 3/8" supporting rods which acted as guides for the mounting. The continuous mode (anticipation) and cutoff microswitches can then be mounted on the mounting.

The ends of the mounting were constructed of 3/8" aluminum plate and the sides of the mounting constructed of 1/8" aluminum plate (Figure 9). To fasten the sides of the mounting to the ends of the mounting, 8 holes (4 on the front side, 4 on the back side) were drilled and tapped to accommodate #8-32 machine screws. Two other holes were drilled on the front side of the mounting for the attachment of the microswitches. Two 25/64" holes for the supporting rods and one 25/64" hole for the threaded rod were drilled through each end of the mounting. This allowed sufficient clearance for the mounting to travel along the rods without binding. A means of driving the mounting by the rotation of the 3/8" threaded rod was

required. A small piece of bar aluminum was acquired and subsequently drilled and tapped for 3/8" threads. A second hole was drilled in the small piece of aluminum and the two ends of the mounting so that the bar aluminum could be fastened to the inside of the mounting. At one end of the mounting the hole for the fastening screw was countersunk because the screw was only 2" long.

APPENDIX II

Another pH-stat

An outgrowth of the work done on the automatic titrator is a pH-stat device, which is presently being used by Dr. J. L. Kice of the organic division. The device consists of a Heath Model EUW-301 Recording Electrometer, a switching mechanism that is operated by the pen carriage, and a motor-driven 1 ml capacity Digi-Pet syringe-type burette (the digital counter on the side of the burette reads directly in thousandths of a milliliter). The recording electrometer has not been modified in any way. The switching mechanism operates in two modes, either on or off (no anticipation).

The device will follow the alkaline hydrolysis of Bunte salts. A generalized Bunte salt would be ϕ-S-SO_3^- where ϕ can be either R or Ar. For instance, C_2H_5-S-SO_3^- would be named S-ethyl thiosulfate, where S indicates the alkyl group is bonded to the sulfur and not the oxygen. The pH will be held constant, and the amount of hydroxyl ion required will be recorded as a function of time. On a recent run using the 1 pH unit span, control was maintained within 0.003 pH for $2\frac{1}{2}$ hours.