A WIDE RANGE, EXTREMELY SENSITIVE HIGH FREQUENCY TITRIMETER

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By

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ABSTRACT

The nature of the response of high frequency titration instruments described in current literature was studied. The investigation included instruments in which the sample solution vessel was placed between the plates of a capacitor type cell and instruments with the sample solution vessel placed in the coil of a resonant circuit.

The effect on the response of these instruments of sample solution temperature changes, dilution, changes in liquid level, changes in cell parameters, and sample solution concentration were determined. These studies confirmed findings of earlier investigations.

A new, truly conductometric high frequency titrimeter was developed. The use of a single turn loop instead of a multiturn coil, in addition to maintaining a critical separation between the titration vessel wall and the loop, reduces the distributed capacity to an absolute minimum. Instrument response with this arrangement is dependent on conductivity changes and independent of dielectric constant changes in the sample solution. Changes in solution composition are indicated by changes in oscillator tube grid current.

Instrument performance was tested with titrations of aqueous solutions of hydrochloric, sulfuric, and boric acids and hydrogen peroxide with sodium hydroxide. Evidence of polybasic neutralization was observed in sulfuric acid and boric acid titrations. In this work the first successful high frequency titration of boric acid was accomplished,

and furthermore presents for the first time evidence of neutralization of the second and third replaceable hydrogen ions. The sulfuric acid titrations substantiate earlier inconclusive evidence of polybasic neutralization.

A successful high frequency titration of three normal hydrochloric acid with four normal sodium hydroxide was carried out, indicating that the new instrument may be used for conductivity studies in a concentration region heretofore unattained.

The angle which the titration curve lines form at the equivalence point obtained in this study for boric acid titrations exactly duplicate the angle obtained in the classical conductometric boric acid titrations carried out by Kolthoff. From this it is deduced that the response of the new instrument is purely resistive.

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INTRODUCTION

In the determination of the end points in high frequency titrations, the sample solution in a vessel is incorporated as a component of a resonant circuit. Changes in the concentrations of ions present in the solution change the electrical properties of the circuit. Changes in the ionic concentrations may be detected through changes in the frequency of an oscillator, if the resonant circuit is the frequency determining element of the oscillator, through changes in the grid or plate currents of the oscillator, or through changes in cell capacitance.

The aim of designers of high frequency titrimeters has been to obtain a response which is a function of the conductivity of the solution only and more truly representative of changes in the concentrations of the ions in the solution. Most of the papers published on high frequency titration since its introduction in 1946 by Jensen and Parrack (10) have been devoted to the constructional details of instruments purported to overcome certain difficulties encountered in the application of the instrument described by Jensen and Parrack (1,2,6).

It appears that individuals in electronics generally are biased in preferring one circuit to others and in a narrow manner defend the merits of their choice. It is believed that this accounts for the variety of instrument models that have appeared. The results obtained with any one instrument of a class are for all practical purposes the

same as those obtained with another and instrumentation is a matter of individual preference.

In a recent book (14) Lingane points out that most of the cited applications of the method are titrations which can be performed as well or better by the ordinary conductance method, and that the greater empiricism, coupled with the usual curvature of the titration lines requiring measurements very near equivalence points are distinct disadvantages. Lingane's observations accurately sum up the relative merits of the method when viewed from the standpoint of work reported in the literature to date.

The historical aspects of high frequency titrations have been reviewed by Jankowski (9) and a very complete bibliography compiled.

Statement of Problem

The discussion which follows is a result of a study undertaken: (1) to construct tried high frequency titration apparatus with the objective of improving their performance and of elucidating the nature of the response and, (2) to construct a new highly sensitative, wide range titrimeter which resulted from a new approach after a more critical evaluation of all the factors affecting instrumental response. Characteristics of the instrument were evaluated and titrations performed to determine whether some of the disadvantages ascribed to the method had been overcome.

Theory pertinent to the instruments constructed is presented.

THEORY

THEORY

Figure 2 (22) shows schematically a parallel circuit made up of a capacitive branch and an inductive branch. The resistance R is a function of the loss in the circuit and is due to the resistance of connecting wires, the coil, and the resistance reflected into the circuit by the load.

The essential properties of the circuit are its resonant frequency f_0, its selectivity Q, and its characteristic impedance Z. The impedance is a vector quantity having both magnitude and phase angle.

For purposes of discussion, the resonant frequency is that frequency f_0 that satisfies the relation

$$\omega L = \frac{1}{\omega C} \qquad (1)$$

where $\omega = 2\pi f$, L is the coil inductance in henrys, and C is the capacity of the condenser in farads.

The selectivity Q of the circuit is given by the relation

$$Q = \frac{\omega L}{R} \qquad (2)$$

The impedance Z is given by the relations

$$Z = \frac{(\omega_0 L)^2}{R + j\left(\omega L - \frac{1}{\omega C}\right)} \qquad (3a)$$

$$Z = \frac{\left(\frac{1}{\omega_0 C}\right)^2}{R + j\left(\omega L - \frac{1}{\omega C}\right)} \qquad (3b)$$

At the resonant frequency

$$\omega_0 L = \frac{1}{\omega_0 C} \qquad (1a)$$

and equation 3a reduces to

$$Z = \frac{(\omega_0 L)^2}{R} \qquad (4a)$$

and equation 3b reduces to

$$Z = \frac{1}{R\,(\omega_0 C)^2} \qquad (4b)$$

The curves of Figure 1 (22) show the magnitude and phase angle of impedance as a function of frequency. The resonant frequency of the circuit in Figure 2 with the values of C and L given is 1000 kc. At resonance, the impedance is at a maximum and is equal to Q times the reactance of either branch at f_0, and the phase angle of impedance is zero. At frequencies below resonance the phase angle of impedance is negative and lower in magnitude than at resonance. At frequencies above resonance the phase angle of impedance is positive and of lower magnitude than at resonance. The circuit is inductive when the phase angle of impedance is negative and capacitive when the phase angle of impedance is positive.

The impedance of a parallel circuit can be broken up into reactive and resistive components.

Figure 2 (22) shows the resistive and reactive components as a function of frequency. The resistance varies much in the same way as

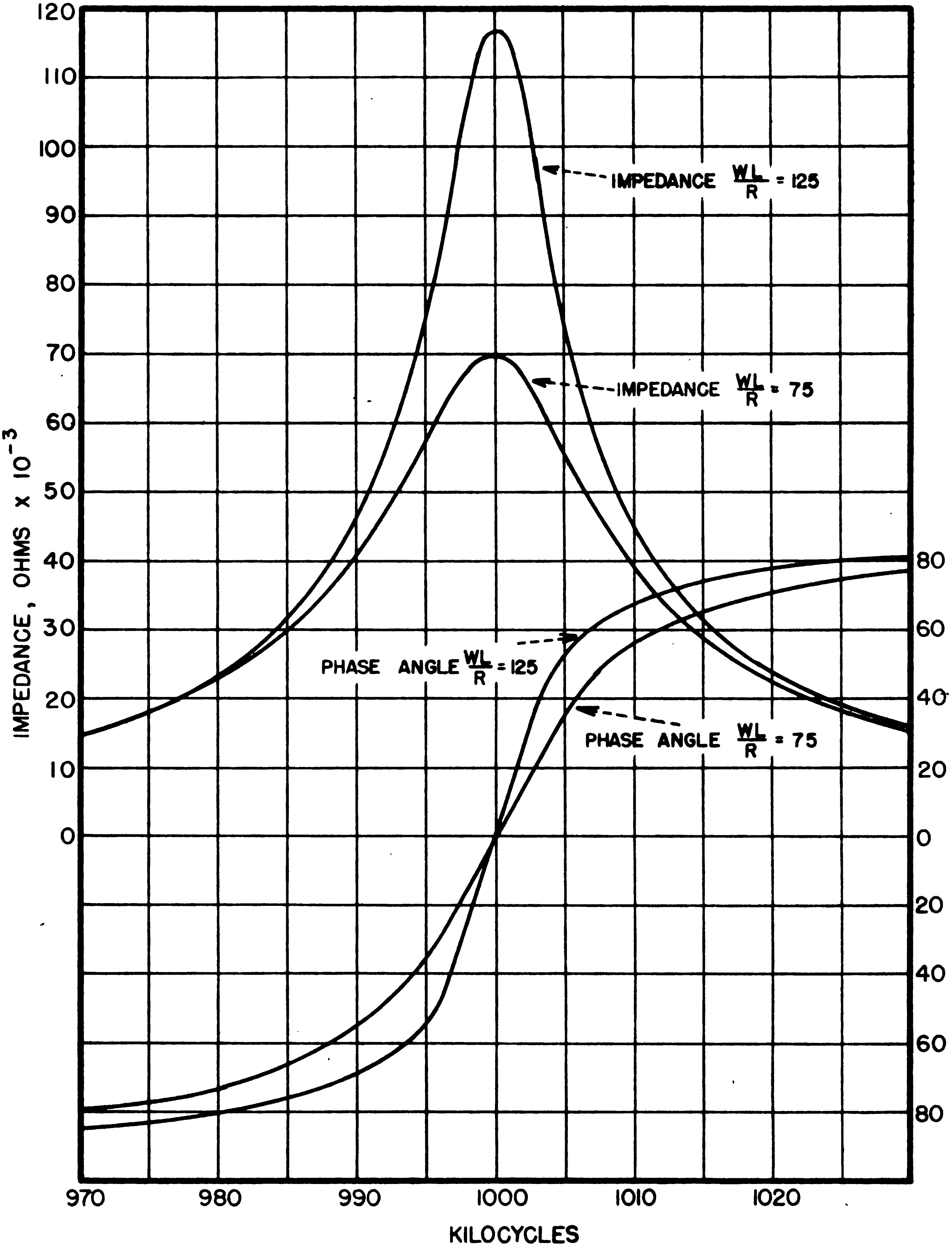


FIGURE I. MAGNITUDE AND PHASE ANGLE OF THE IMPEDANCE OF THE CIRCUIT IN FIGURE 2 AS A FUNCTION OF FREQUENCY.

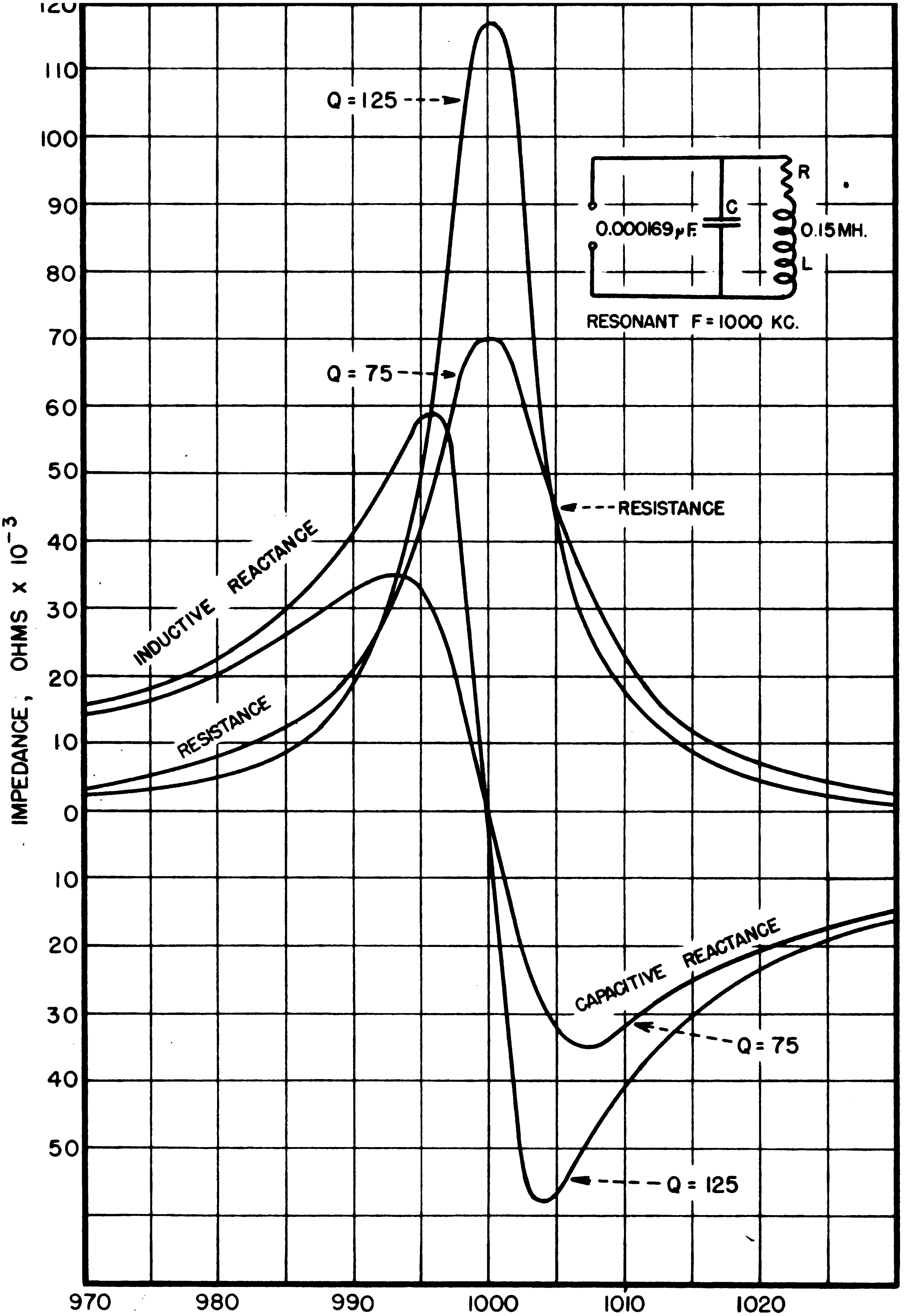


FIGURE 2. RESISTANCE AND REACTANCE COMPONENTS OF A PARALLEL CIRCUIT AS A FUNCTION OF FREQUENCY.

does impedance. The reactance curve shows a maximum inductive reactance at a frequency below resonance equal to $f_0(1-1/2Q)$, and a maximum capacitive reactance at a frequency above resonance equal to $f_0(1+1/2Q)$. At resonance the reactance curve passes through zero, the resistance curve passes through its maximum, and therefore, at resonance the parallel circuit is equivalent to a pure resistance equal to the characteristic impedance of the circuit.

Curves as shown in Figures 1 and 2 are known as resonance curves.

The cells used in high frequency titrimeters are of two types. One is constructed so that the solution is the dielectric material between the plates of a condenser and is connected across the tuning condenser of the parallel circuit. Another cell type places the solution within the field of the coil along its axis. In either case, the solution may reflect capacity or resistance into the tuned circuit. The effect on the electrical properties of the parallel circuit can be deduced by examining the resonance curves of Figures 1 and 2.

An increase in R will lower Q (equation 2), a lower Q will result in a broadening of the resonance curve (Figure 1), and lower the impedance, (equation 3a, equation 3b, and Figure 1). An increase in line current will be detected when R is increased. Another effect of increased R is a decrease in the phase angle of impedance. This will result in a slight shift in frequency when the parallel circuit is incorporated in an oscillator. This point will be discussed in greater detail under oscillators.

If the solution in the cell reflects a capacity change into the parallel circuit, the resonant frequency of the circuit will change (equation 1) displacing the curves either up or down along the frequency axis. Therefore, when the parallel circuit is made a part of an oscillator circuit, a change in frequency will be detected if the dielectric constant of the solution changes.

The fact that a change in the dielectric constant of a solution will result in a frequency change is obvious in the case of the capacitor type cell. However, when a solution is in the coil of the parallel circuit the situation is slightly different, and the reason for capacity effects may not suggest itself. Every coil has associated with it a distributed capacity as a result of dielectric stress between various parts of the coil. This distributed capacity acts as though it were lumped across the terminals of the coil and is in effect connected across the tuning condenser of the parallel circuit. A change in the dielectric constant of the solution changes the value of distributed capacity across the coil and results in a new resonant frequency. The conditions for resonance given by equation 1 still hold, but it must be remembered that C is the sum of the capacity of the tuning condenser and the value of distributed capacity associated with the coil. If the capacity of the tuning condenser is C_1 and the distributed capacity of the coil is C_2, equation 1 may be rewritten as

$$\omega L = \frac{1}{\omega(C_1 + C_2)} \qquad (5)$$

Since the parallel circuit is only one part of the complete oscillator circuit, the response of high frequency titrimeters to changes in solution composition are not fully explainable on the basis of the properties of the parallel circuit alone. To be complete, the discussion must be extended to include the conditions that must be satisfied in order to promote sustained oscillations in a typical oscillator.

Figure 3 is a schematic diagram of the Colpitts oscillator circuit. The parallel resonant circuit has L in parallel with the series combination of C_1 and C_2. The vacuum tube is able to act as an oscillator through its ability to amplify. The power input required by the grid is much less than the amplified output. Therefore, a portion of the output power may be fed back into the grid circuit and oscillation will take place.

The feedback in the Colpitts circuit is provided to the grid circuit by applying to the grid that portion of the voltage developed across the parallel circuit that appears across C_1. In the series connection of C_1 and C_2 both condensers will have the same charge Q at any instant. This charge Q is not to be confused with the Q or selectivity of the parallel circuit. The capacity of a condenser is defined as

$$C = \frac{Q}{V} \qquad (6)$$

where C is the capacity in farads, Q the charge in coulombs, and V the potential across the plates. Since both condensers have the same charge

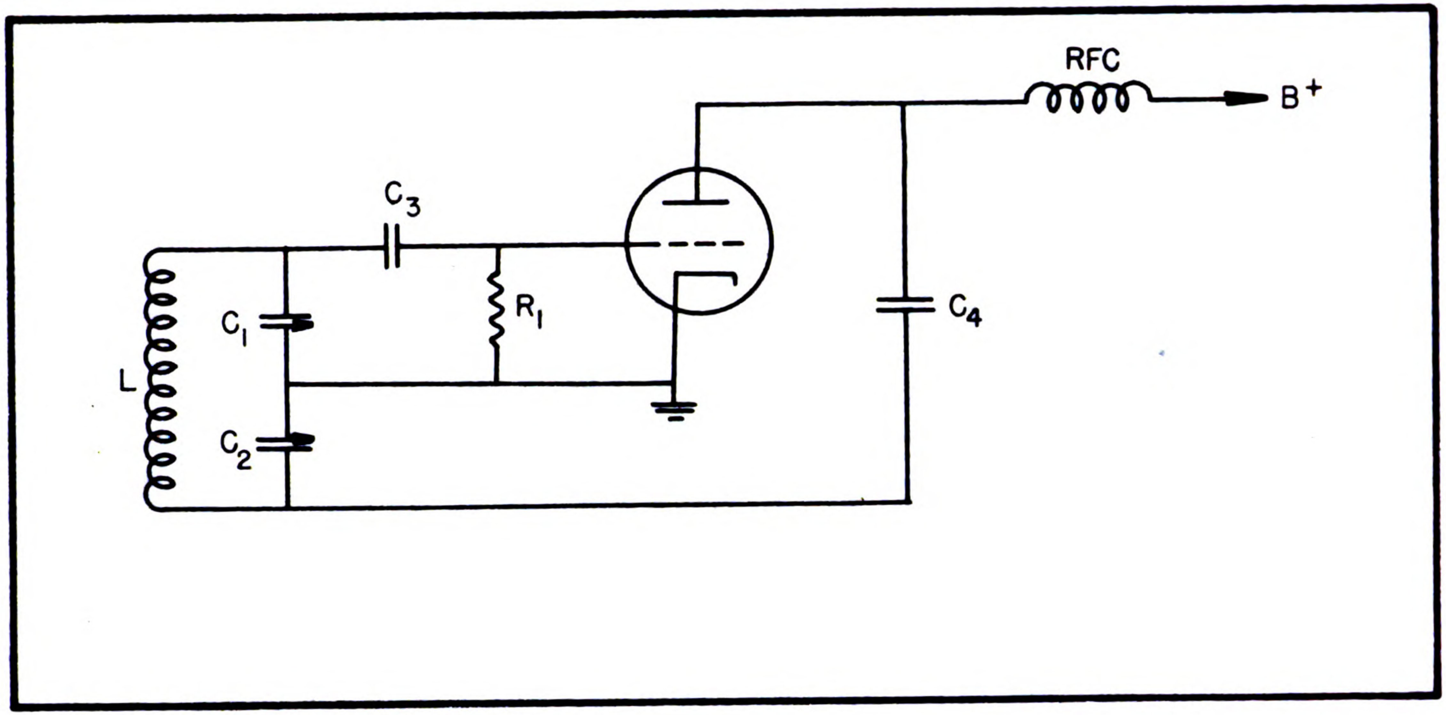


FIGURE 3. COLPITTS OSCILLATOR CIRCUIT.

$$\frac{C_1}{C_2} = \frac{V_2}{V_1} \tag{7a}$$

$$V_1 = V_2 \frac{C_2}{C_1} \tag{7b}$$

Equation 7b shows that feedback may be varied by changing the ratio of C_2 to C_1, the excitation increasing with smaller values of C_1.

The conditions that must be satisfied in order to maintain sustained oscillations in an oscillator is that the alternating current generated by the vacuum tube oscillator have a frequency such that the voltage which the generated oscillations apply to the grid of the tube is exactly 180 degrees out of phase with the oscillations of the equivalent plate voltage (23). These conditions are satisfied in the case of the Colpitts oscillator when the parallel circuit is tuned to offer a capacitive reactance to the generated frequency. Referring to Figure 2, it will be seen that the generated frequency will be higher than the resonant frequency of the parallel circuit as defined by equation 1. The operating point of the oscillator on the impedance curve of Figure 1 will be the point at which the phase angle of impedance is of the proper value to satisfy the conditions outlined above for sustained oscillations to take place.

The oscillator adjusts itself automatically to these conditions. In the discussion of the parallel circuit it was pointed out that an increase in R which occurs with an increase in the conductivity of a solution in high frequency titration, results in a decrease in the phase angle of impedance and in order to compensate for this change the oscillator will adjust itself to a new frequency where the operating conditions are satisfied.

A change in the value of the capacity in the parallel circuit will upset the operating conditions of the oscillator and a frequency shift will be necessary to restore the conditions once again.

When the frequency changes of a vacuum tube oscillator are measured, some problems arise. One is to separate the frequency shift due to changes in dielectric constant which determines the amount of capacity in the circuit from the frequency shift due to changes in conductivity which determines the amount of resistance in the circuit.

In an instrument in which the parallel circuit and associated cell are not included in the circuit of an oscillator, the separation of capacitive and resistive changes is quite simple. Examples of such instruments are those of Hall and Gibson (6), and Fujiwara and Hayashi (5). The principle and method of measurement involved in the latter circuit is discussed elsewhere (20). The curves of Figures 1 and 2 are obtained by this method.

The parallel circuit is tuned to resonance at the beginning of a titration in the application of this type of instrument. The parallel circuit therefore satisfies the conditions of equation 1. Increases in cell capacity can be compensated for by removing capacity from a variable capacitor placed in parallel with the cell capacity. According to equation 5, if C_2 increases by an amount ΔC, C_1 can be decreased by an amount ΔC and resonance will be restored. The change of capacity

Δ C can be evaluated from a calibrated dial installed on the rotor of C_1. Usually resonance is indicated by a maximum voltage reading on a vacuum tube voltmeter placed across the terminals of the parallel circuit. Since the impedance curve is flat at this point some difficulty in determining the exact point of resonance may arise. Small changes in capacity may even be undetectable.

The amplitude of the voltage appearing across the coil is a function of the Q of the circuit. Changes in voltage readings may be interpreted in terms of resistance. In general, the sensitivity of the method when applied to high frequency titration is much less than the sensitivity of other methods. Furthermore, the voltage applied to the parallel circuit must be free of harmonics of the fundamental frequency. At resonance the circuit impedance is high to the fundamental component of the applied voltage, but is low to any harmonics. Consequently, harmonic components will cause high line currents that will mask the small line current due to the fundamental component.

No mention is made by Fujiwara and Hayashi (5) whether or not their oscillator was free of harmonics.

The principles outlined above for separating resistive and capacitive components responsible for measurable changes in resonant frequency and Q of a parallel circuit when not included in an oscillator circuit do not apply when the parallel circuit is part of the oscillator circuit. As previously pointed out, the parallel circuit in the Colpitts oscillator is tuned to be resonant to a frequency slightly higher than the

output signal frequency of the oscillator. Restoring the frequency of the oscillator to its original output frequency after a frequency shift has occurred by adjustment of a shunting capacity compensates for the frequency shift due to both resistance and capacity. Other factors that influence the output frequency such as changes in plate supply voltage, grid excitation, and grid bias are also compensated. Frequency changes are therefore the result of the interaction of many variables. The component due to a change in the dielectric constant of the solution is practically impossible to determine.

Oscillators may be stabilized to make them insensitive to variations in tube characteristics (15) which would simplify things somewhat, but whether a true separation of the variables of capacity and resistance are accomplished would be open to debate.

Furthermore, it is conceivable that a solution may show a dielectric constant change tending to increase the output frequency of an oscillator and a conductivity change tending to decrease the output frequency, resulting in a net change of zero (7).

Returning to the schematic diagram of the Colpitts oscillator circuit of Figure 3, a resistor R_1 is connected from the grid of the tube to ground. Before oscillations start there is no voltage applied to the grid, and therefore no grid current. The bias on the tube is zero and a large plate current flows. The initial surge of current through the tube when the cathode reaches the temperature at which electron emission begins, sets up an alternating current in the parallel circuit and an alternating voltage across it. Feedback of part of this voltage to the grid drives the grid positive with respect to the cathode. Electrons are attracted from the cathode to the grid and current flows through the resistor R_1 commonly called the grid-leak resistor. The voltage drop across the resistor makes the grid negative with respect to the cathode. The value of the grid bias is the product of the average value of the grid current and the value of the grid-leak resistor. As the amplitude of oscillations builds up the bias increases and eventually a steady state is attained where the grid bias and the amplitude of the oscillations remain constant. The voltage and current relations existing in an oscillator under steady state conditions are shown in Figure 4 (23).

The instantaneous value of plate voltage is the sum of the plate supply voltage and the alternating voltage developed between the plate and cathode, Figure 4a. The instantaneous value of grid voltage is the sum of the grid bias voltage and the voltage developed across the feedback capacitor C_1 between cathode and grid by the current in the tuned circuit, Figure 4b. The alternating plate-cathode voltage and alternating grid-cathode voltage are 180 degrees out of phase.

The grid is driven positive for a period of time less than the period of a half cycle. The plate current and grid current flows in pulses, Figures 4c and 4d. The plate current pulse is longer than the grid current pulse. The tube conducts as soon as the instantaneous grid voltage is slightly more positive than cutoff on the upward part

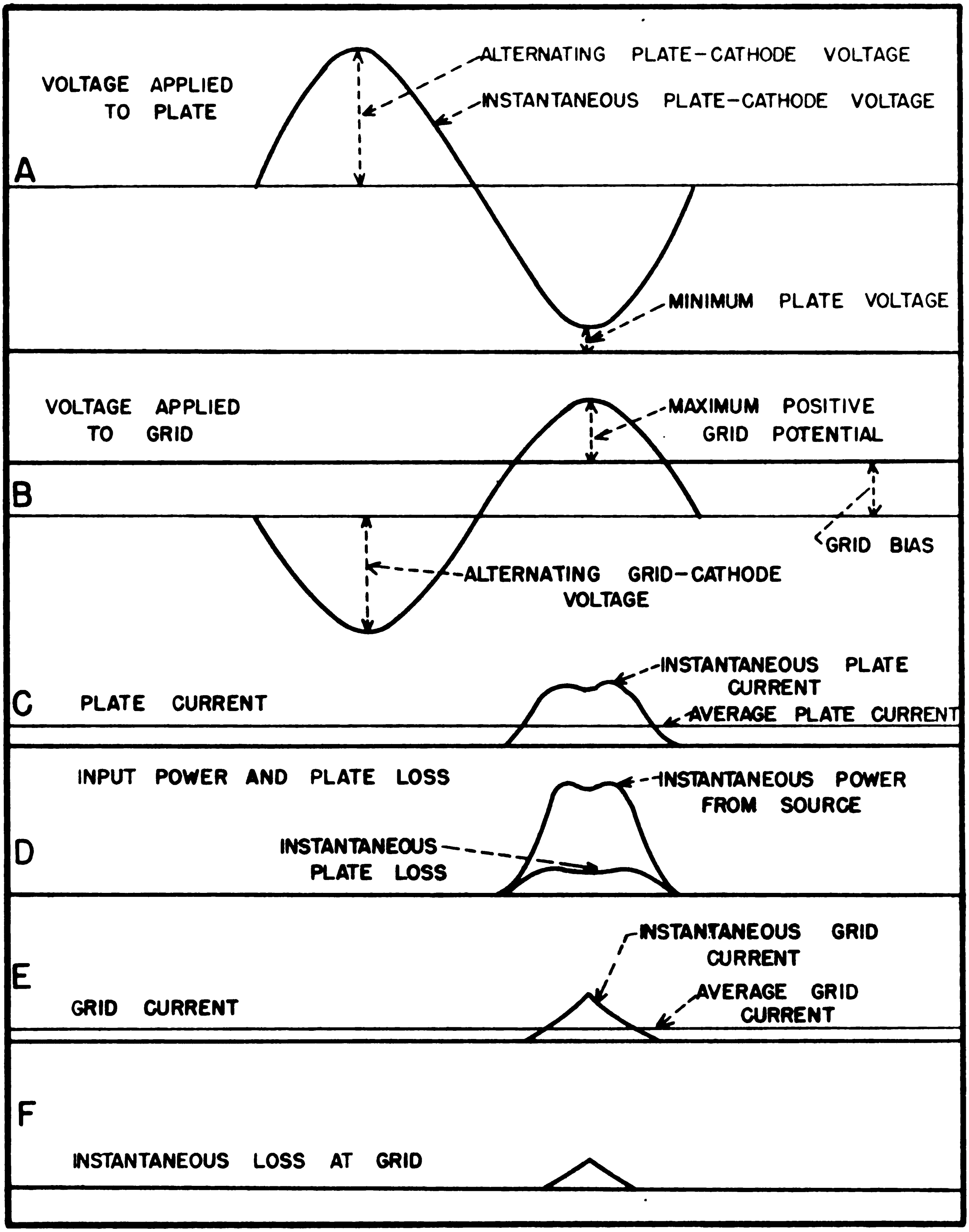


FIGURE 4. VOLTAGE AND CURRENT RELATIONS EXISTING IN AN OSCILLATOR UNDER STEADY STATE CONDITIONS.

of the cycle and grid current does not flow until the grid is driven positive with respect to the cathode some time later. Likewise the grid current ceases sometime before the plate current cuts off on the downward part of the cycle. The slight distortion at the peak of the plate current pulse is the result of the grid robbing the electron stream on the way to the plate of a supply of electrons which constitute the grid current. This distortion results in the generation of harmonics.

The power supplied by the plate supply is equal to the plate supply voltage times the average value of the plate current pulse taken over a full cycle. Part of this power is delivered to the resonant circuit in the form of alternating current energy and part of it is dissipated at the plate of the tube in the form of heat, Figure 4d. The heating is due to the impact of electrons on the plate of the tube.

The power loss at the grid is very nearly equal to the product of the average grid current and the crest value of the alternating grid-cathode voltage. The power loss at the grid is the sum of the power losses due to the heating of the grid by the impact of electrons and the heating of the grid-leak resistor. The power losses in the grid circuit are supplied by energy obtained from the resonant circuit.

When the resistance of the resonant circuit is increased by an increase in the conductivity of a solution in the cell of a high frequency titrimeter, the steady state conditions of Figure 4 are upset. In addition to the frequency changes discussed earlier, the amplitude of the oscillations will tend to decrease. The original oscillating current in the resonant circuit in flowing through the added resistance consumes more energy than is supplied from the plate supply source. Immediately the alternating plate-cathode voltage decreases, increasing the minimum plate voltage and increasing the amplitude of the plate current pulses. The resonant circuit receives additional energy, and a new equilibrium point is reached where the enlarged plate current pulses supply sufficient energy to maintain oscillations in the higher resistance circuit. The oscillations will be reduced in amplitude, and consequently the feedback voltage across C_1 is reduced in amplitude, less grid current flows, and bias is decreased until equilibrium is reestablished.

In summary, if the effect of a change in the concentration of a solution in the cell of a high frequency titrimeter is purely resistive and reflects an increased resistance into the resonant circuit as a result of an increase in conductivity, a slight frequency shift will be detected, plate current increases, grid current decreases, and grid bias decreases. Any of these changes may be measured and by this means the course of a titration may be traced.

A capacity change will produce the same type of response. Once again the problem of separating the components due to resistive and capacitive effects arises.

It is believed that a solution to the problem has been found and that an instrument has been developed in which the response is so predominantly resistive that for all practical purposes is not affected by changes in the dielectric constant of the solution in the cell.

EXPERIMENTAL

EXPERIMENTAL

Preparation of Reagents

Reagent grade acetic, hydrochloric, sulfuric, phosphoric and C. P. oxalic acid was used to prepare acid solutions. These were compared to sodium hydroxide which was standardized against primary grade potassium acid phthalate.

Solid C. P. sodium chloride and reagent grade sodium fluoride, calcium chloride, ammonium oxalate, silver nitrate were weighed out to the nearest 0.1 of a mg. employing weights calibrated against Bureau of Standards calibrated weights, N. B. S. Test No. 87925. These solids were dissolved and diluted at 20 degrees C. in a calibrated one liter volumetric flask. The concentration of the sodium chloride solution was checked against the silver nitrate solution by the Fajans' method.

The concentration of the calcium chloride solution was determined by the permanganate method. The potassium permanganate was standardized against primary standard grade sodium oxalate.

Reagent grade boric acid was used to prepare a solution which was compared to standardized sodium hydroxide. C. P. d-mannitol was employed (12).

Hydrogen peroxide solutions were prepared from three percent reagent grade hydrogen peroxide. Its concentration was determined by an iodimetric method (13). The sodium thiosulfate solution employed had been standardized against primary standard grade potassium dichromate.

Incidental Instrumentation

The operating frequencies of the oscillators used in this study were determined with a U. S. Army Signal Corps BC-221-D frequency meter, a U. S. Army BC-1255-A heterodyne frequency monitor, and a General Radio Company 758-A wavemeter.

Other instruments included a Clough-Brengle Company Model OCA signal generator, a Heathkit Model V-5 vacuum tube voltmeter, a Heathkit Model O-7 oscilloscope, a Radio Corporation of America Model 162-C Rider Channalyst, and a U. S. Navy Type ARB superheterodyne communications receiver.

A Sola 120 v. a. constant voltage transformer was used to regulate line voltage.

Calibrated pipets and burets were used for all titrations.

The Parallel Resonant Circuit Titrimeter

At the time experimental work was begun, several instruments had been described in the literature (1,2,3,6,8,10,15). These instruments were of the type employing an oscillator of some sort, with the solution vessel placed either in the coil of a tank circuit, or between the plates of a condenser making up part of the tuning capacity of a tank circuit. Frequencies used ranged from 2 mc. up to 350 mc.

At this time the nature of the response of these instruments to changes in circuit parameters and to changes in solution composition had not been established.

Past experience in the field of electronics suggested that the properties of a resonant circuit could be studied quite simply (21) using units that were readily available. Mizushima (17) had earlier applied the method to the measurement of dipole moments with some success.

The principle of the method is evident from the schematic diagram of Figure 5. A parallel resonant circuit which includes the titration cell C_x, was loosely coupled to a signal generator. The output of the oscillator could be adjusted to any frequency between 100 kc and 30 mc, and was modulated by a frequency of 400 cps.

When the parallel resonant circuit was tuned to the frequency of the signal generator output, the voltage or current indicated in the detector circuit was a maximum. The voltage or current indicated by the detector at the maximum was a function of the Q of the circuit containing the filled cell. Changes in circuit capacity were measured by means of the calibrated Micro Pot dial attached to the C_1 drive mechanism.

The arrangement of the apparatus as finally employed is shown in Figure 6. Details of the probe making up C_x of the schematic diagram are given in Figure 7. The copper foil plates were held securely between two concentrically fitted soft glass test tubes. The number of test tubes that can be fitted to make the combination shown in Figure 7 are relatively few, but it is estimated that at least a half a dozen suitable combinations can be found per 100 test tubes.

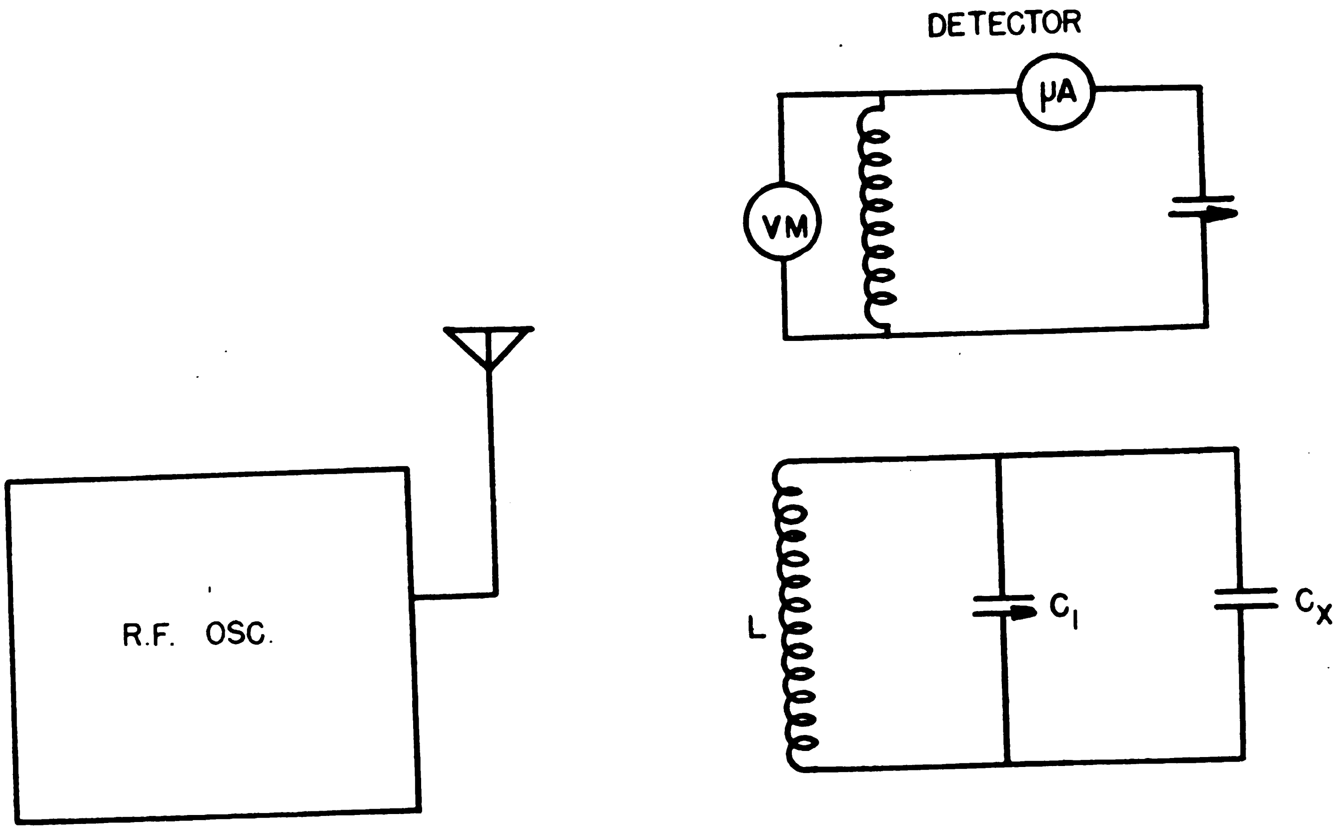


FIGURE 5. SCHEMATIC DIAGRAM OF ELEMENTARY HIGH FREQUENCY TITRIMETER.

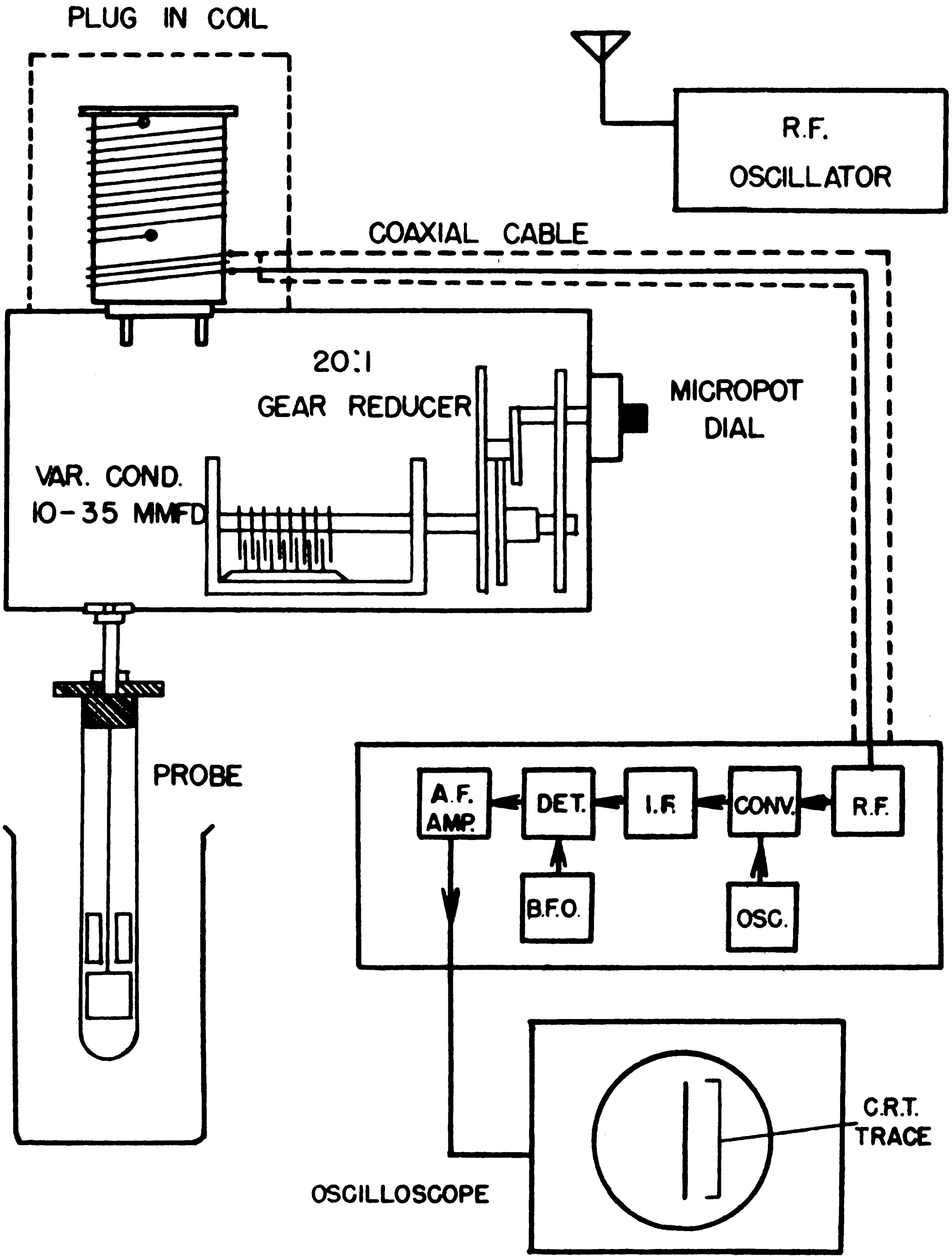


FIGURE 6. APPARATUS EMPLOYED IN EARLY HIGH FREQUENCY TITRATIONS.

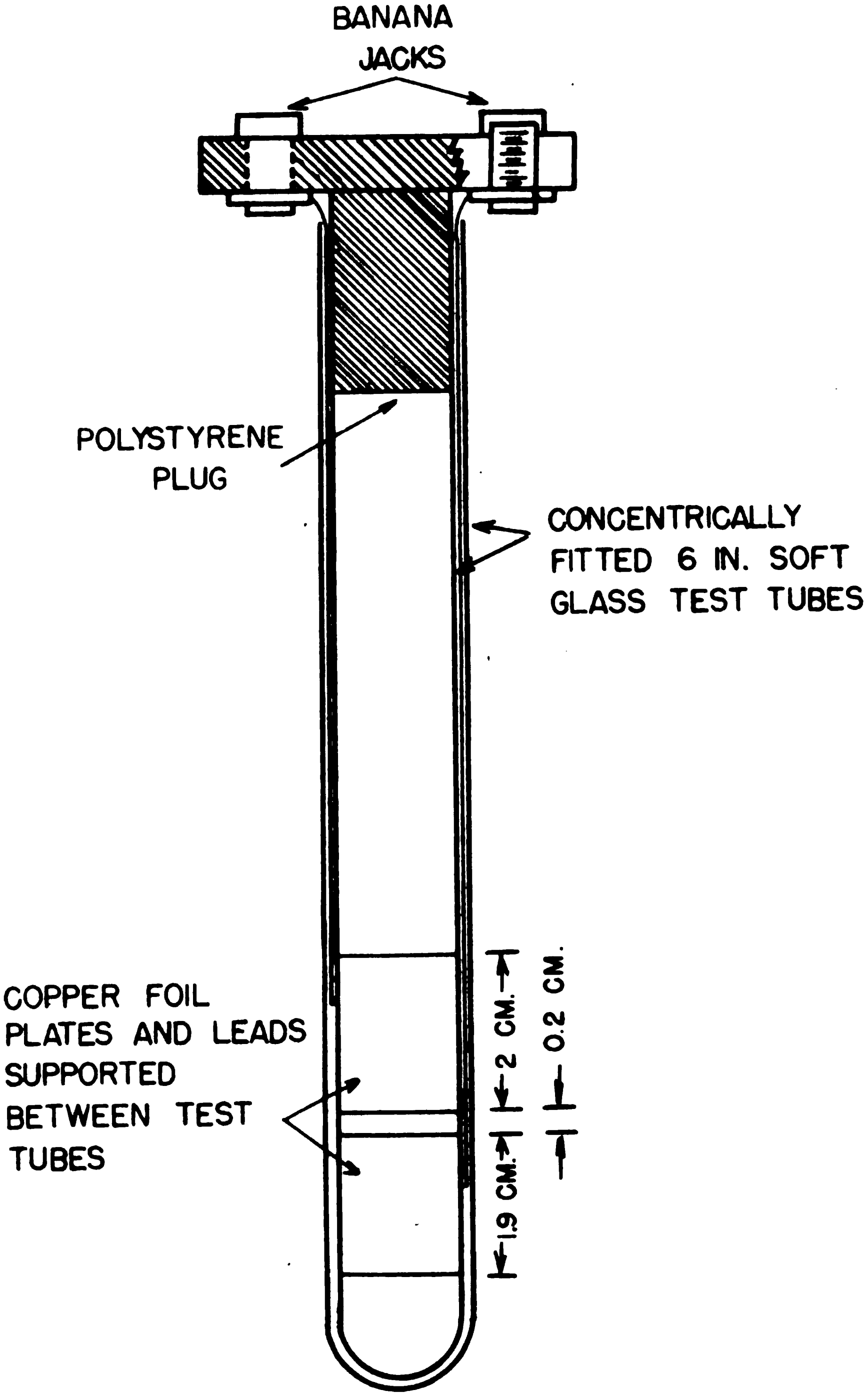


FIGURE 7. PROBE DETAILS.

Initially, the condenser C_1 was adjusted to approximately one half of its maximum capacity, the proper coil for the frequency range selected was plugged into its socket, and the signal generator adjusted so that its output frequency was the resonant frequency of the parallel circuit. Resonance was indicated by maximum length of the vertical line on the oscilloscope screen. The output of the receiver was the 400 cps. modulation frequency of the input signal after demodulation in the second detector of the receiver. The automatic volume control circuit of the receiver was turned off to insure a constant over-all receiver gain throughout the experiments. A grid was placed over the oscilloscope screen to facilitate measurement of output amplitude. The reference point for amplitude measurements was the amplitude measured at the beginning of a titration.

Some of the undesirable features of the apparatus were immediately apparent. The maximum of the resonance curve of the parallel circuit was quite broad, making accurate capacity measurements difficult. The probe as designed was sensitive to changes in the level of the solution and the effect could not be eliminated. This effect was obviously due to the arrangement in which the leads connecting the plates of the probe to the terminals at the top of the probe represented a small amount of the total surface area of the condenser. In addition, the probe was sensitive to changes in its position in the beaker and to body capacity. The sensitivity of the method was believed to be inadequate for analytical purposes.

This work could have been continued further, and the difficulties mentioned overcome by using the conventional type of cell as shown in Figures 16 and 17 and employing circuits of higher Q. Recently the method was employed by Fujiwara and Hayashi (5) to obtain the response curves for circuits in which the solution was placed in a vessel within the inductance of a parallel circuit.

A modification of the apparatus of Figure 6 in which a crystal filter circuit was substituted for the parallel circuit at the input of the receiver was investigated. A crystal filter circuit was constructed utilizing a 456 kc. quartz crystal, but the high noise level at the frequency made further work with the unit impossible. It was found that the sources of the noise being fed into the receiver could not be eliminated without curtailing other work being carried out in the same building.

It is believed that the unit merits some additional consideration and under more favorable conditions its full potential may be realized.

Fortunately, at the time these problems were being encountered, several excellent papers appeared (4,7,19) establishing the effect of circuit parameters on the response of most of the instruments in use at that time. Almost any shape of titration curve could be explained, and the limitations of the method clearly pointed out. It was now possible to go ahead with the construction of an experimental high frequency titrimeter and by a series of simple tests determine its characteristics. Knowing these, the instrument could then be applied intelligently to the particular system to be studied.

The Frequency Measuring Instrument

Before making a decision on the type of instrument to be constructed, the titrimeters for which sufficient details were available in published papers were evaluated. The instrument considered to offer the most in terms of flexibility, sensitivity, and stability, in addition to being easy to construct, was the titrimeter reported by Anderson, Bettis, and Revinson (1). Jensen and Parrack (10) used a tuned plate-tuned grid oscillator found to be unstable by others (1,2,6). Blaedel and Malmstadt (2) used a Clapp oscillator using a 6AC7 tube for work at frequencies of 30 mc. and below. The frequency limitations of the tube would restrict the use of any instrument in which it was used to this frequency range which was undesireable. The 350 mc. equipment reported by the same authors (3) required elaborate machining operations which could not be undertaken. The apparatus of West, Burkhalter, and Broussard (24) seemed to be too complicated for the results obtained in return.

Anderson et al. (1) used a grid dip oscillator circuit employing a type 955 tube. The tube could be used up to frequencies of 500 mc. if necessary and required relatively little power. No tuning adjustments were necessary, the operating frequency being that assumed by the oscillator at the beginning of a titration. Changes in solution concentration were followed by observing changes in the grid current of the oscillator.

It was decided to convert the instrument into one in which changes in frequency were measured during a titration. The mechanical layout of the instrument was changed, including the design of the cell.

A schematic diagram of the oscillator is shown in Figure 8. The power supply circuit diagram appears in Figure 9. The physical layout of the instrument is shown in the top and bottom views of the chassis in Figure 10 and Figure 11.

Care was taken to keep all leads to an absolute minimum, and in the layout of the parts, an effort was made to produce the most symmetrical layout possible. The tube and its associated components were mounted on a subchassis constructed from 3/16 inch thick aluminum plate. The subchassis is located at the extreme left in Figure 11. Access to the tube was provided through a hole in the top of the main chassis around which a suitable shield assembly was secured. These details appear in Figure 12 and Figure 13.

For frequencies up to 60 mc. the operating frequency of the oscillator was changed by using coils having varying numbers of turns. The coil shields were made of heavy guege copper and were firmly attached to the substantial bases of the coil forms, Figure 15. When plugged into position a spring collar attached to the chassis gripped the lower edge of the shield firmly, completing the shielding to the chassis, in addition to preventing any physical movement of the coil assembly during a titration, Figure 12 and Figure 13.

The cell was designed so that the polyethylene vessel could be removed by simply sliding it up vertically out of the bands and the

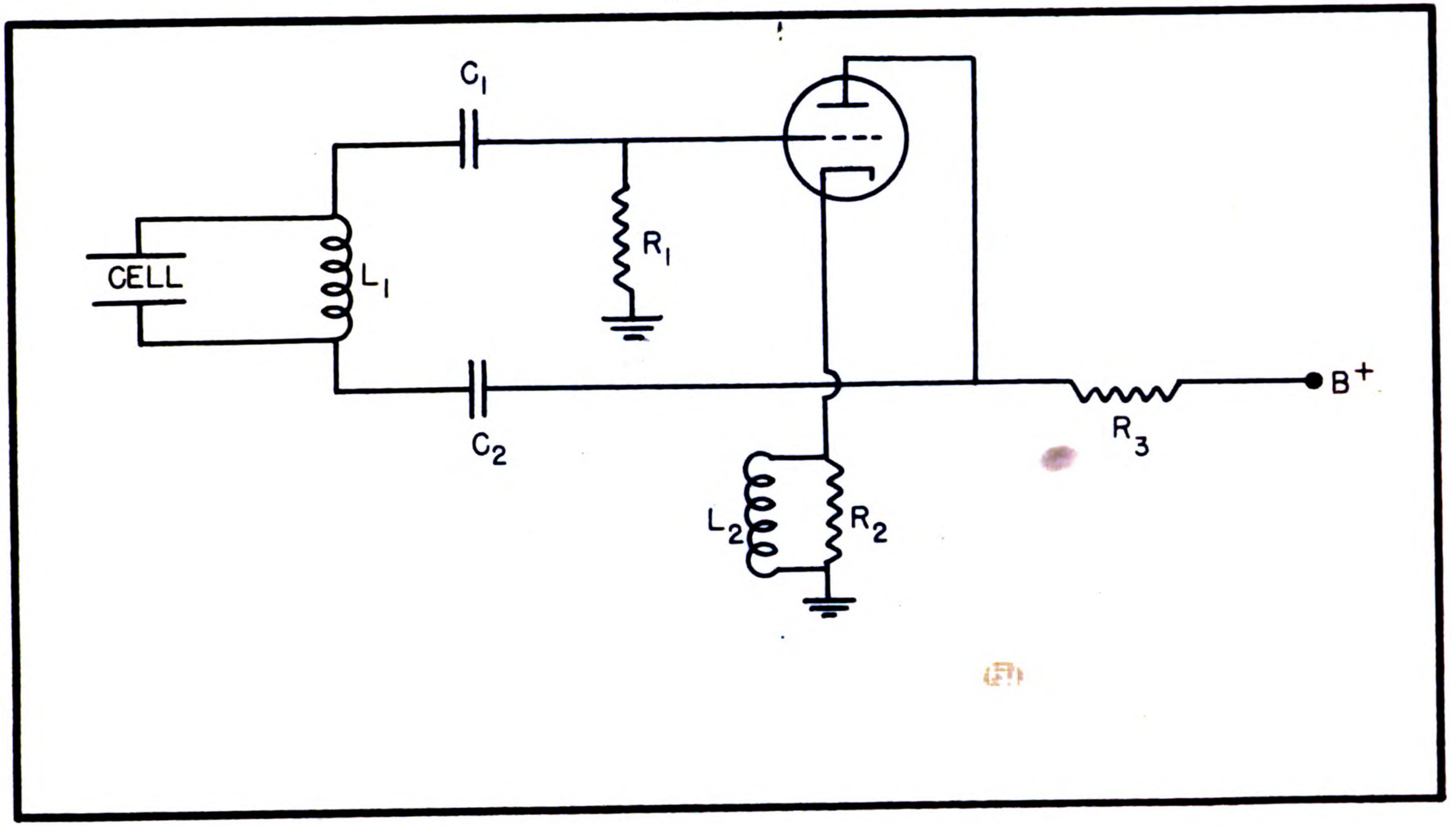


FIGURE 8. OSCILLATOR CIRCUIT OF FREQUENCY MEASURING INSTRUMENT.

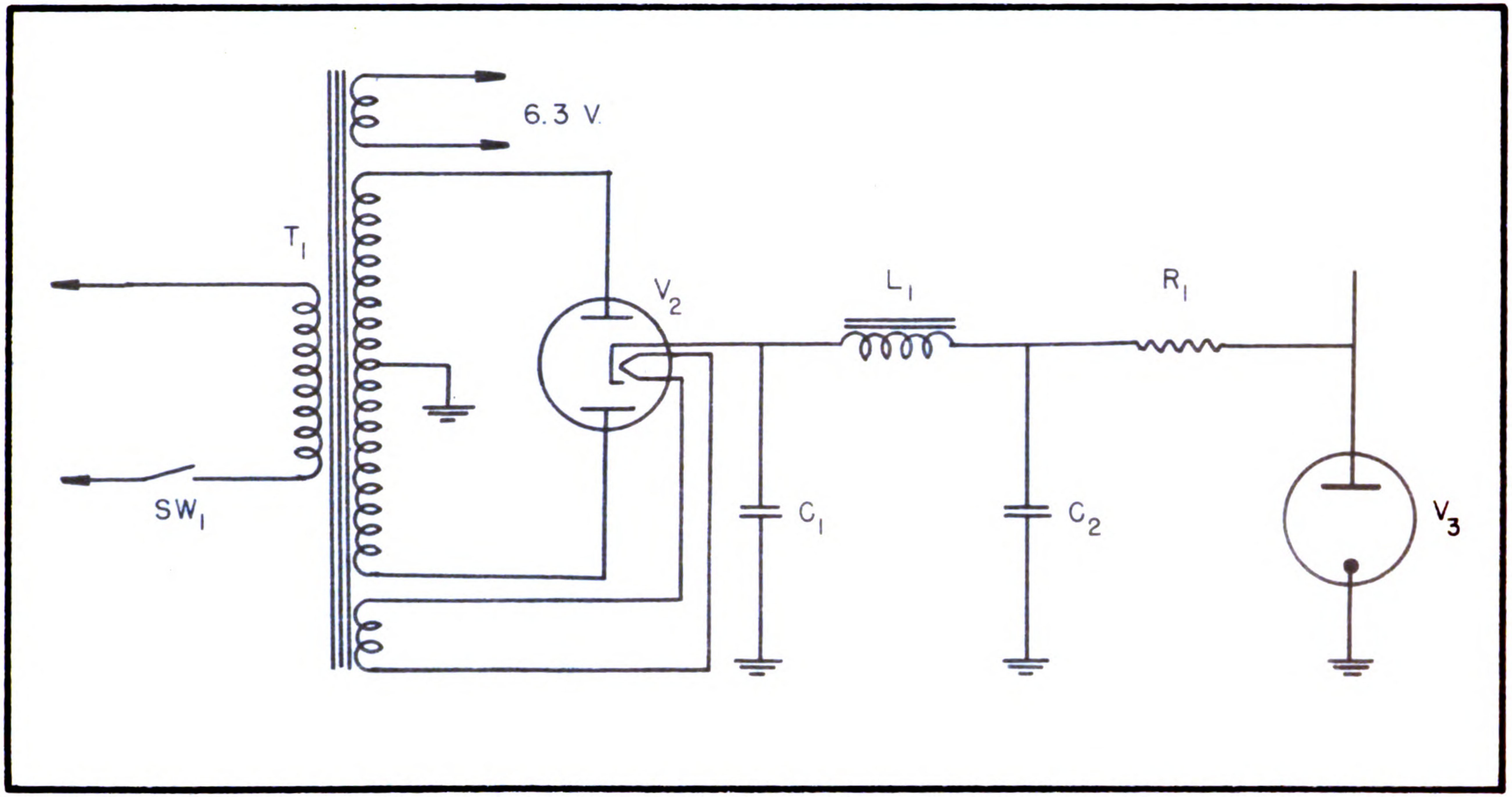


FIGURE 9. POWER SUPPLY CIRCUIT.

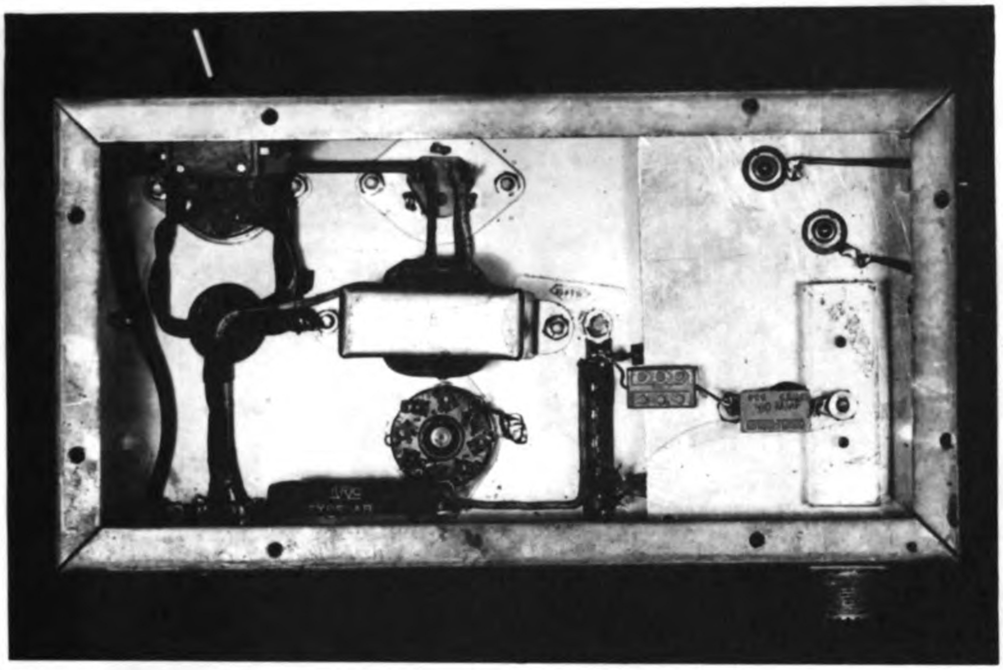


FIGURE 10. TOP VIEW OF MAIN CHASSIS.

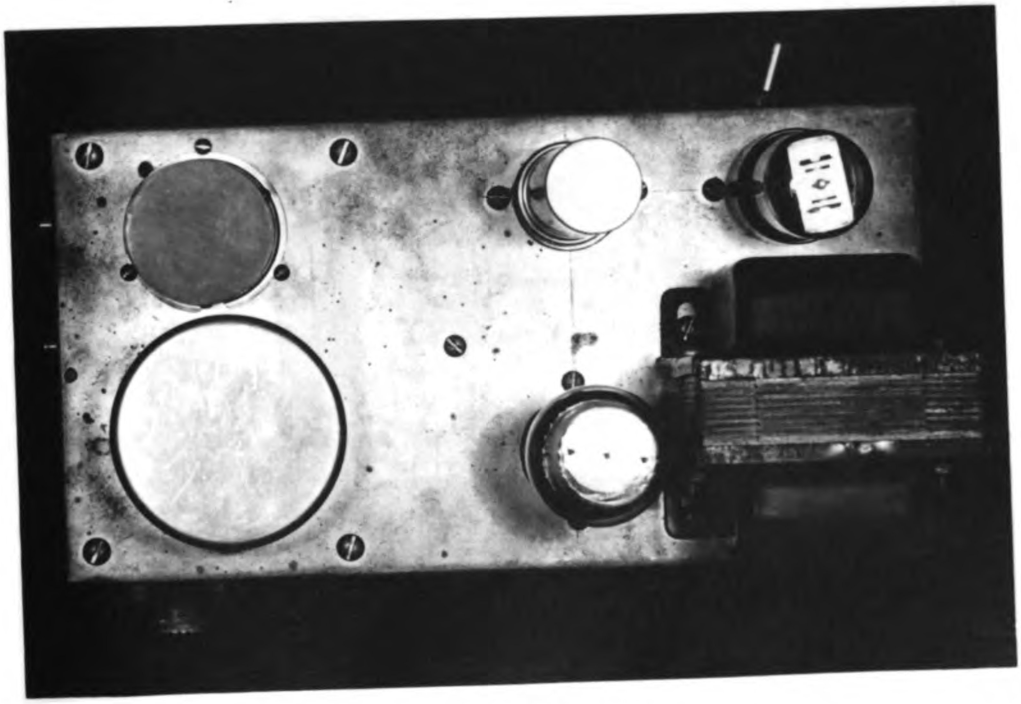


FIGURE 11. BOTTOM VIEW OF MAIN CHASSIS.

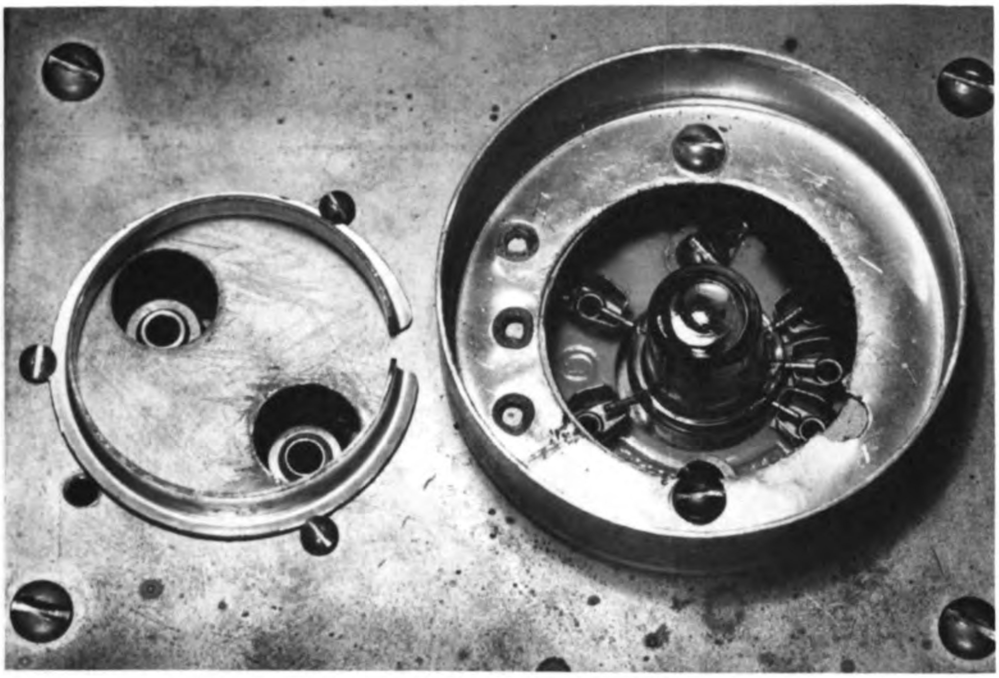


FIGURE 12. CLOSEUP OF COIL AND 955 TUBE SOCKETS.

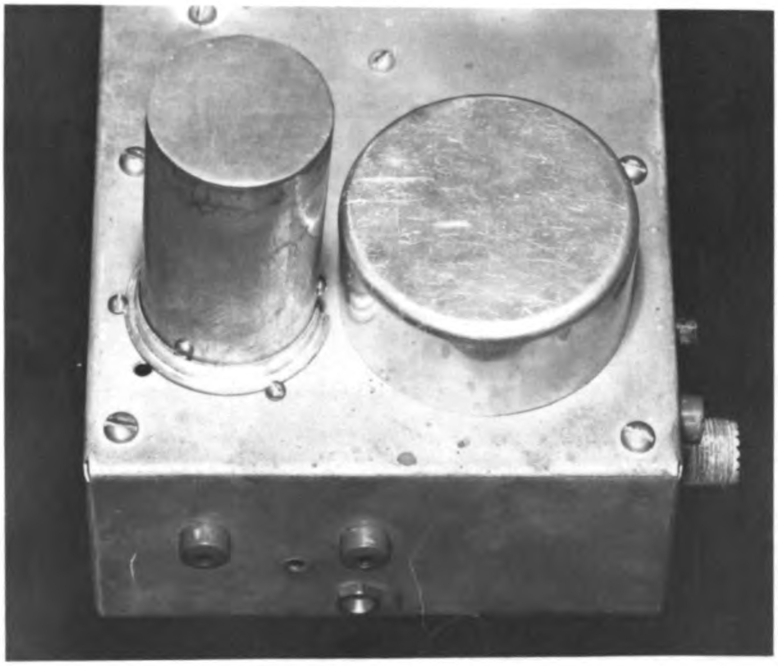


FIGURE 13. CLOSEUP OF COIL AND TUBE SHIELD IN POSITION.

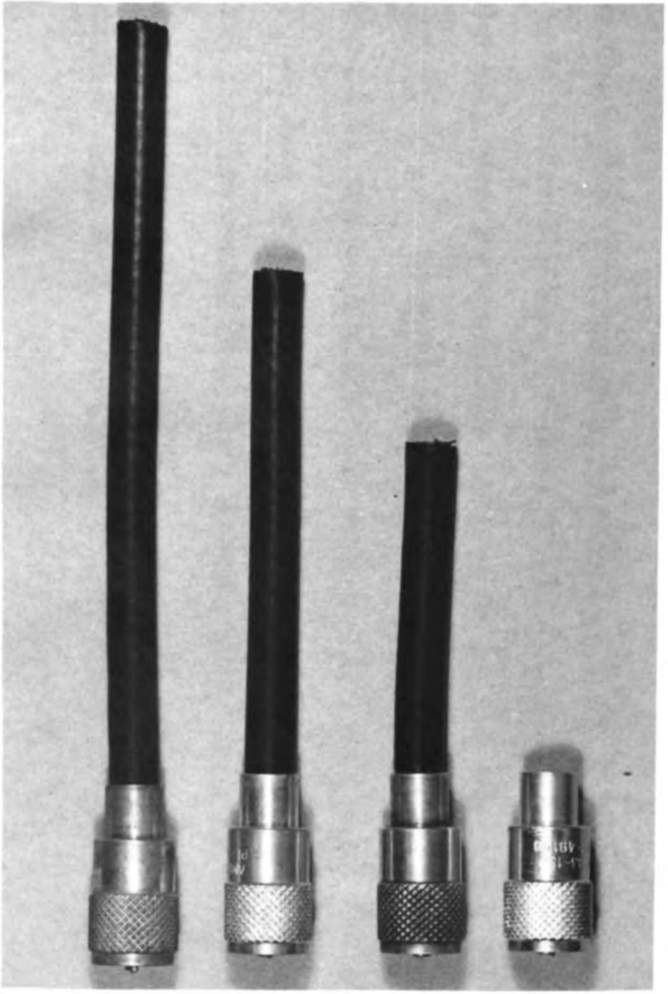


FIGURE 14. FEEDBACK CAPACITORS.

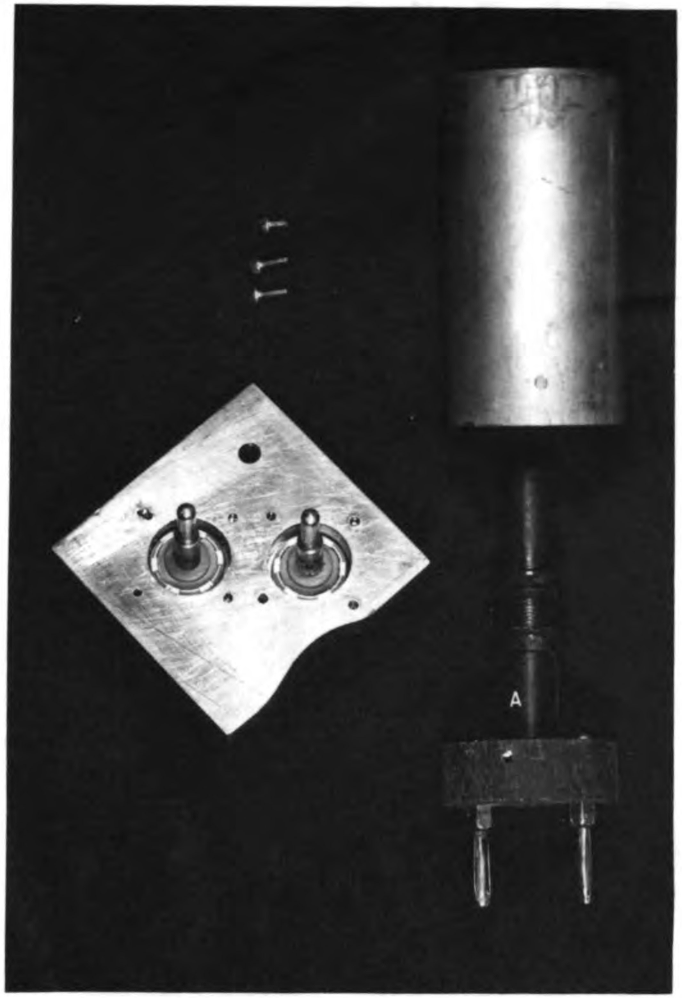


FIGURE 15. (A) COIL ASSEMBLY, (B) BASE PLATE WITH COAXIAL CONNECTORS.

remainder of the cell assembly. The fit was snug enough to prevent any movement of the vessel relative to its surroundings during a titration. The bands making up the plates of the capacitor were supported firmly and insulated from the remainder of the unit by polystyrene spacers attached to the walls of the heavy guage aluminum box which served to shield the sensitive circuit elements from outside influences as shown in Figure 16 and Figure 17. The shielding of the unit was completed by a snug fitting grounded ring installed in the upper shield assembly and a positive contact between the main chassis and the aluminum shield of the cell was provided by means of a third banana jack and plug. When the cell was plugged into position and secured to the base plate by means of a screw as shown in Figure 18, it was found that the hands could be placed anywhere on the instrument without causing a detectable shift in frequency.

Blaedel and Malmstadt (2,3) had shown that in order to extend the useful range of frequency measuring instruments up to more practical regions of conductivities, frequencies of 100 mc. and above were necessary. The highest frequency obtainable using coils in the instrument was approximately 80 mc. In order to reach 120 mc. a half wave line had to be constructed to replace the coils previously used. The equivalence of a half wave line to a parallel circuit is discussed elsewhere (20).

The line was constructed from Amphenol RG 8/U coaxial cable and terminated in Amphenol type PL-259 male coaxial cable connectors. The male coaxial cable connectors at the ends of the line were plugged in

FIGURE 16. TITRATION VESSEL INSERTED INTO POSITION INSIDE OF BANDS OF CAPACITY TYPE CELL.

FIGURE 17. CAPACITY TYPE CELL WITH UPPER SHIELD ASSEMBLY IN POSITION.

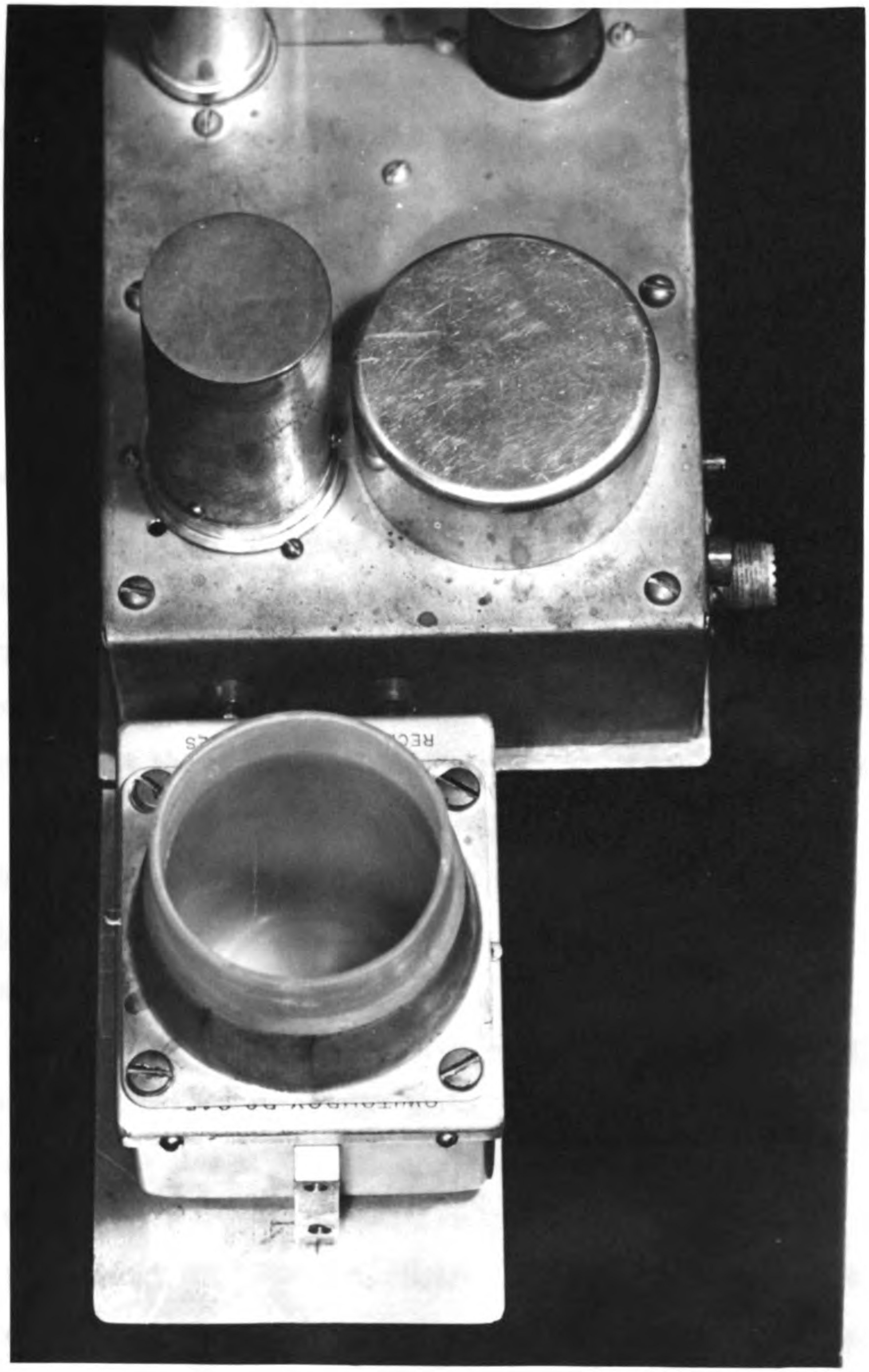


FIGURE 18. CAPACITY CELL PLUGGED INTO POSITION IN SIDE OF MAIN CHASSIS.

and firmly secured to two female receptacles mounted on a substantial base plate made of 3/8 inch thick brass. The bottom view of the base plate is shown in Figure 15. The spacing of the banana plugs soldered to the center conductors of the female receptacles was made the same as the spacing of the terminal plugs of the coils previously used. After removing the spring collar from the chassis the base plate plugged into position as shown in Figure 19.

The entire line and base plate appear in Figure 42 above the BC-221-D frequency meter.

Increasing the operating frequency of the titrimeter to 120 mc. required additional changes to be made in the cell. Bands could no longer be used because this construction led to greater values of cell capacity than could be tolerated. In place of bands two small plates curved to fit the contours of the polyethylene vessel were substituted. The polystyrene spacers that previously had supported the bands were left in position to center the vessel and to prevent physical displacement of the vessel during a titration. These details appear in Figure 21 and Figure 22.

Coupling to the frequency meter was provided through a small capacitance from the oscillator plate to the Amphenol female receptacle mounted on the side of the chassis. It was found that a short antenna connected to the frequency meter provided sufficient signal for measuring purposes at the lower frequencies. With this arrangement interaction between the oscillator and frequency meter could not occur.

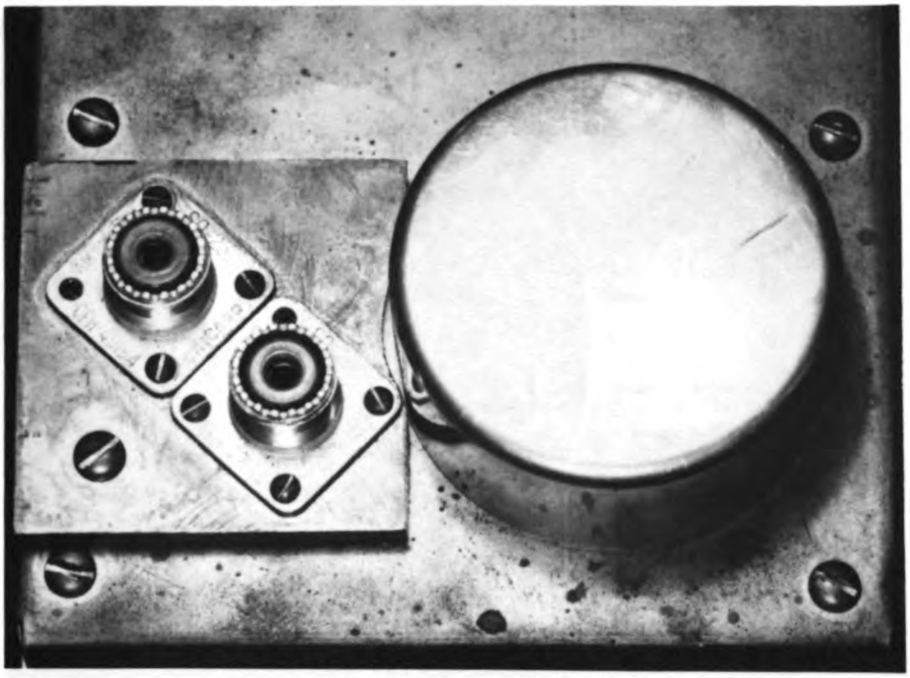


FIGURE 19. BASE PLATE WITH FEMALE COAXIAL RECEPTACLES PLUGGED INTO POSITION ON MAIN CHASSIS.

FIGURE 20. FEEDBACK CAPACITORS IN POSITION ON BASE PLATE.

FIGURE 21. TITRATION VESSEL INSERTED INTO POSITION IN 120 mc. CAPACITY CELL.

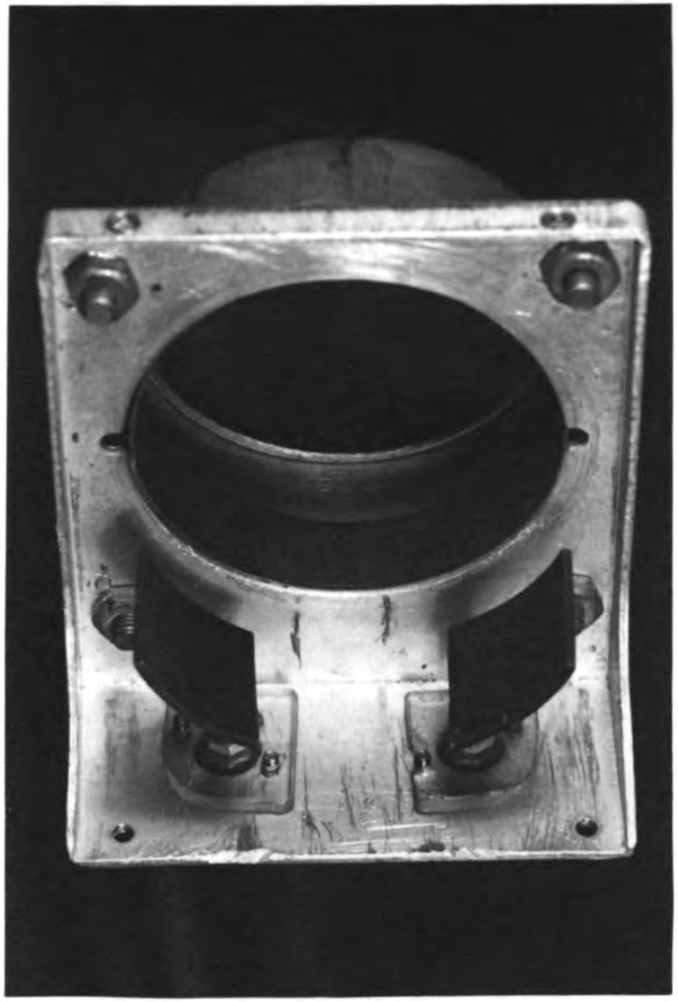


FIGURE 22. UPPER SHIELD ASSEMBLY AT 120 mc. CAPACITY CELL SHOWING CAPACITOR PLATES.

The frequency meter used was a U. S. Army type BC-221-D heterodyne frequency meter. The highest fundamental frequency of the calibrated oscillator in the frequency meter was 20 mc. When used in conjunction with the 120 mc. titrimeter, a higher harmonic of the fundamental frequency of the frequency meter oscillator had to be used in order to obtain an audible beat note. The beat frequency was amplified by feeding the audio output signal of the frequency meter into the audio channel of an R. C. A. Rider Channelyst. Ample volume was provided in the earphones after amplification.

The frequency stability of the oscillator in the frequency meter was checked against the 5000 kc. standard frequency signal of WWV, National Bureau of Standards, Washington, D. C. After a twelve hour warm up period the oscillator showed a downward drift in frequency of 2 kilocycles in a 30 minute period.

The method used for the test was as follows. The 5000 kc. signal of WWV was tuned in on a U. S. Navy type AHB receiver. The oscillator in the frequency meter was adjusted to zero beat with WWV. Every five minutes for a period of thirty minutes the frequency meter oscillator was retuned to zero beat. The results of the test are recorded in Table I.

When performing a titration, a harmonic of the frequency meter oscillator was adjusted to zero beat with the 120 mc. signal of the titrimeter oscillator after each increment of titrant had been added. The frequency stability for the combination of the two oscillators was

TABLE I

FREQUENCY STABILITY OF FREQUENCY METER OSCILLATOR*

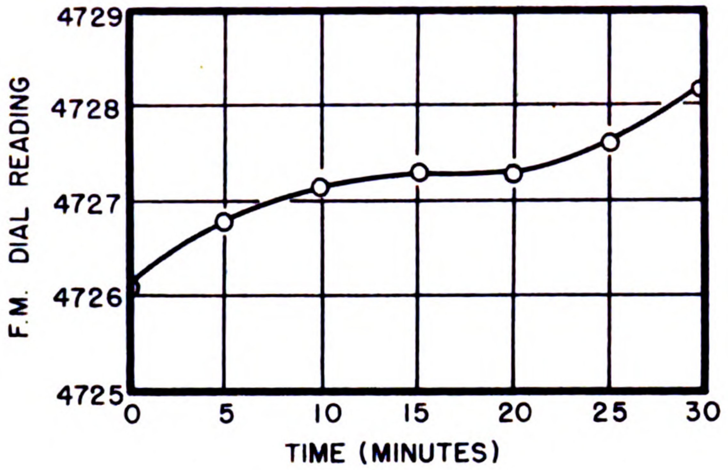
Time min.	Zero Beat Dial Reading	Frequency kc.
0	1375.9	5000
5	1375.9	5000
10	1375.9	5000
15	1375.8	4999
20	1375.8	4999
25	1375.8	4999
30	1375.7	4998

Maximum frequency drift: 2 kc. down

*WWV, National Bureau of Standards, 5000 kc. standard frequency

determined over a 30 minute period. Figure 23 is a plot of the results of this test.

It was observed in the course of the work that frequency drifting increased immediately upon inserting the filled titration vessel into position in the cell assembly. It was reasoned that temperature changes taking place in the solution was the cause of the increased frequency drift. The titration vessel containing a dilute sodium chloride solution in which was immersed the tip of a Beckman thermometer adjusted to the expected temperature range was installed into position in the titrimeter. The dial readings at zero beat on the



~2.3 FM Div/Kc

FIGURE 23. TITRIMETER FREQUENCY STABILITY AT 120 MC.

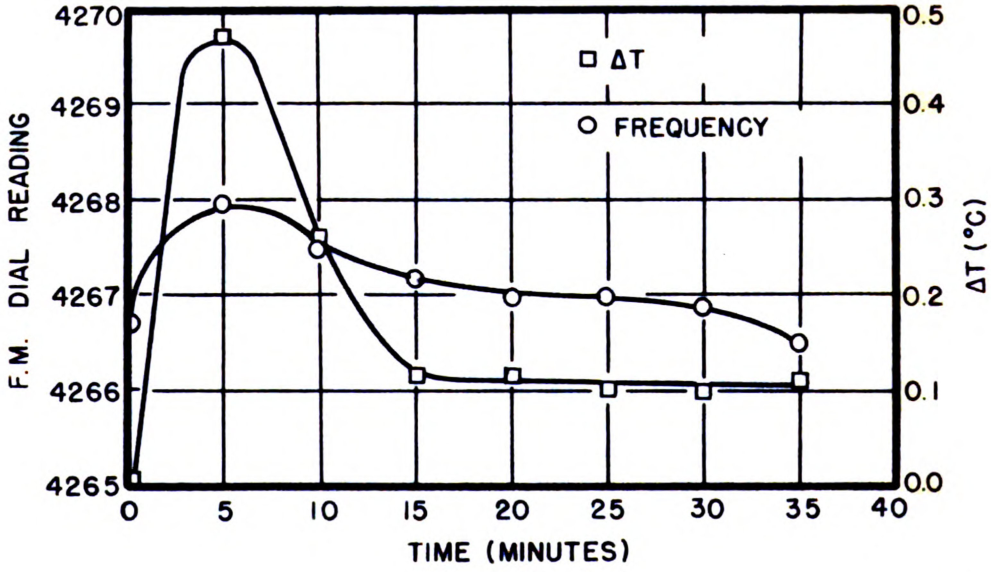


FIGURE 24. INFLUENCE OF SOLUTION TEMPERATURE CHANGES ON FREQUENCY.

frequency meter were recorded together with the temperature of the solution every five minutes for a thirty-five minute period. Figure 24 is a plot of the results. The results indicate that frequency drift is at a maximum when the change in the temperature of the solution is at a maximum. Obviously, temperature changes taking place in the solution are a source of frequency drift, but cease after approximately ten minutes have elapsed. Before beginning a titration the solution was allowed to stand for at least ten minutes to permit temperature equilibrium to be established.

The instrument responded to changes in liquid level and dilution as shown by the curves of Figure 25 and 26. Installation of the grounded ring in the upper shield assembly of the cell renders the instrument insensitive to changes in liquid level above the ring but has no effect on the response due to dilution. Re-examination of the curves of Figure 25 and Figure 26 shows that the effects oppose one another and within a certain volume range can be made to cancel each other. It was found that if titrations were carried out within the range of volume between 100 and 110 ml., the effects were for all practical purposes eliminated as indicated in Figure 27. The effect on an actual titration curve can be seen in Figure 45. It will be noted that in Figure 45 the initial slope of the lower curve is positive and the initial slope of the upper curve is very nearly zero. The lower curve of Figure 45 was obtained in the volume range 160 to 170 ml. and the upper curve in the volume range 100 to 110 ml.

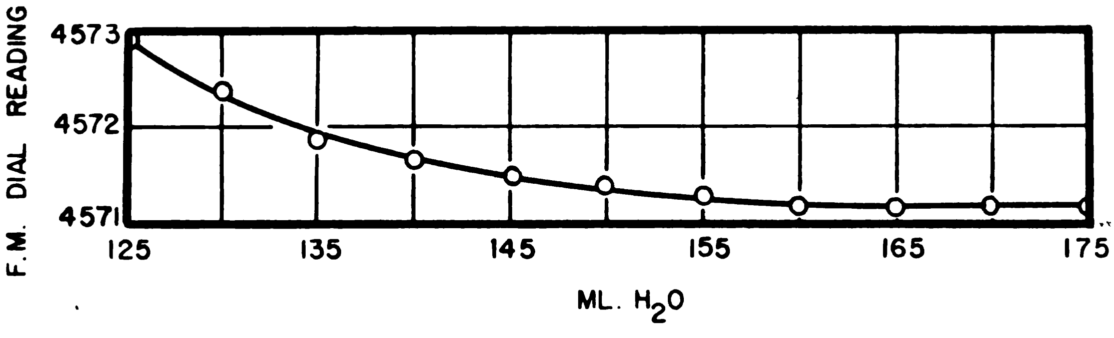


FIGURE 25. INFLUENCE OF CHANGES IN LIQUID LEVEL ON FREQUENCY.

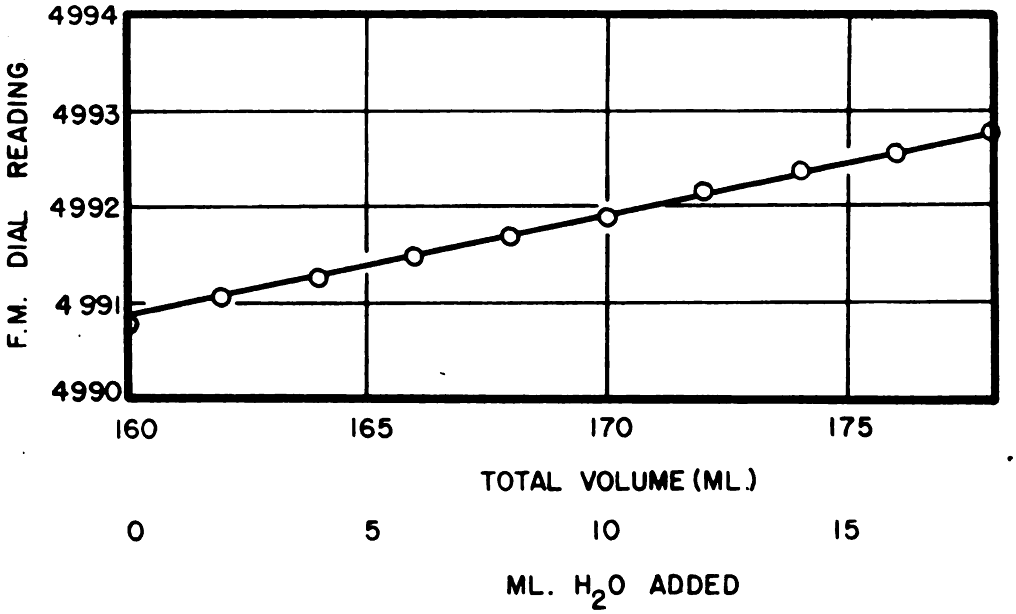


FIGURE 26. INFLUENCE OF CHANGES IN LIQUID LEVEL AND DILUTION ON FREQUENCY.

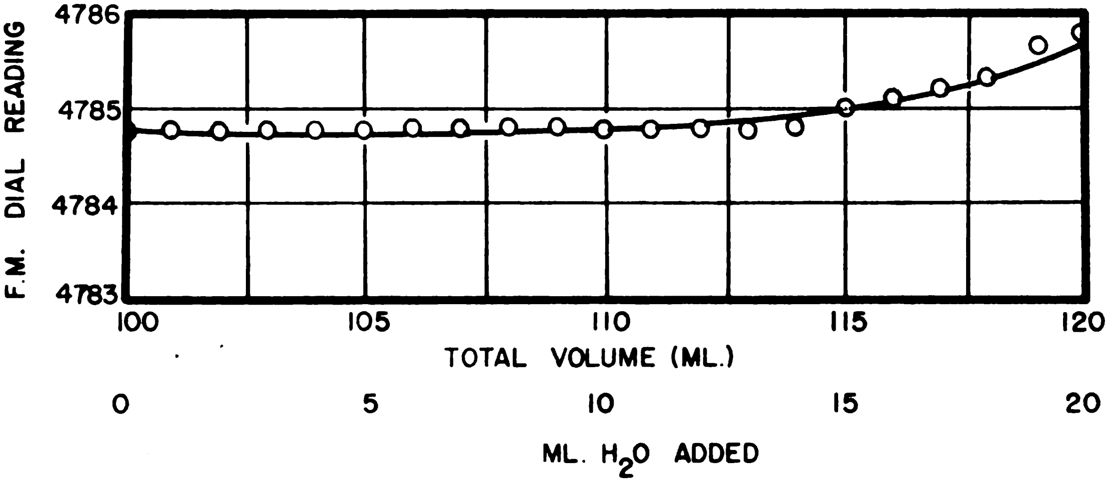


FIGURE 27. GRAPH SHOWING ELIMINATION OF RESPONSES DUE TO DILUTION AND CHANGE IN LIQUID LEVEL IN THE VOLUME RANGE 100 TO 114 ML.

A sensitivity or response curve was obtained to test the concentration range in which the instrument responds. The same technique as used by others was employed (2,3,4,7,19). Initially the vessel was filled with 125 ml. of distilled water. One ml. increments of a 1.0 N sodium chloride solution were added and the frequency changes recorded. The sensitivity curve, Figure 28, was obtained by plotting the frequency meter dial readings against the logarithm of the sodium chloride concentration. The curve is a typical one for frequency measuring instruments reported earlier by others (2,3,4,7,19).

It has been shown (2,3,4,7,19) that if the abscissa was the logarithm of the specific resistance of the sodium chloride solution instead of its concentration, the curve would apply to any aqueous electrolyte placed in the same cell at the same frequency, and it would be unnecessary to obtain response curves for more than one electrolyte. It follows, that the position of the midpoint of the curve on the abscissa and its slope is a function of the frequency, the cell parameters, the solvent, and the ionic strength of the solution (2,3,4,7,19).

It is evident that a titrimeter of this type has adequate sensitivity between certain limits that are fixed once the operating frequency and cell parameters are selected. To perform a successful titration under these conditions, the specific conductivity of the solution must be adjusted so that the endpoint will fall somewhere within the limits shown by the sensitivity curve.

The cell parameters are variable to a limited degree and are partially determined by the amount of loading the oscillator can

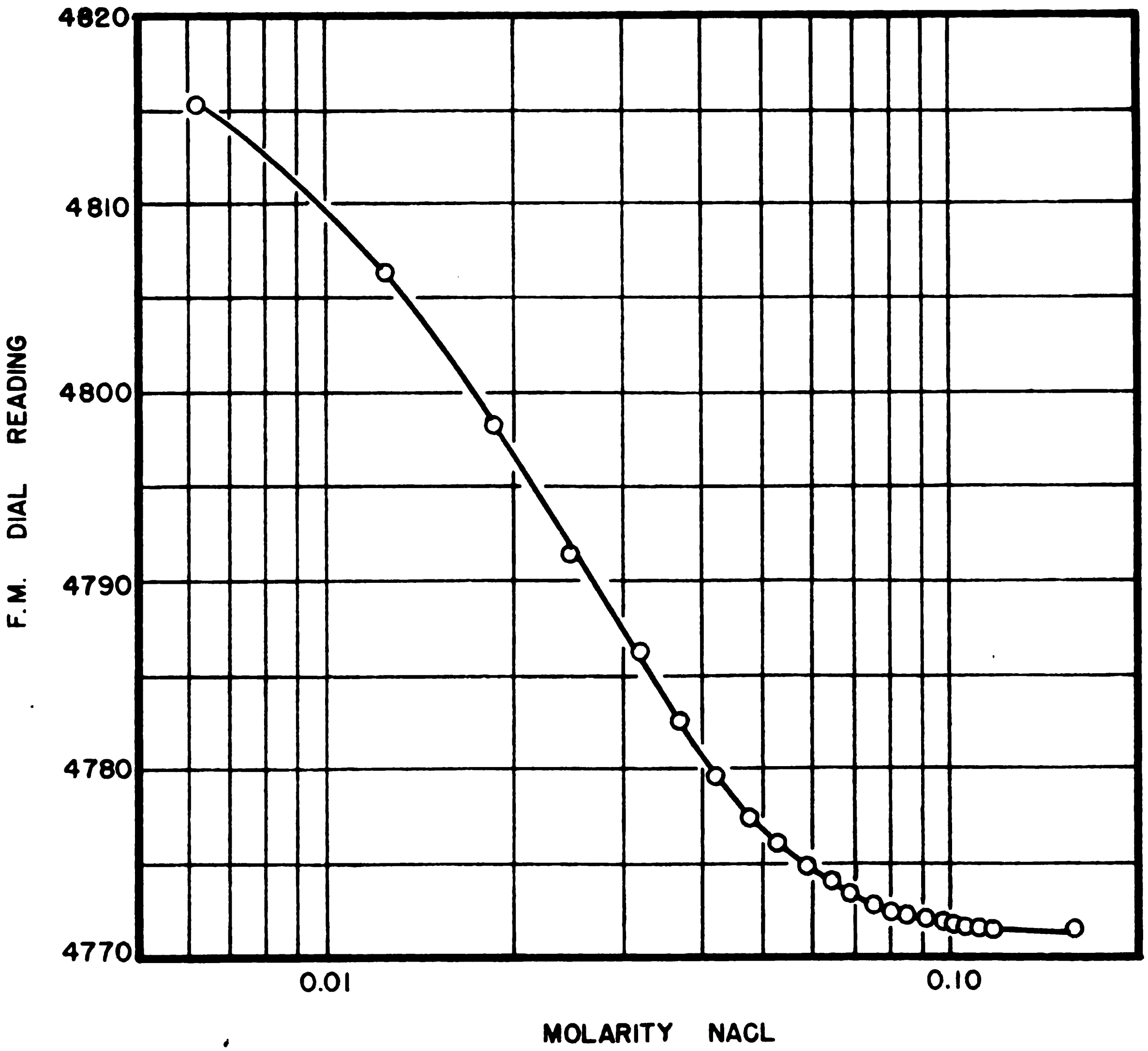


FIGURE 28. SENSITIVITY CURVE OF 120 MC. FREQUENCY MEASURING INSTRUMENT.

withstand and still maintain sustained oscillations and the total capacity permissible across the particular inductance in the parallel circuit (22,23). As the operating frequency is increased, sensitivity is extended to the regions of higher ionic strengths, but the area of the cell plates must be reduced accordingly which reduces the over-all sensitivity of the apparatus at the higher concentrations (19).

The cell of Figures 16 and 17 could be used up to 60 mc., but in order to utilize a frequency of 120 mc. the cell plate area had to be reduced to that shown in Figure 22.

The Wide Range Titrimeter*

Relatively few instruments had been constructed in which the solution was placed in a vessel in the field of the coil of a parallel resonant circuit. With a few exceptions (24) titrimeters utilizing the above principle were reconstructions of the instrument reported by Jensen and Parrack (10,16). Some workers experienced considerable difficulty in the application of the instrument to titrations (1,2,5). The concensus seemed to be that the instrument was unstable and easily went out of oscillation. It was reasoned that this erratic behavior was the result of large increases in the distributed capacity associated with the coil.

The Q of a parallel resonant circuit is decreased by an increase in distributed capacity much in the same way as it is reduced by an increase in the resistance reflected into it by an increase in load. Hence, when

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* U. S. patent application made.

a solution is placed within the field of a coil, the increased distributed capacity together with the normal increase in the series resistance of the circuit due to the conductivity of the solution, could result in such heavy power demands upon the oscillator that it would cease to function completely. This seemed to be a logical explanation for the difficulties experienced by some workers in the application of Jensen and Parrack's instrument.

It was observed that all of the instruments of the coil loaded type had low operating frequencies, consequently the coils employed were of the multiturn type which have associated with them relatively high values of distributed capacity. The distributed capacity is in shunt with the inductance, thus making the coil equivalent to a parallel resonant circuit having a natural resonant frequency. The natural resonant frequency sets an upper limit to the frequency at which the coil is useful in providing an inductive reactance (22). Inserting a solution of high dielectric constant within the coil should markedly affect the natural resonant frequency of the coil, and erratic behavior could be expected of any oscillator in which the parallel circuit was a circuit element.

In order to improve on instruments in which the solution to be titrated was placed within the field of the coil, some means of preventing or minimizing changes in distributed capacity had to be found.

As a starting point the inductance was reduced to a one turn loop constructed of 1/4 inch copper tubing to give it mechanical rigidity.

This construction reduced the distributed capacity to a minimum and the small amount associated with the loop was believed to be distributed mainly along the circumference of the loop. Further, it was reasoned that if the diameter of the titration vessel was substantially smaller than the diameter of the loop, the solution would be removed out of the range of the field of the distributed capacity of the loop, and changes in the dielectric constant of the solution would have relatively little effect.

With the design of the inductance fixed in this manner the operating frequency of the titrimeter would fall in the frequency range between 70 mc. and 100 mc. A harmonic of the fundamental of the BC-221-D frequency meter oscillator providing a suitable beat note in this range could not be found. For this reason the frequency meter was discarded and the instrument converted to one in which changes in solution composition were detected through changes in titrimeter oscillator grid current.

If the premise concerning distributed capacity was correct, the proposed design would make the response of the instrument mainly dependent upon changes in solution conductivity, and the problem of separating resistive and capacitive components eliminated. Hence, grid current readings would be truely indicative of conductivity changes, as should any changes in the operating frequency of the oscillator. Furthermore, any masking of conductivity changes by changes in dielectric constant would be eliminated resulting in an increase in sensitivity.

The loading on the oscillator was controlled by varying the volume of solution in the field of the loop. With solutions of higher conductivity this is accomplished by withdrawing the titration vessel vertically along the axis perpendicular to the plane of the loop. Loading could also be reduced by enlarging the diameter of the loop, which would be analogous to loosening the coupling between two tightly coupled circuits in a radio transmitter.

It seemed that the proposed design would extend the range of the titrimeter to more practical regions of conductivity, with the possibility of covering the range of fairly concentrated solutions.

It was found that the frequency measuring instrument could be easily converted to an instrument of the proposed design. A schematic of the instrument appears in Figure 29. The power supply circuit is shown in Figure 9. The details of the cell assembly appear in Figure 30.

The new cell assembly was attached to the chassis in the same position occupied previously by the capacity type cell. The loop leads were terminated in banana plugs and spaced to match the spacing of the insulated banana jacks in the side of the chassis that served as the terminals to the grid and plate of the 955 tube. The feedback and tuning capacitors C_1 and C_2 were short lengths of Amphenol RG-8/U coaxial cable and plugged into the female Amphenol receptacles mounted on the top of the chassis previously used for attaching the 120 mc. half wave line in place. These details are shown in Figures 14, 20, and 30.

Amphenol RG-8/U coaxial cable has a nominal capacity of 29.5 mmfd. per foot. Therefore, the length of coaxial cable used plus the small

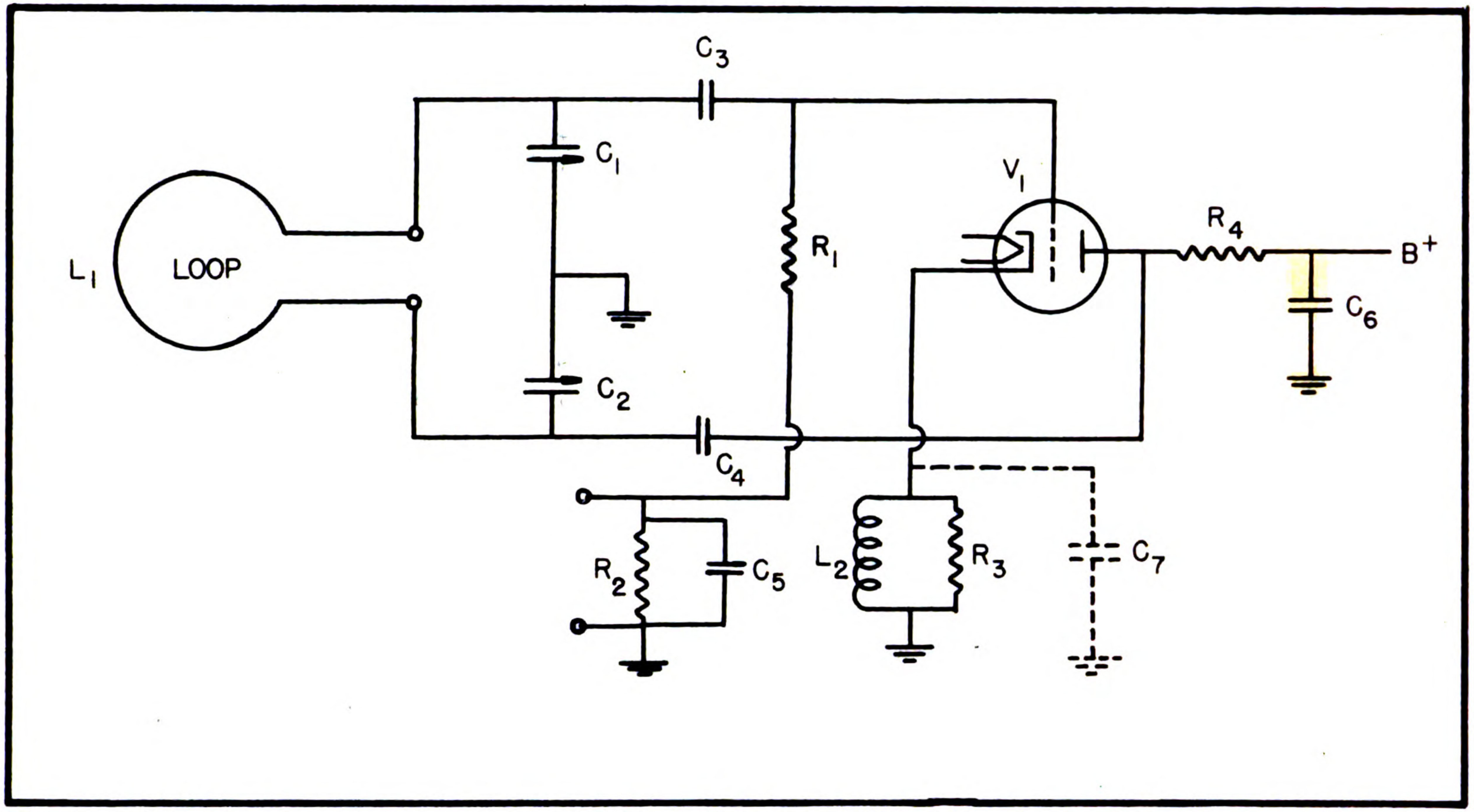

FIGURE 29. OSCILLATOR CIRCUIT OF WIDE RANGE TITRIMETER.

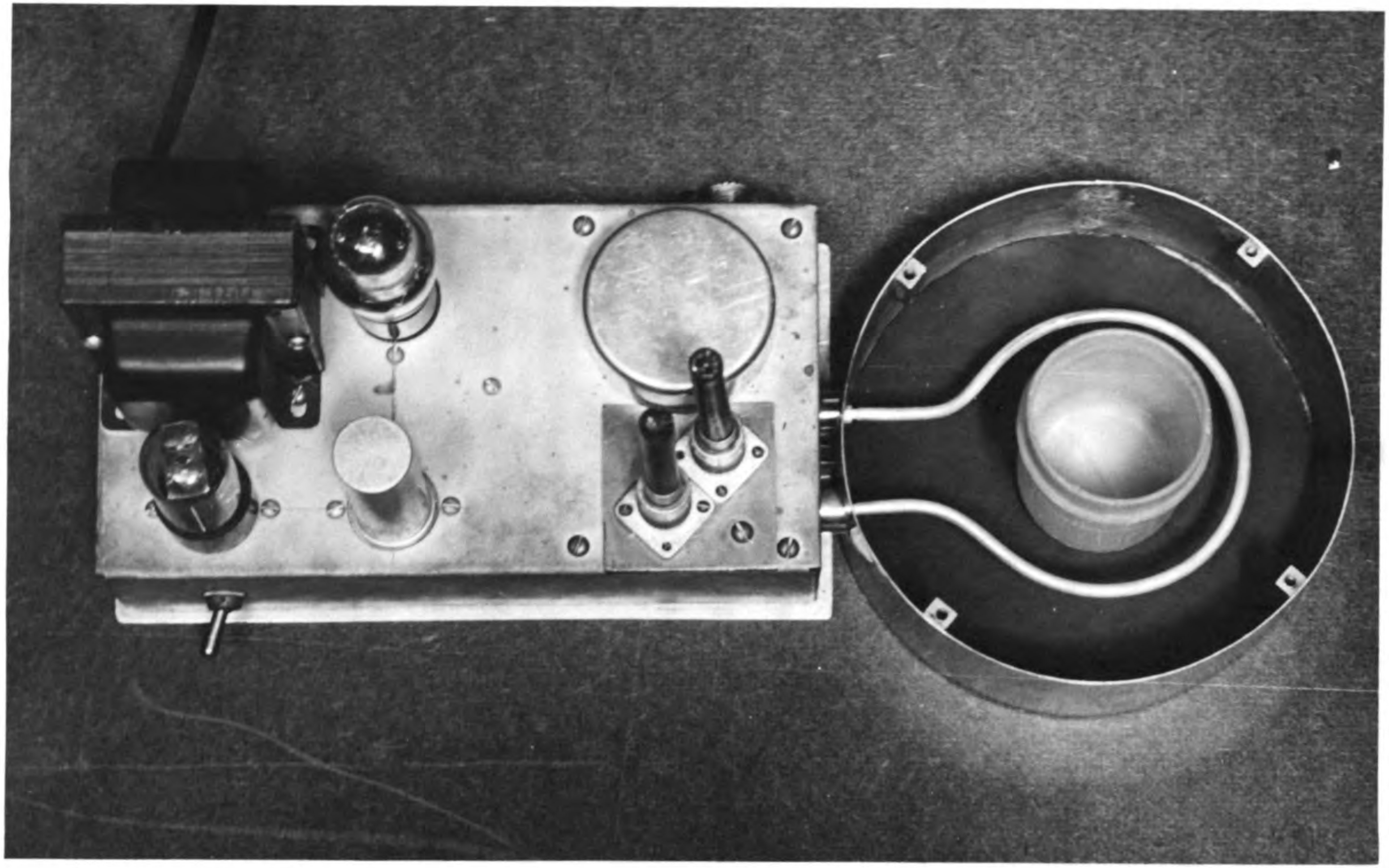

FIGURE 30. WIDE RANGE TITRIMETER WITH COVER REMOVED FROM CELL ASSEMBLY SHOWING TITRATION VESSEL IN POSITION IN LOOP.

amount of capacity associated with the Amphenol plugs and jacks determined the capacity of C_1 and C_2. Obviously a range of capacity was obtained simply by varying the length of the coaxial cable attached to the plug. By this means any ratio of C_1 to C_2 could be obtained to provide the proper feedback requirements as the situation demanded.

Since the total capacity in C_1 and C_2 was entirely between the inner and outer conductors of the coaxial cable and the outer conductor was grounded, C_1 and C_2 were completely shielded from outside influences. If the conventional type of tuning capacitor had been used, stray capacities would exist between the tuning capacitor, ground, and neighboring objects that would vary with temperature changes, vibration, and condenser setting. This variation in stray capacity would be a source of oscillator instability, and would be particularly serious at the operating frequencies of 70 mc. and above. The polyethylene dielectric separating the inner conductor from the outer conductor in the coaxial cable has a dielectric constant of 2.29 and a power factor of 0.0004 at all frequencies from 60 cycles up to 100 mc. per second, a water absorption of 0.005 per cent, a softening temperature between 103 and 105 degrees Centigrade. The mechanical stability of the coaxial cable is excellent and the outer protective vinyl covering is nonhygroscopic and impervious on exposure to acids, alkalies and oils (18). All of the above desirable properties of the coaxial cable and the rigid construction of connectors, brackets, plates, etc., contributed greatly to the electrical and mechanical stability of the titrimeter.

In order to facilitate the measurement of changes in the grid current of the oscillator, a 1000 ohm resistor was inserted in series with the grid-leak resistor. The terminals of the 1000 ohm resistor were brought out to two banana jacks mounted on one side of the chassis, providing a convenient and positive connection to the grid current meter.

The Sargent Model XXI Polarograph was adapted for the measurement of oscillator grid current. By inserting the standard 290,000 ohm resistor supplied with the instrument in one of the dropping mercury electrode lead jacks, the unit performed as a potentiometer. The principle is illustrated in Figure 31. The leads normally connected to the dropping mercury electrode assembly plugged in the second jack of the polarograph, were connected to the terminals of the 1000 ohm resistor in series with the grid-leak resistor. A part of the grid bias developed by the oscillator appears at the terminals A and B and was usually less than 0.20 volts. With a span voltage of one volt on the polarograph any voltage between zero and one volt could be placed across the standard resistor by an adjustment of the bridge control.

If the potential across the standard resistor was equal to the bias developed across the 1000 ohm resistor no current would flow in the circuit made up of the 1000 ohm resistor, the leads A and B and the standard resistor. If the bias developed by the oscillator changed, current would begin to flow in the circuit in a direction dependent on whether the bias was greater or less than the percentage of the polarograph span voltage applied to the standard resistor.

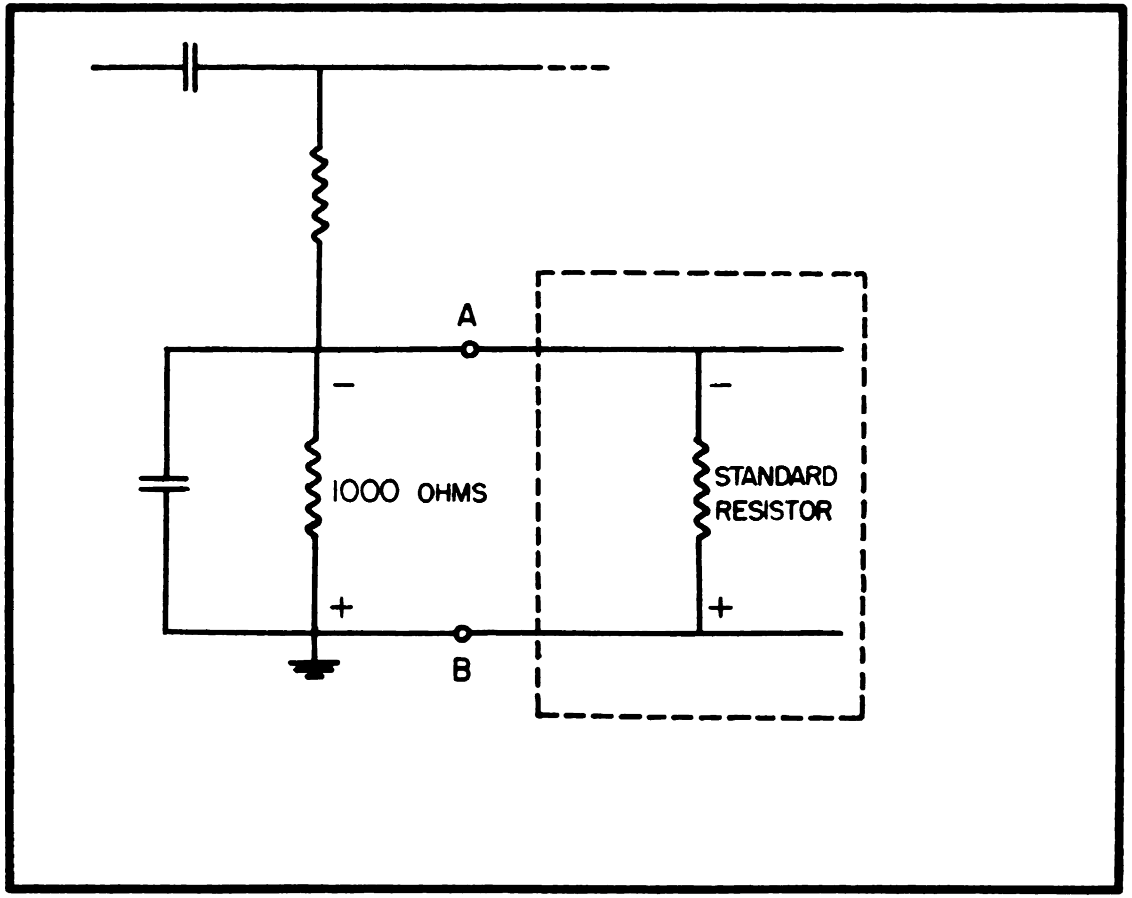

FIGURE 31. GRID CURRENT MEASURING CIRCUIT.

The scale of the current measuring meter of the polarograph is 280 mm. in length. Twenty values of current measuring sensitivity ranging from 0.003 microamps per mm. to 1.500 microamps. per mm. can be selected by means of a twenty position switch. After performing a few exploratory titrations a sensitivity could be selected with which the current changes encountered in the course of a titration covered the entire 280 mm. length of the recorder scale.

Sensitivity curves were obtained for the titrimeter by the same procedure previously used in connection with the frequency measuring instrument. The curves appear in Figures 32 and 33 and the corresponding instrument adjustments appear in Table II.

In obtaining the curves two loops of different diameters were employed. Various combinations of C_1 and C_2 and vessel position were also used. As shown in Figure 34, vessel position one indicates a maximum volume of solution was within the field of the loop. In vessel position two, Figure 35, a smaller volume of solution was in the field of the loop since the vessel had been withdrawn by an amount equal to the width of the ring that had been inserted between the lip of the vessel and the ring attached to the aperture in the top of the shield assembly of the cell.

A point of interest in connection with the curves is that in order to reach the more concentrated ranges, the loop diameter was increased, resulting in a lowered operating frequency. In all titrimeters previously reported, in order to extend their range of sensitivity to regions

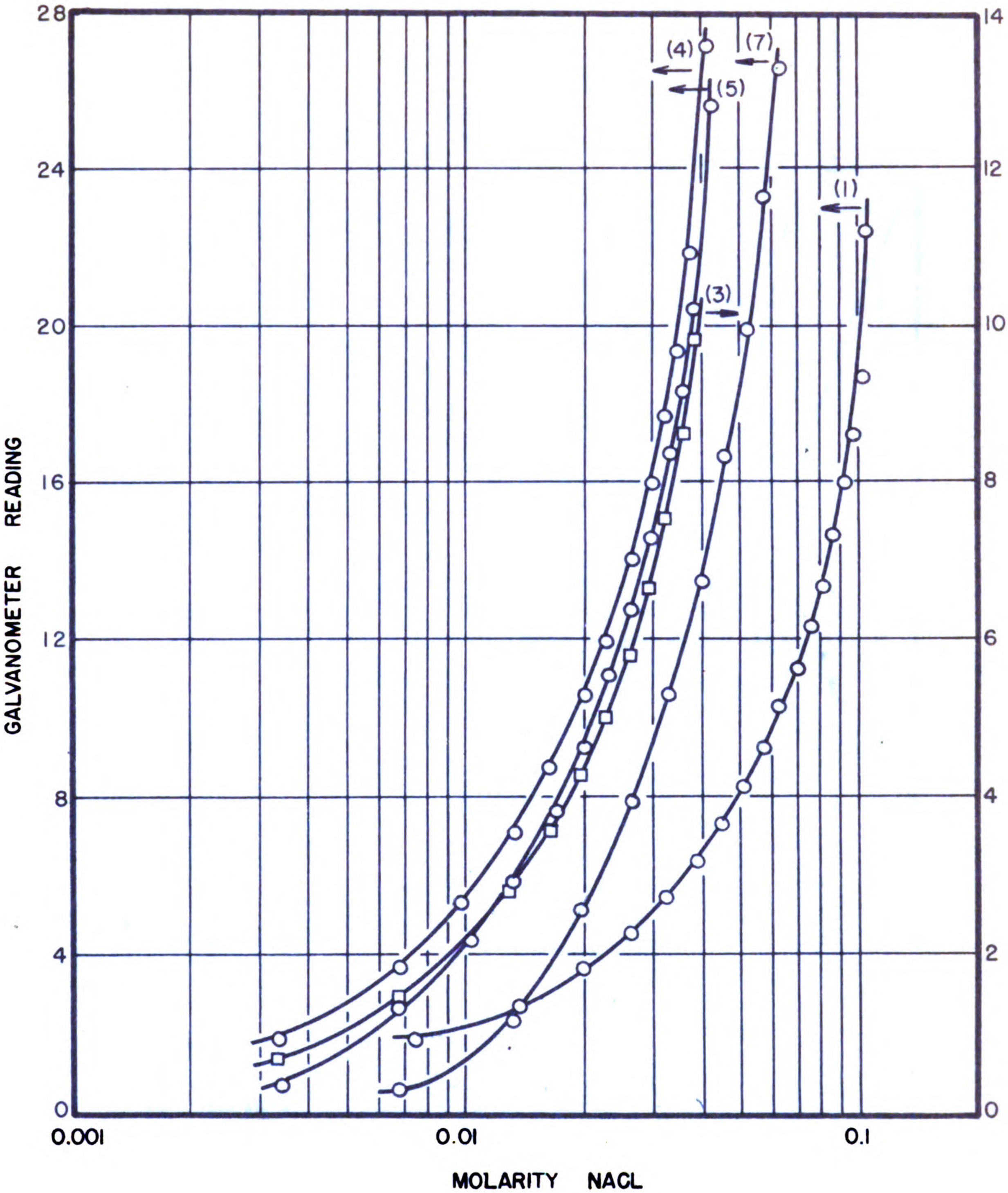

FIGURE 32. WIDE RANGE TITRIMETER SENSITIVITY CURVES.

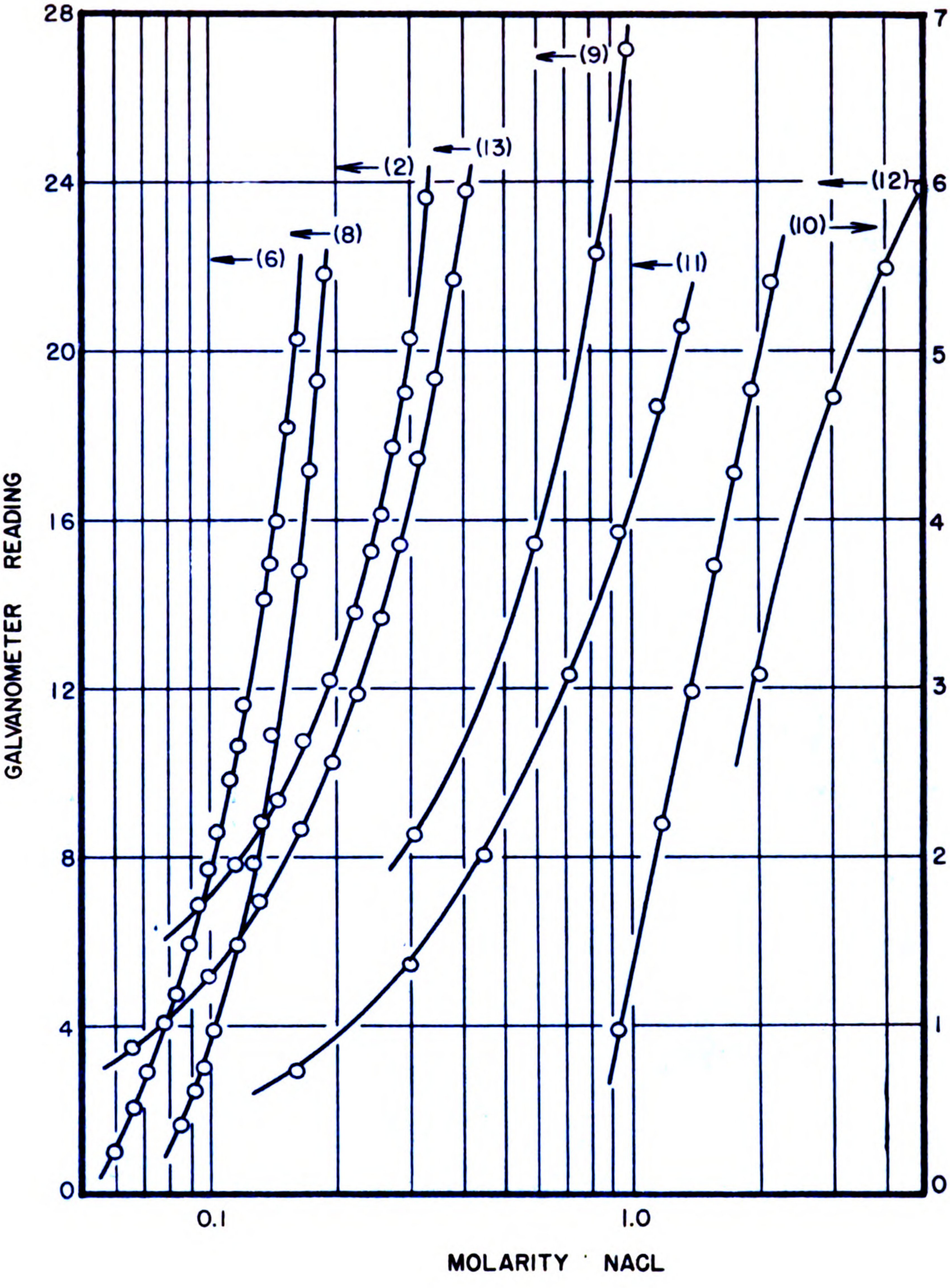

FIGURE 33. WIDE RANGE TITRIMETER SENSITIVITY CURVES.

TABLE II

WIDE RANGE TITRIMETER ADJUSTMENTS PERTAINING TO SENSITIVITY CURVES*****

Curve Number	C_1*	C_2*	Loop**	Frequency (mc.)	Vessel Position***	Sensitivity (μa/mm.)	Bridge Setting (% of 1 v. span)
1	2	1	2	88	1	0.15	8.5
2	2	1	2	88	2	0.15	8.5
3	2	3	2	83	1	0.15	8.0
4	2	3	2	83	1	0.06	6.5
5	3	5	2	90	1	0.06	7.0
6	5	2	2	94	2	0.06	7.2
7	5	2	2	94	1	0.06	8.8
8	5	2	2	94	2	0.06	7.7
9	2	1	1	82	1	0.15	14.0
10	2	1	1	82	2	0.15	13.2
11	2	1	1	82	2	0.06	12.9
12	2	1	1	82	2	0.06	10.4
13****	2	1	1	82	1	0.40	30.6

* Capacitor	Length of Coaxial Cable (See Figure 15)
1	10 cm.
2	11 cm.
3	19 cm.
5	male connector only

** Loop	Diameter
1	10 cm.
2	7.5 cm.

*** Vessel Position. Refer to Figure 34 and 35. In vessel position 2 the titration vessel is raised and supported on a ring 2 cm. in width.

**** Refer to Figure 29. L_2 and R_3 short circuited by connecting cathode directly to ground.

***** Curves 1, 2, 3, 5, 6, 8, and 13 were terminated at the point of completely damped oscillations.

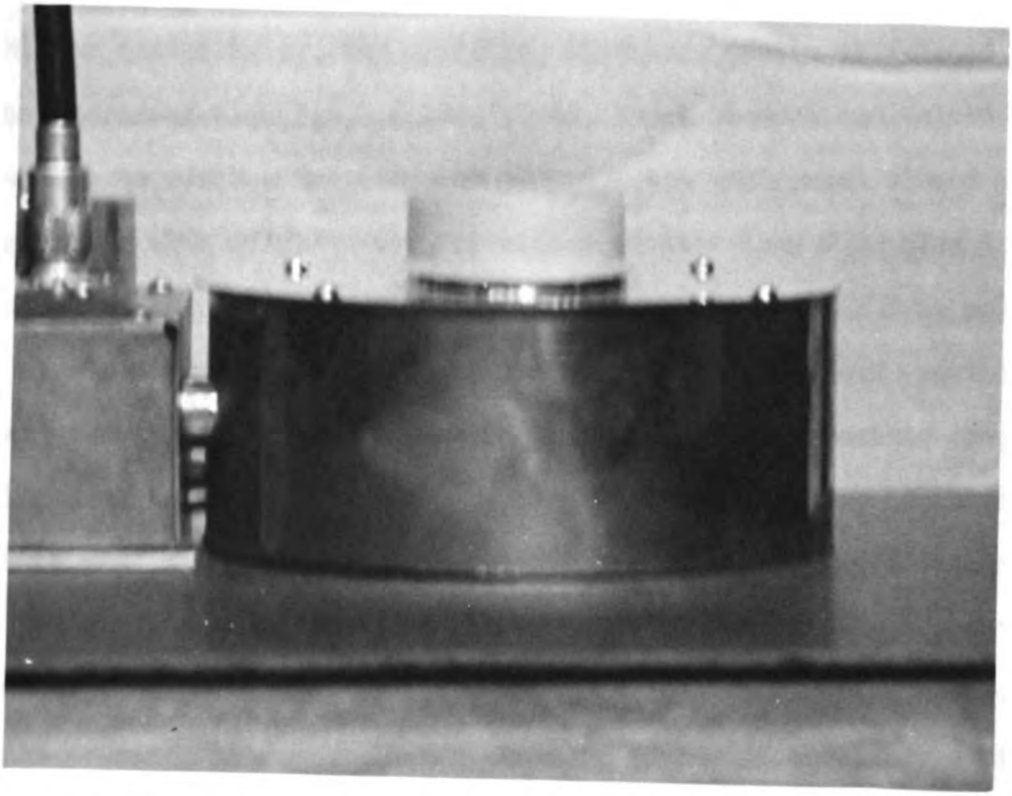

FIGURE 34. VESSEL POSITION ONE.

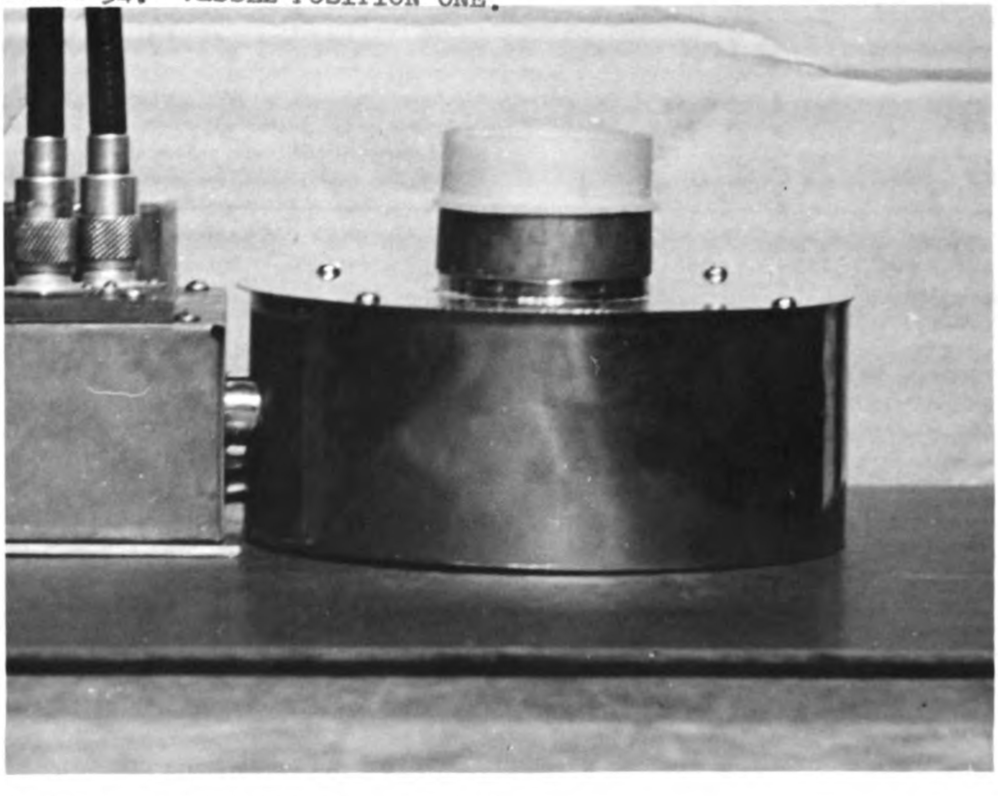

FIGURE 35. VESSEL POSITION TWO.

of higher conductivity, the operating frequency of the oscillator had to be increased (1,2,3,6,7,8,19). Even though Blaedel and Malmstadt (3) were able to reach a frequency of 350 mc., the instrument showed no sensitivity with solution concentrations greater than 0.3 molar in terms of sodium chloride or 0.1 molar in terms of hydrochloric acid. The same authors (3) were able to vary the loading on their oscillator by adjustment of vessel position in the end of the concentric line employed at the above frequency, but only the sensitivity of the instrument to changes in solution composition was reduced. The adjustment did not shift the region of maximum sensitivity for higher concentrations of sodium chloride or hydrochloric acid. Withdrawing the vessel in the present instrument lowers the sensitivity of the instrument somewhat, but at the same time extends the range of the instrument to higher conductivity regions. Thus it appears that in the present instrument, operating frequency is of little significance and any region of conductivity may be reached by varying loop diameter, vessel position, or feedback. The operating frequency of the oscillator is the frequency assumed by the oscillator with the particular dimension loop and tuning capacity selected in order to work in a specific range of conductivity.

The combinations of loop, vessel position and feedback capacity used in obtaining the sensitivity curves by no means exhaust the possibilities. Intermediate curves could be obtained with intermediate values of cell parameters.

Curve 12 shows a curvature which suggests that a point of inflection had been reached, but the curvature is believed to be due to the manner in which the data for the points on the curve were obtained. Instead of adding electrolyte to the solution in the vessel, the vessel was first filled with 5 molar sodium chloride solution and distilled water added in measured portions until the solution was 4 molar. At this point the vessel was filled to capacity. The vessel was removed after recording the initial and final recorder readings and a portion of the solution removed permitting further dilution. The original position of the vessel in the cell assembly was not perfectly reproducible. This could account for the curvature observed.

As indicated in Table II, some of the curves were terminated at the point of completely damped oscillations which was due to excessive loading.

How the shape of a titration curve is affected by the concentration at which the titration is carried out may be predicted from the sensitivity curves and has been adequately discussed by others (2,3,4,7,19). The wide range titrimeter is unique insofar as theoretically an infinite number of sensitivity curves are available through adjustments of vessel position, loop diameter, lengths of C_1 and C_2, and ratio of C_1 to C_2, so that excessive curvature or reversal of titration curves as different concentrations of sample and titrant are used can be eliminated by a proper adjustment of the titrimeter.

The voltage impressed across the 1000 ohm resistor in series with the grid-leak resistor by the polarograph places a small amount of fixed bias on the oscillator. The effect of varying amounts of fixed bias on the sensitivity curves is shown in Figure 36. An increased bias reduces the shope of the sensitivity curve slightly. The effect shown in Figure 36 resulted from a 100 per cent increase in bias. Ordinarily, variations in fixed bias are less than 10 per cent. Therefore, it may be assumed that adjustments of the bridge control on the polarograph have a negligible effect on sensitivity curves.

The instrument responded to changes in liquid level as shown by Figure 37. Data for the curve were obtained by adding measured increments of 0.25 molar sodium chloride to an initial volume of 90 ml. of 0.25 molar sodium chloride. When the liquid level is above the grounded band in the top of the cell shield assembly, the instrument no longer responds to changes in liquid level.

The effects of changes in liquid level and dilution were checked by adding distilled water in measured increments to 75 ml. of 0.25 molar sodium chloride. The effects were found to oppose one another which accounts for the maximum in the curve of Figure 38.

A Modification of the Wide Range Titrimeter

The 120 mc. line employed with the frequency measuring instrument was substituted in the place of C_1 and C_2 and the magnitude of the grid bias indicated that the oscillator was oscillating vigorously with C_7, shown in Figure 29, in the circuit. The sensitivity curves of Figures 39 and 40 were obtained utilizing the 120 mc. line and a line

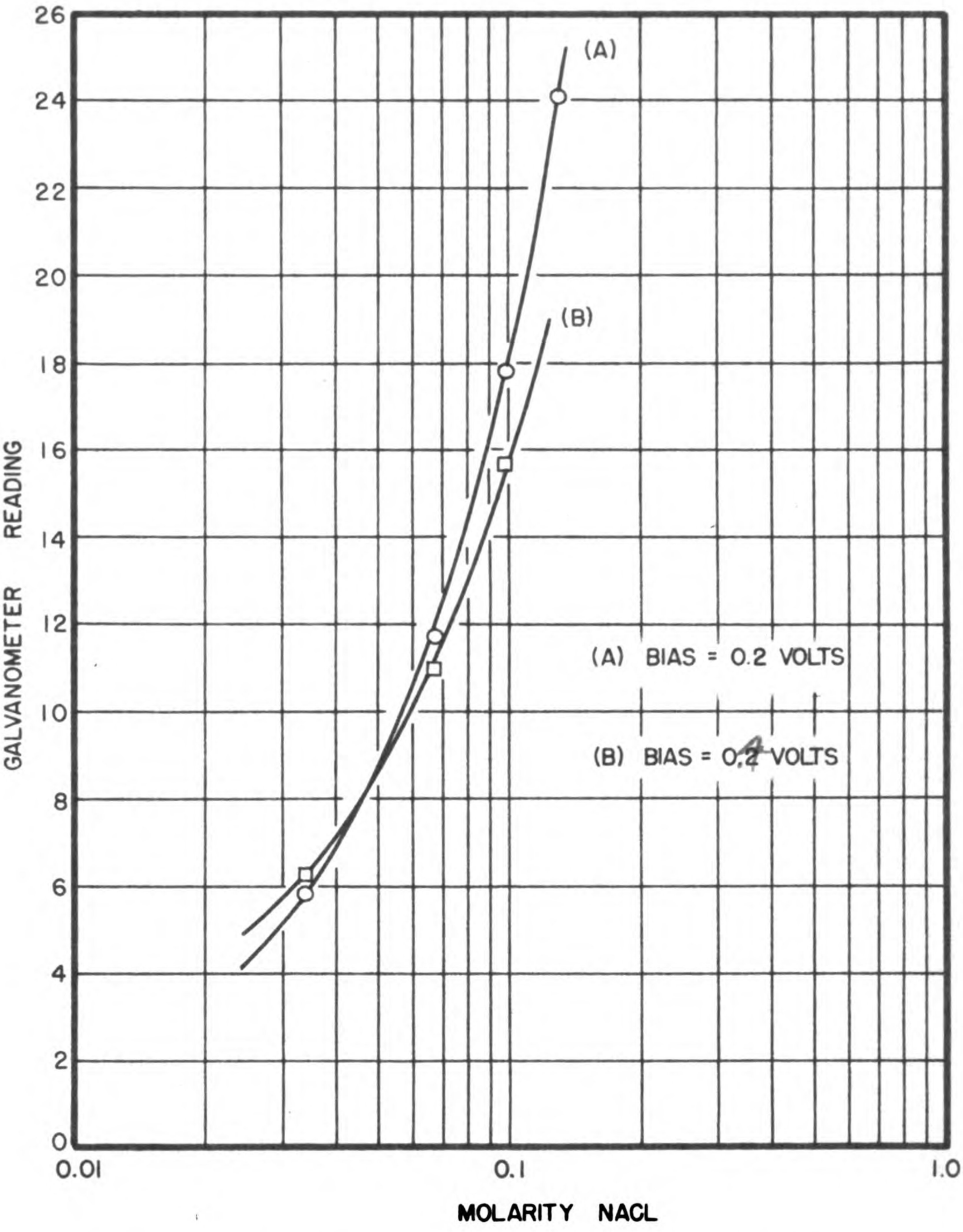

FIGURE 36. EFFECT OF FIXED BIAS ON SENSITIVITY CURVES.

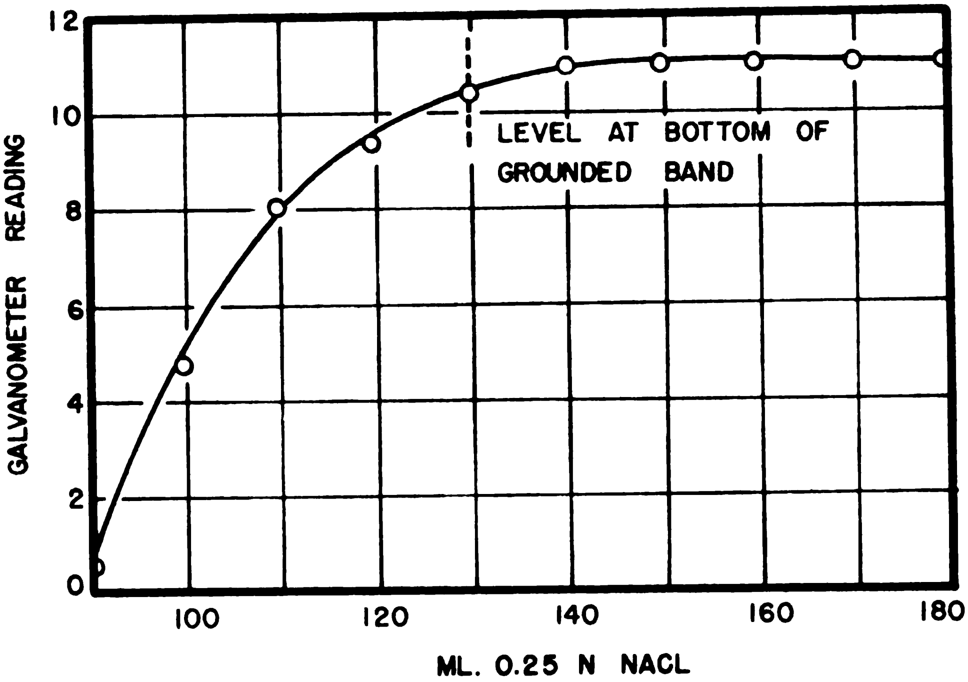

FIGURE 37. RESPONSE OF WIDE RANGE TITRIMETER TO CHANGES IN LIQUID LEVEL.

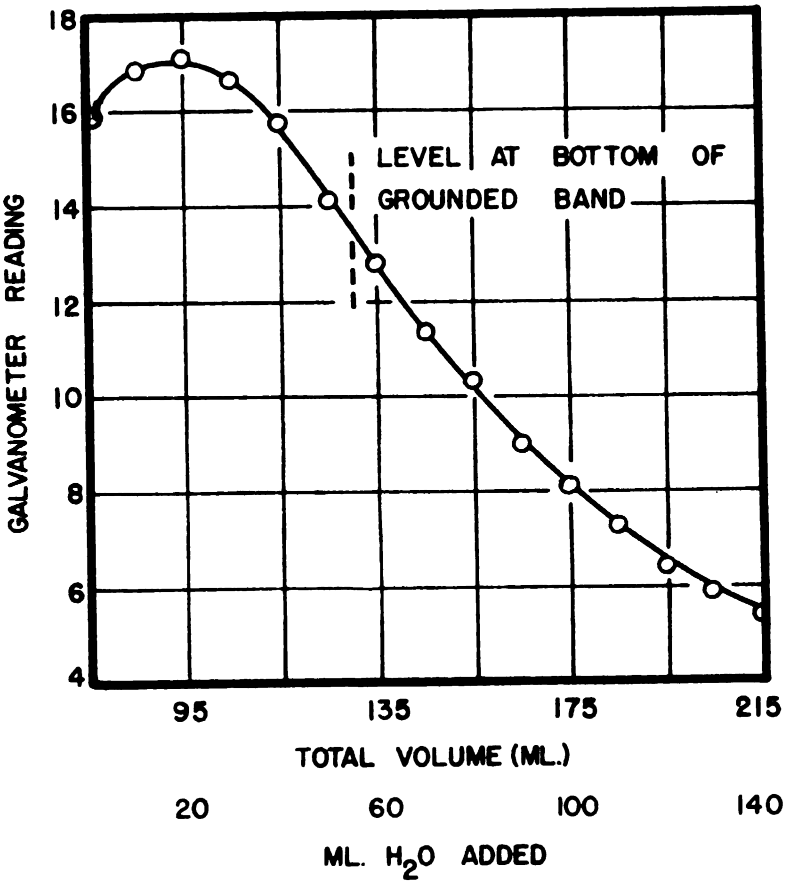

FIGURE 38. RESPONSE OF WIDE RANGE TITRIMETER TO CHANGES IN LIQUID LEVEL AND DILUTION.

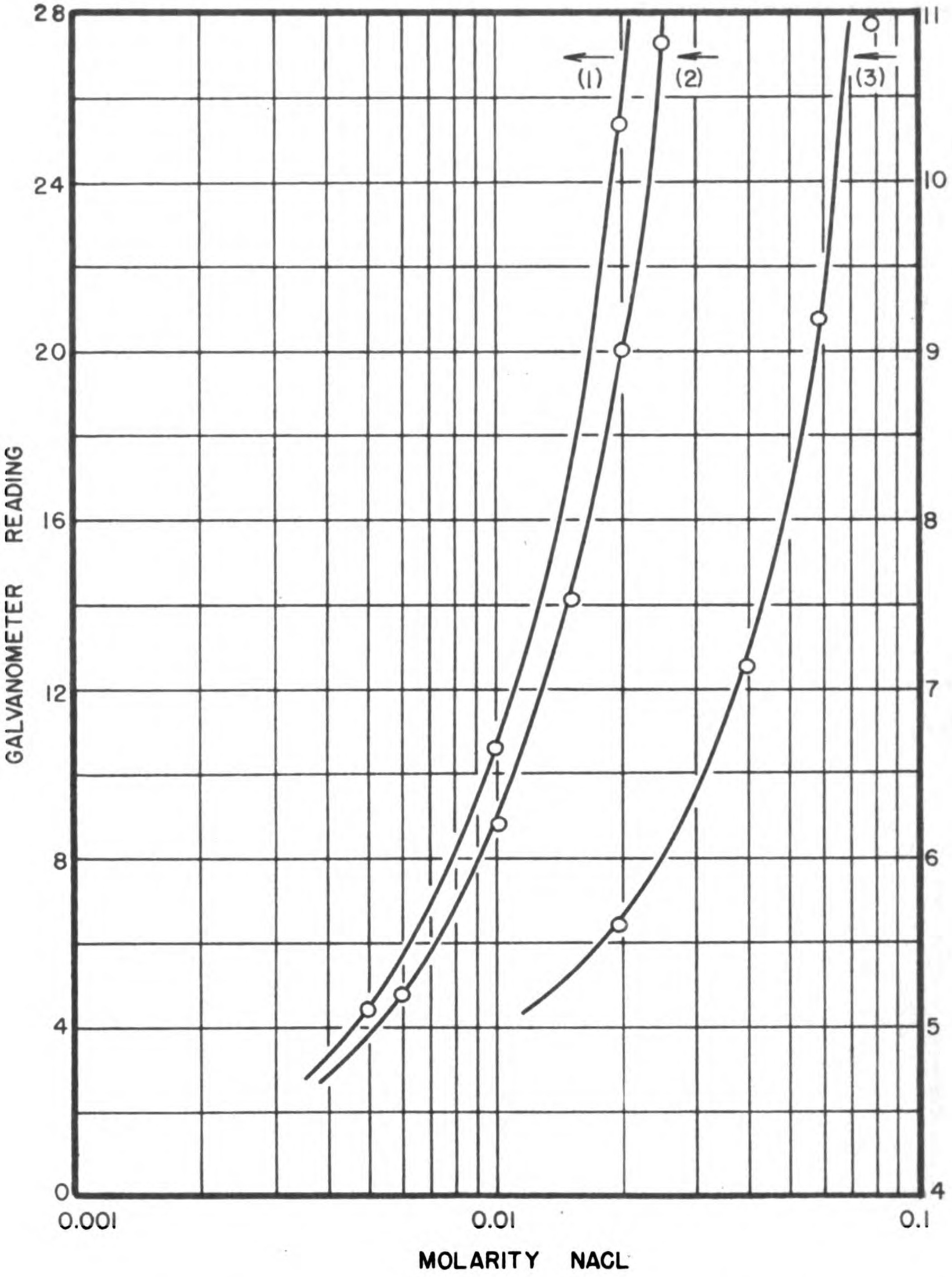

FIGURE 39. SENSITIVITY CURVES OF MODIFIED WIDE RANGE TITRIMETER.

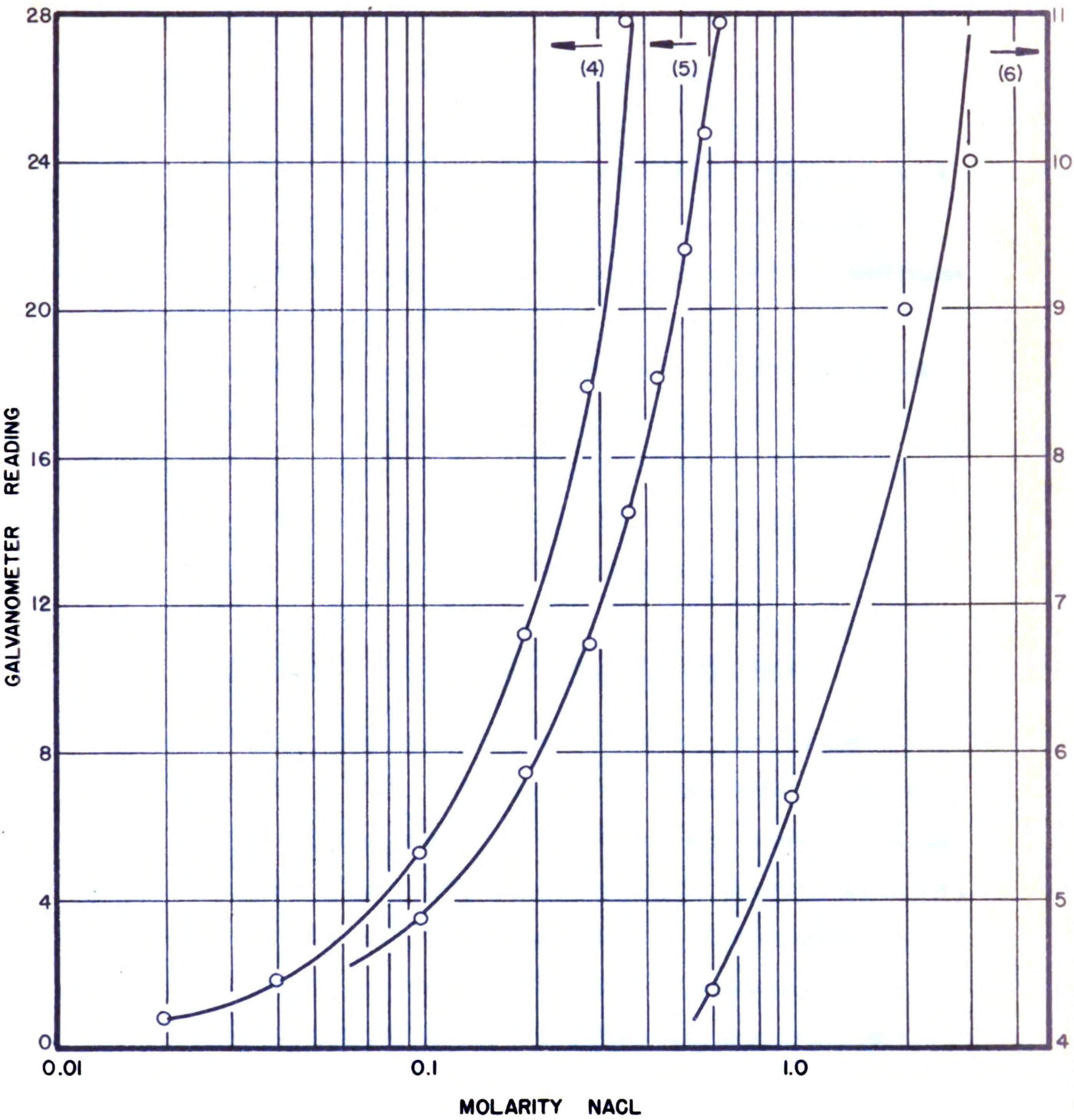

FIGURE 40. SENSITIVITY CURVES OF MODIFIED WIDE RANGE TITRIMETER.

approximately one-third longer. The sensitivity curves are similar to those obtained with the wide range instrument and the data pertaining to the curves are given in Table III.

The mode of oscillation was not definitely established, but it is believed that it is similar to the mode of oscillation in a ring oscillator, which suggests that a titrimeter may possibly be constructed using a conventional ring oscillator.

The frequency of the oscillator was monitored as electrolyte was added to distilled water in the vessel and the operating frequency of the oscillator increased with increasing conductivity. In all other titrimeters, including the wide range titrimeter previously discussed, the frequency decreased with increasing conductivity.

Titrations With Frequency Measuring Instrument

All electronic apparatus was warmed up for two hours before use. A measured volume of sample to be titrated was transferred to the vessel and diluted to a minimum total volume of 100 ml. with a measured volume of distilled water. The vessel was inserted in the field of the plates, a motor driven paddle stirrer introduced and the solution stirred for ten minutes to attain temperature equilibrium. The frequency meter oscillator was adjusted to zero beat with the instrument oscillator. The dial reading of the frequency meter was recorded. Increments of reagent were added from a 50 ml. or 10 ml. buret, as the situation required, and the frequency meter restored to zero beat after each

TABLE III

ADJUSTMENTS OF MODIFIED WIDE RANGE TITRIMETER PERTAINING TO SENSITIVITY CURVES

Curve Number	Loop*	Line**	Frequency (mc.)	Sensitivity (μ-a/mm.)	Bridge (% Span)	Vessel Position***
5	1	1	91	0.15	11.2	1
6	1	1	91	0.15	17.0	4****
4	1	2	103	0.15	10.8	1
3	2	1	95	0.15	10.8	1
2	2	2	108	0.06	8.8	2
1	2	2	108	0.06	8.8	1

* Refer to Table II

** Line 1 117.5 cm. RG8/U Coaxial Cable
Line 2 85.0 cm. RG8/U Coaxial Cable

*** Refer to Table II

**** Vessel raised 3 cm.

increment had been added. The titration was carried beyond the equivalence point. The frequency meter dial readings were plotted against ml. of reagent added. Curves were drawn through the points. The equivalence point was read at the point where two curves intersected.

Preliminary qualitative titrations of hydrochloric acid and sulfuric acid with sodium hydroxide were carried out to test instrument performance at 12.2 mc. A standard solution of phosphoric acid was then titrated with sodium hydroxide at this frequency.

Other neutralization reactions were carried out at 38.8, 60, and 120 mc. The results are listed in Table IV and VI.

A series of precipitation reactions were carried out at 120 mc. The results are listed in Table V and VII.

Titrations With the Wide Range Titrimeter

The titrimeter oscillator and polarograph A. C. circuit was warmed up for two hours or longer. A measured volume of sample was prepared for titration by dilution with a measured volume of distilled water to a minimum total volume of 150 ml. The titration vessel was lowered into the field of the loop and adjustments made to the apparatus according to the procedure given below. After these adjustments had been made, a motor driven glass paddle stirrer was installed in position, increments of titrant were added, recorder readings taken, and the ml. of titrant added plotted against recorder readings. Curves were drawn through the points and the equivalence point read at the intersection of the curves.

An illustration of the arrangement of the apparatus is shown in Figure 41. The titrimeter was connected to the 110 volt A. C. power line through a Sola constant voltage transformer to minimize fluctuations in line voltage.

Procedure for the Proper Adjustment of the Wide Range Titrimeter

The 7.5 cm. loop and the 10 cm. lengths of C_1 and C_2 are plugged into their respective positions in the titrimeter. The selector switch of the Heathkit vacuum tube voltmeter is turned to the D. C. minus position, and the range switch to the three volt scale. The common lead of the voltmeter is connected to the chassis of the titrimeter and the D. C. lead connected to the grid of the 955 tube. A ground lead is connected from the chassis of the titrimeter to the same ground connection used for the polarograph external ground placing the chassis of both instruments at the same potential. If this is not done, erratic operation of the recorder results.

The D. M. E. leads from the polarograph are connected to the color coded banana jacks on one side of the titrimeter chassis. The positive D. M. E. lead is connected to the red jack and the negative lead to the black jack. With this connection of the D. M. E. leads, the D. M. E. switch is switched to the minus position. No damping of the polarograph circuit is used, i.e., damping switch turned off.

Before the vessel is lowered into the field of the loop, the grid bias indicated on the vacuum tube voltmeter should be approximately

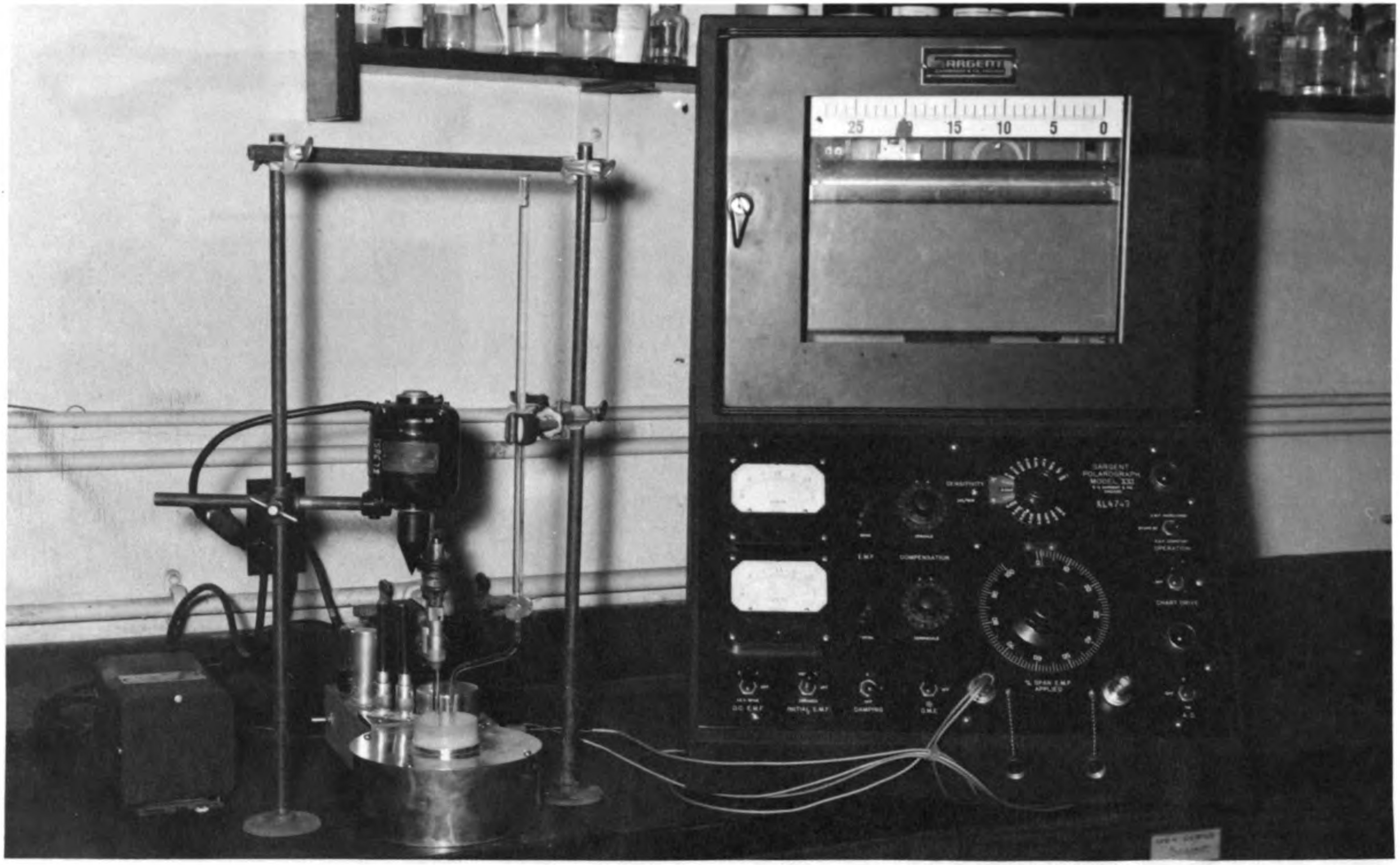

FIGURE 41. WIDE RANGE TITRIMETER, POLAROGRAPH, AND ASSOCIATED APPARATUS SET UP FOR TITRATIONS.

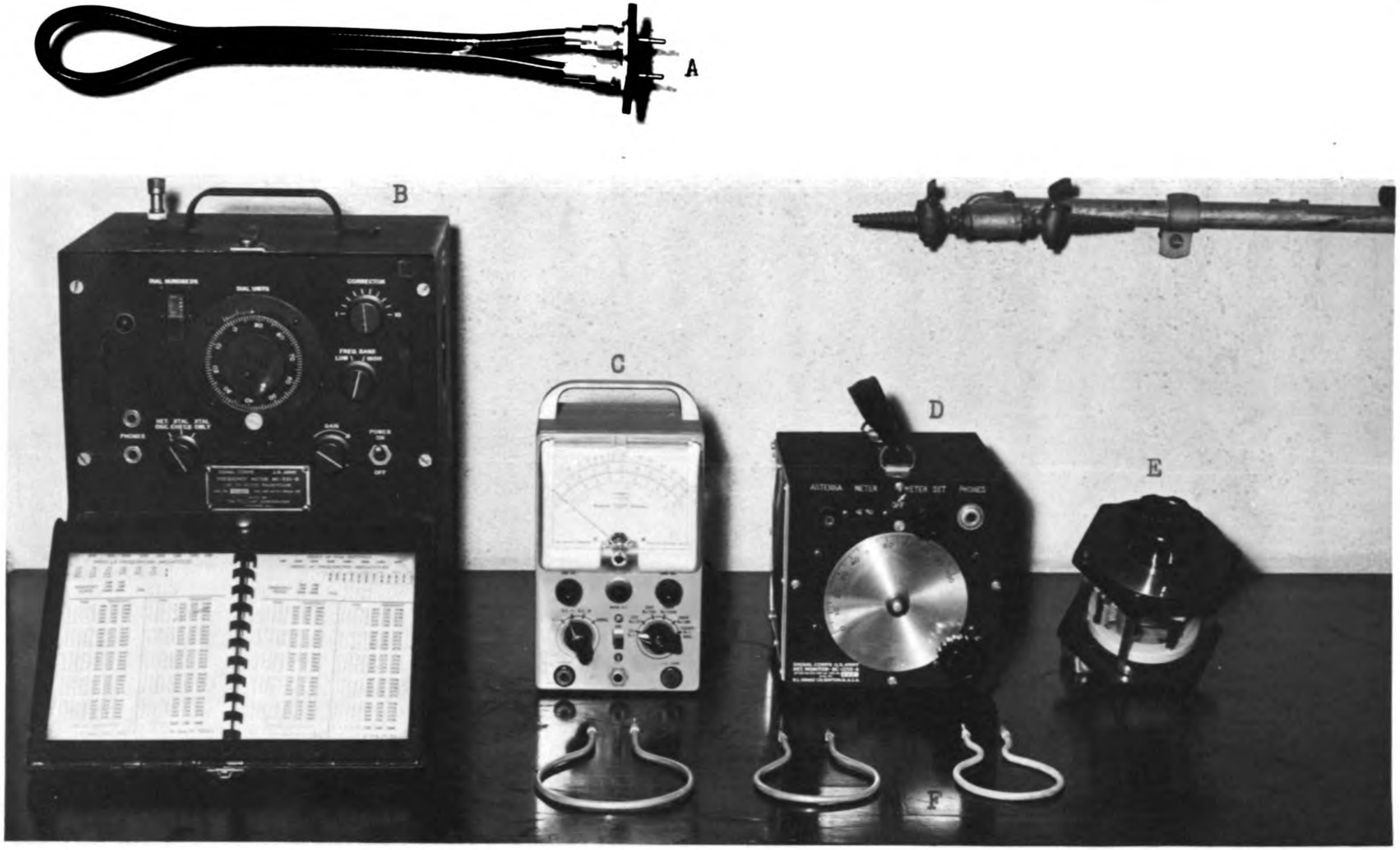

FIGURE 42. (A) 120 mc. HALF WAVE LINE; (B) BC-221-D FREQUENCY METER; (C) HEATHKIT MODEL V-5 VACUUM TUBE VOLTMETER; (D) BC-1255-A HETERODYNE FREQUENCY MONITOR; (E) GENERAL RADIO MODEL 758-A WAVE METER; (F) LOOPS 1, 2, AND 3 FOR WIDE RANGE TITRIMETER.

1.2 volts. If the voltmeter indicates a bias of approximately 0.6 volts, the oscillator is out of oscillation and is in need of servicing.

The vessel containing the sample to be titrated is slowly lowered into the field of the loop and the grid bias voltage changes on the vacuum tube voltmeter observed. As the vessel is lowered into the field of the loop, the solution begins to absorb energy from the tank circuit of the oscillator which shows up as a decrease in grid bias. As the vessel is lowered slowly into the field of the loop the grid bias voltage decreases gradually, and will be at a minimum when the vessel is at its lowest point, i.e., vessel position one of Figure 36. If in the course of lowering the vessel into the field of the loop a sudden decrease in grid bias is observed, usually in the vicinity of 0.7 volts, and the voltmeter indicates a steady value of approximately 0.6 volts upon further lowering of the vessel, the solution is too concentrated and is overloading the oscillator. If the vessel is within one quarter of an inch of position one when the oscillator goes out of oscillation, longer lengths of C_1 and C_2 are substituted in place of the 10 cm. lengths used up to this point. If it is found that the oscillator will not remain in oscillation with the vessel in position one when the lengths of C_1 and C_2 have been extended to 25 cm., the 10 cm. loop should be employed and the above procedure repeated.

The instrument has its greatest sensitivity when the vessel is lowered to its maximum, and therefore the initial adjustments of the titrimeter should be made to permit the sample to be titrated with the vessel in position one. However, satisfactory results may be obtained with the vessel in other positions.

To select an intermediate vessel position, the vessel is lowered slowly into the field of the loop until the oscillator goes out of oscillation, and then the vessel is raised very slowly until a sudden increase in grid bias indicates the oscillator has resumed oscillation. The proper width spacing band is selected and slipped into position on the vessel to maintain the vessel in the position attained in the above adjustment. Figure 37 is an illustration of an intermediate vessel position.

With extreme concentrations, such as 3 molar hydrochloric acid, the 10 cm. loop and intermediate lengths of C_1 and C_2 are used. In addition, a 100 mmfd. mica condenser is installed between the cathode of the 955 tube and ground. The impedance in the cathode circuit of the oscillator makes the oscillator more sensitive to loading at the lower concentrations, but limits the upper range of the instrument to approximately one molar hydrochloric acid. Bypassing the impedance permits hydrochloric acid in concentration greater than 3 molar to be titrated. The grid bias indicated on the voltmeter before the vessel is lowered into the field of the loop is approximately two volts when the bypass condenser is installed, indicating increased amplitude of oscillations. The condenser is shown in the schematic diagram of Figure 29 as C_7.

In the titration of a strong acid adjustments are made so that the oscillator is just in oscillation at the beginning of a titration to obtain a complete titration curve. In the titration of a weak acid the adjustments are made so that at the completion of the titration the oscillator is at the point of going out of oscillation. Further adjustments of the apparatus are made after the results of an exploratory titration have been analyzed. These adjustments include changing the ratio of C_1 to C_2. This adjustment varies the feedback to the grid of the oscillator. Figure 32 shows the effect of different ratios of C_1 to C_2. Curves 5 and 7 are excellent examples. The data pertaining to the curves given in Table II shows that increased feedback shifts the sensitivity curve to regions of higher conductivity. Comparing curves 5 and 7 with curve 1 shows that C_1 to C_2 ratios other than unity result in steeper curves. Confining a titration to the straighter portions of sensitivity curves, or adjusting the titrimeter to operate on a steeper curve will all but eliminate excessive curvature of titration lines.

It is recommended that new workers familiarize themselves in this phase of the operation of the instrument by collecting data for sensitivity curves using a wide variety of adjustments and plotting curves such as those shown in Figures 32 and 33. In the operation of the titrimeter there is no substitute for experience.

Polarograph Adjustments When Used in Conjunction With the Wide Range Titrimeter

After the titrimeter has been adjusted properly, the span voltage of the polarograph is adjusted to one volt or less. Better control of the voltage is attained with lower values of span voltage. Thus, if a voltage of 0.1 volts is to be applied to the titrimeter, and the span voltage is one volt, the bridge is set to ten per cent of the span. If a 0.4 volt span is used the bridge setting is 25 per cent. It is easier to adjust the bridge to the proper value at the lower span voltage because the increment per dial division is considerably less, and backlash and over travel in the adjustment of the bridge control produce correspondingly smaller variations in applied voltage.

The chart and pen are removed from the recorder and the chart drive switch turned to the on position and the operation switch is turned to the E. M. F. constant position. With these settings the current measuring circuit of the polarograph is self balancing.

A current measuring sensitivity of 0.06 microamps. per mm. is satisfactory for most titrations. The range used in this study was 0.06 to 1.5 microamps. per mm.

The polarograph bridge setting depends on the type of system being titrated. In the titration of a strong acid, the per cent of span voltage is so selected that at the beginning of the titration the recorder pointer is near the 280 mm. limit. If a weak acid is titrated, the applied voltage is such that the pointer is near the zero limit.

The current measuring circuit of the polarograph is balanced against the potential of the standard cell in the instrument before commencing the titration.

If in the course of an exploratory titration the pointer travels over the entire 280 mm. length of the recorder scale before the titration is completed, the remainder of the titration curve may be obtained by adjusting the appropriate compensation control moving the pointer up or down on the scale as required and continuing the titration as before. The points corresponding to this latter part of the titration curve are obtained by calculating the increments between points from the data and combining the two portions of the curve. The initial reading of the recorder after the upscale or downscale compensation has been made will correspond to the last point obtained before the adjustment, and the increment between this point and the succeeding point will locate the latters position on the graph. All successive points are located in this manner.

The data collected in the exploratory titration is used to determine the maximum current change during the titration and the proper adjustment of the polarograph sensitivity control can then be made to confine the titration to the 280 mm. length of the recorder scale in all succeeding titrations.

Performance of the Parallel Resonant Circuit Titrimeter

No actual titrations were carried out with this instrument for the following reasons. It was sensitive to body capacity, the probe position in the beaker, and changes in solution level.

The exact point of resonance was difficult to determine since the resonance curve was quite broad at the maximum. The presence or absence of harmonics of the fundamental frequency of the oscillator could not be established.

Performance of the Frequency Measuring Titrimeter

A series of neutralization and precipitation reactions were carried out to test the performance of the instrument. The results are listed in Tables IV to VII.

Phosphoric acid was titrated at 12.2, 38.6, and 120 mc. Two breaks were observed in all of the titration curves. At the two lower frequencies the second break was not as pronounced as at 120 mc. This is shown in typical curves for 12.2 and 120 mc. titrations reproduced in Figure 43.

Oxalic acid was titrated at 38.3 and 60 mc. Two break titration curves similar to those obtained with phosphoric acid at these frequencies were obtained.

Acetic acid was titrated at 60 and 120 mc. A typical 120 mc. titration curve is shown in Figure 44. Curves for titrations at 60 mc. showed more curvature than those at 120 mc.

Best precision was obtained in a series recorded in Table VI. The titrations were carried out with the tip of the buret extending below the surface of the solution in the titration vessel.

The deviations from the theoretical equivalence points of all high frequency titrations are considerably higher than those generally obtained employing indicators. The deviations are less at the higher frequencies. Straighter lines of the titration curves facilitated the location of a more accurate end point.

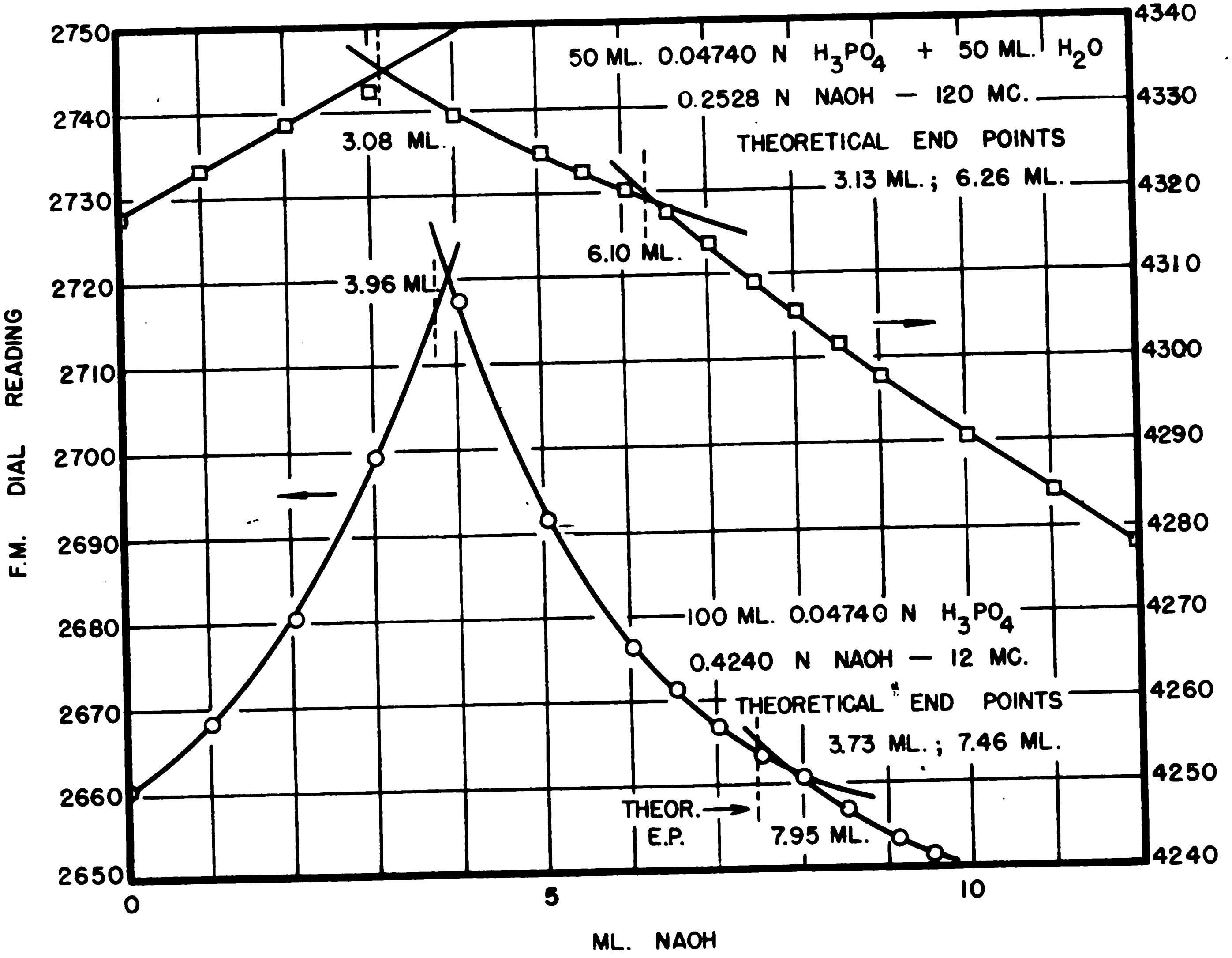

FIGURE 43. TITRATION OF H_3PO_4 WITH NAOH.

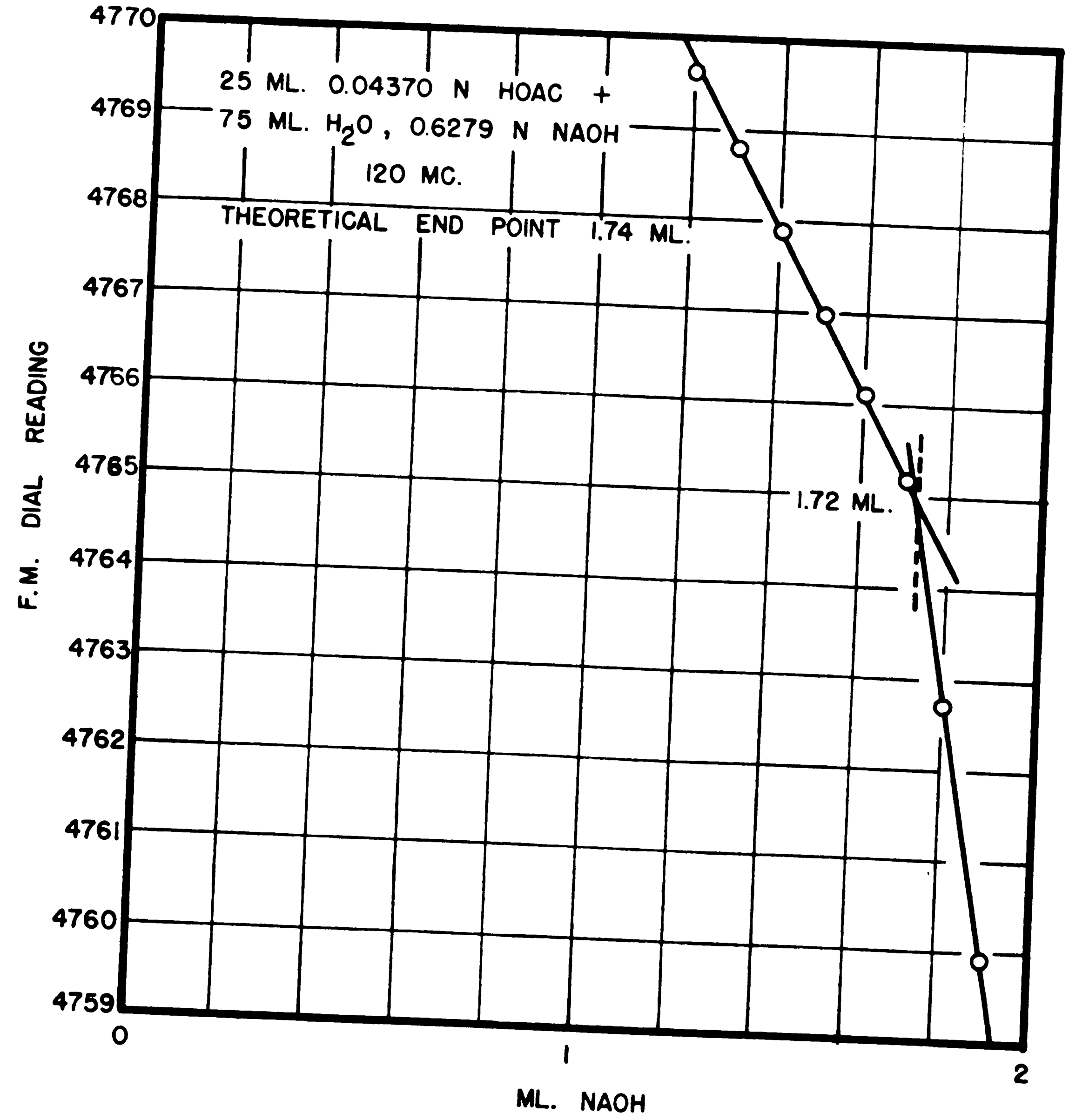

FIGURE 44. TITRATION OF HOAC WITH NAOH.

A series of precipitation reactions was carried out at 120 mc. The results are listed in Tables V and VII. A typical titration curve for the titration of silver nitrate with sodium chloride is shown in Figure 45. All titrations yielded straight line titration curves. In the titration of sodium fluoride with calcium chloride deviations of the order of 100 parts per thousand were obtained but in the reverse titrations the deviations varied two to six parts per thousand.

Blaedel and Malmstadt (2,3) constructed frequency measuring instruments. A full comparison between their instruments and the one constructed for this study cannot be made.

The precision of the order of 3 parts per thousand in their neutralization titrations at 30 mc. were superior to the precision of the order of 12 to 60 parts per thousand obtained in this study at 38.8 mc. An elaborate, precise frequency meter at their disposal obviously accounts for the contrast in results. They were able to measure changes in frequency resulting from the addition of 0.05 ml. increments of titrant. Near the equivalance point the frequency change was less than 100 cycles per second which would be impossible to detect with the audio method employed in this study.

The above authors (2) constructed a 100 mc. instrument but found that the instrument was unstable. They abandoned testing its performance because no great gain in response sensitivity in the concentration range of 0.05 molar sodium chloride was noted.

A stable 120 mc. instrument was successfully constructed for the present work and a practical titration cell designed. With more

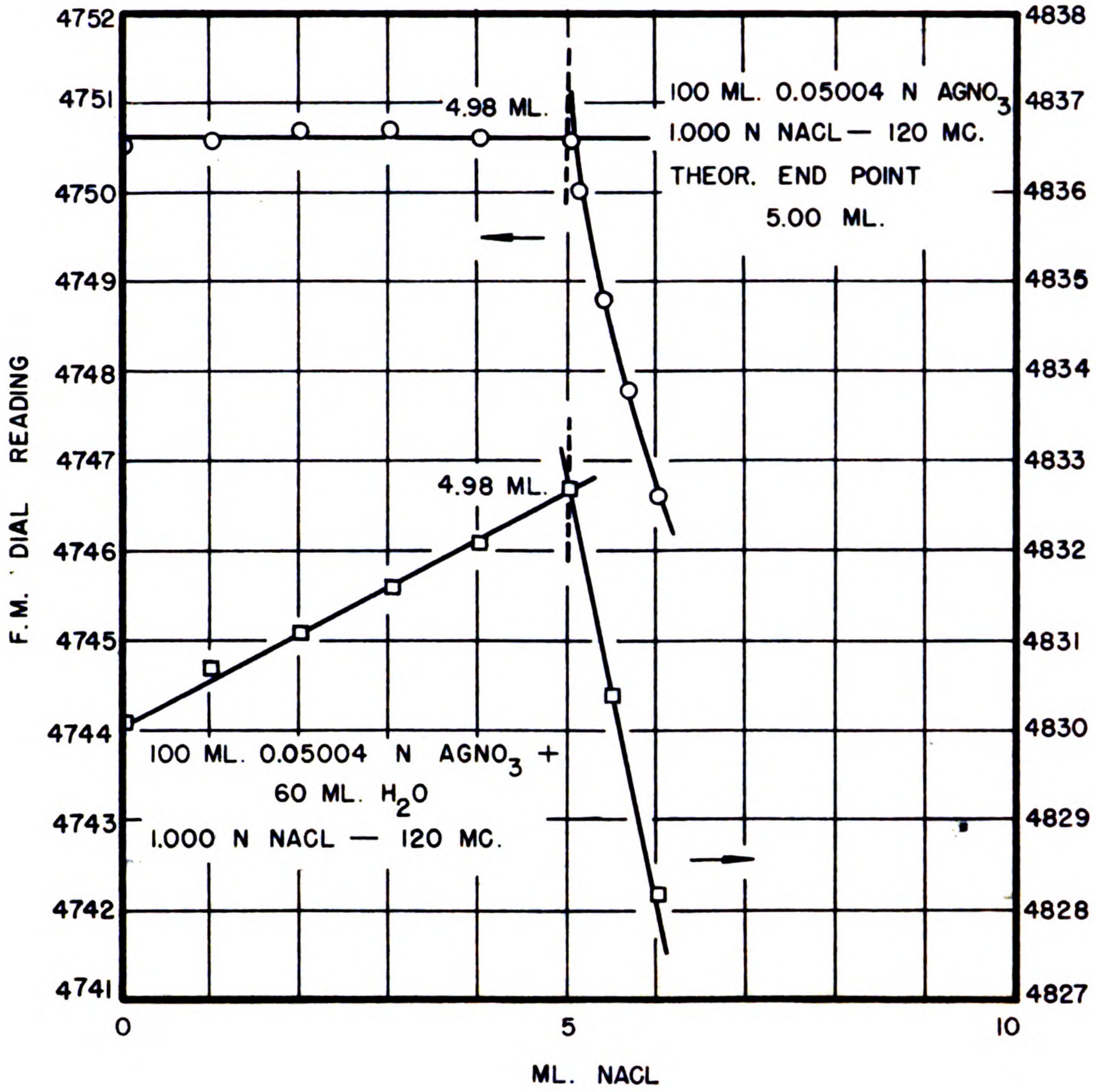

FIGURE 45. TITRATION OF $AGNO_3$ WITH NACL.

TABLE IV

ACID BASE TITRATIONS WITH FREQUENCY MEASURING INSTRUMENT

Frequenty	Acid	Ml. Taken	N. Acid	N. NaOH	Theor. E.P.	H.F. E.P.	Dev. P.P.T.
12.2 mc.	H_3PO_4**	100	0.04740	0.4240	3.73 7.46	3.96 7.95	+61.7 +65.7
38.8 mc.	H_3PO_4	100	0.04740	0.4240	3.73 7.46	3.88 7.90	+40.2 +57.0
38.8 mc.	H_3PO_4	50*	0.04740	0.4240	1.87 3.73	1.93 3.94	+32.1 +56.3
38.8 mc.	$H_2C_2O_4$	100	0.04988	0.2528	9.86 19.71	10.25 19.94	+39.6 +11.5
38.8 mc.	$H_2C_2O_4$	100	0.04988	0.2528	9.86 19.71	10.30 20.00	+44.6 +14.5
60 mc.	HOAc	50*	0.04370	0.2528	8.70	8.88	+20.7
60 mc.	$H_2C_2O_4$	100	0.04988	0.2528	9.86 19.71	10.10 19.95	+24.3 +12.0
120 mc.	H_3PO_4	50*	0.04740	0.2528	3.13 6.26	3.08 6.10	-16.0 -25.6
120 mc.	H_3PO_4	100	0.04740	0.2528	6.26 12.52	6.11 12.15	-24.0 -27.9
120 mc.	H_3PO_4	100	0.04740	0.2528	6.26 12.52	6.16 12.20	-16.0 -25.6
120 mc.	HOAc	50*	0.04370	0.2528	8.70	8.76	+ 6.9

* Diluted to 100 ml.

** Phosphoric acid titrated to the phenolphthalein endpoint.

TABLE V

PRECIPITATION REACTIONS WITH FREQUENCY MEASURING INSTRUMENT

Frequency	Substance Titrated	Normality	Ml. Taken*	Titrant	Normality	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
120 mc.	NaCl	1.00	2.20	$AgNO_3$	0.05004	--	--	No endpoint
120 mc.	NaCl	1.00	1.13	$AgNO_3$	0.05004	--	--	No endpoint
120 mc.	$AgNO_3$	0.05004	15.00	NaCl	0.05108	14.69	14.75	+ 4.8
120 mc.	$AgNO_3$	0.05004	15.00	NaCl	0.05108	14.69	14.85	+10.9
120 mc.	$AgNO_3$	0.05004	14.98	NaCl	0.05108	14.68	14.72	+ 2.7
120 mc.	$AgNO_3$	0.05004	14.96	NaCl	0.05108	14.66	14.58	- 5.4
120 mc.	$AgNO_3$	0.05004	15.00	NaCl	0.05108	14.69	15.00	+21.1
120 mc.	NaF	0.05	48.98	$CaCl_2$	0.02026	12.09	10.47	-134.0
120 mc.	NaF	0.05	49.88	$CaCl_2$	0.02026	12.31	10.72	-129.0
120 mc.	NaF	0.05	49.98	$CaCl_2$	0.02026	12.33	10.98	-109.5
120 mc.	NaF	0.05	49.95	$CaCl_2$	0.02026	12.30	11.04	-102.0
120 mc.	NaF	0.05	49.90	$CaCl_2$	0.02026	12.31	10.95	-110.7
120 mc.	$CaCl_2$	0.02026	20.00	NaF	0.15	27.40	27.45	+ 1.82
120 mc.	$CaCl_2$	0.02026	20.00	NaF	0.15	27.40	27.58	+ 6.57
120 mc.	$CaCl_2$	0.02026	19.98	NaF	0.15	27.39	27.22	- 6.21
120 mc.	$CaCl_2$	0.02026	15.00	$(NH_4)_2C_2O_4$	0.2000	15.20	15.00	-13.2
120 mc.	$CaCl_2$	0.02026	15.00	$(NH_4)_2C_2O_4$	0.2000	15.20	15.13	- 4.6
120 mc.	$CaCl_2$	0.02026	15.00	$(NH_4)_2C_2O_4$	0.2000	15.20	15.02	-11.8
120 mc.	$CaCl_2$	0.02026	15.00	$(NH_4)_2C_2O_4$	0.2000	15.20	15.07	- 8.6

* All samples were diluted to an initial volume of 100 ml.

TABLE VI

ACID-BASE TITRATIONS WITH FREQUENCY MEASURING INSTRUMENT

Frequency	Acid	Ml. Taken*	N. Acid	N. NaOH	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
120 mc.	HOAc	25.00	0.04370	0.6279	1.74	1.75	5.75
120 mc.	HOAc	25.00	0.04370	0.6279	1.74	1.74	0.00
120 mc.	HOAc	25.00	0.04370	0.6279	1.74	1.74	0.00
120 mc.	HOAc	25.00	0.04370	0.6279	1.74	1.74	0.00
120 mc.	HOAc	25.00	0.04370	0.6279	1.74	1.72	11.50

* All samples diluted to an initial volume of 100 ml.

TABLE VII

PRECIPITATION REACTIONS WITH FREQUENCY MEASURING INSTRUMENT

Frequency	Substance Titrated	Normality	Ml. Taken	Titrant	Normality	Theor. E.P.	H.F. E.P.	Dev. P.P.T.
120 mc.	$AgNO_3$	0.05004	100*	NaCl	1.000	5.00	4.99	2.0
120 mc.	$AgNO_3$	0.05004	100*	NaCl	1.000	5.00	4.98	4.0
120 mc.	$AgNO_3$	0.05004	100**	NaCl	1.000	5.00	4.95	10.0
120 mc.	$AgNO_3$	0.05004	100**	NaCl	1.000	5.00	4.98	4.0

* Diluted to an initial volume of 160 ml.
** Initial volume 100 ml.

precise frequency measuring equipment better titration results could be obtained.

Blaedel and Malmstadt (3) constructed a sturdy, stable, and elaborate instrument which operated at 350 mc. The sensitivity was extended to 0.3 molar sodium chloride which is considerably beyond the practical limit obtained in this study with the 120 mc. instrument. They have shown that in order to increase the sensitivity range for a capacity cell type frequency measuring instrument, higher frequencies have to be employed.

Performance of the Wide Range Titrimeter

Sulfuric acid was titrated with standard sodium hydroxide at several concentrations. The results are tabulated in Table VIII. The precision of the titrations varied from zero to six parts per thousand.

Two breaks were observed in every titration curve. A typical sulfuric acid titration curve is shown in Figure 46. Anderson et al. (1), had previously reported some evidence of a double break in sulfuric acid titration curves.

Hydrochloric acid was titrated at concentrations from 0.1 normal up to three normal. The precision of the titrations listed in Table IX varied between one and two parts per thousand. The theoretical endpoint for the titration of three normal hydrochloric acid with four normal sodium hydroxide was determined by comparison of the two solutions using methyl red indicator. Curves typical of the titration are shown in Figures 47 and 48.

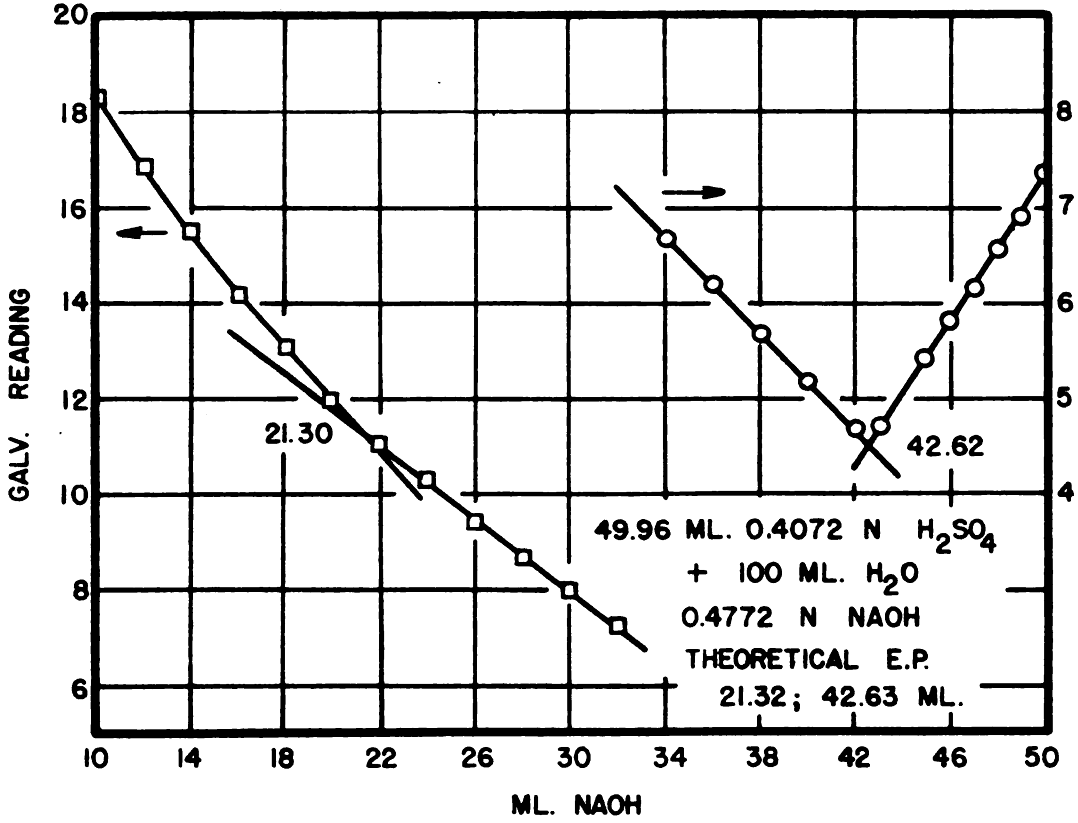

FIGURE 46. TITRATION OF H_2SO_4 WITH NAOH.

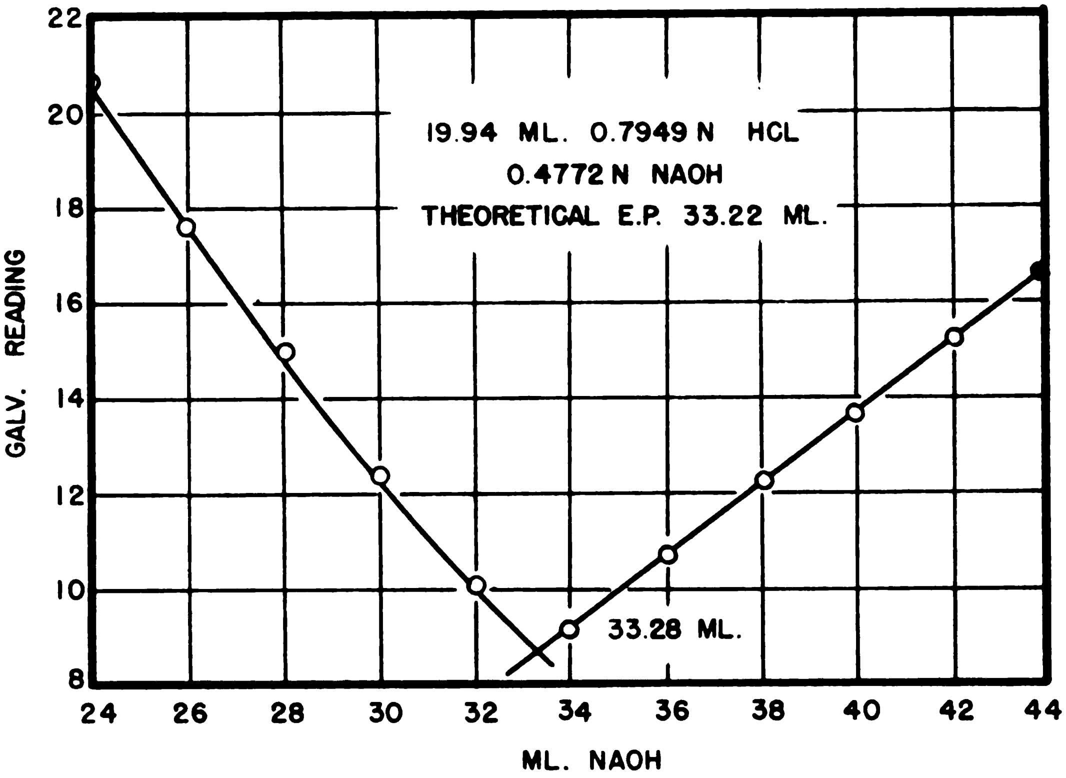

FIGURE 47. TITRATION OF HCL WITH NAOH.

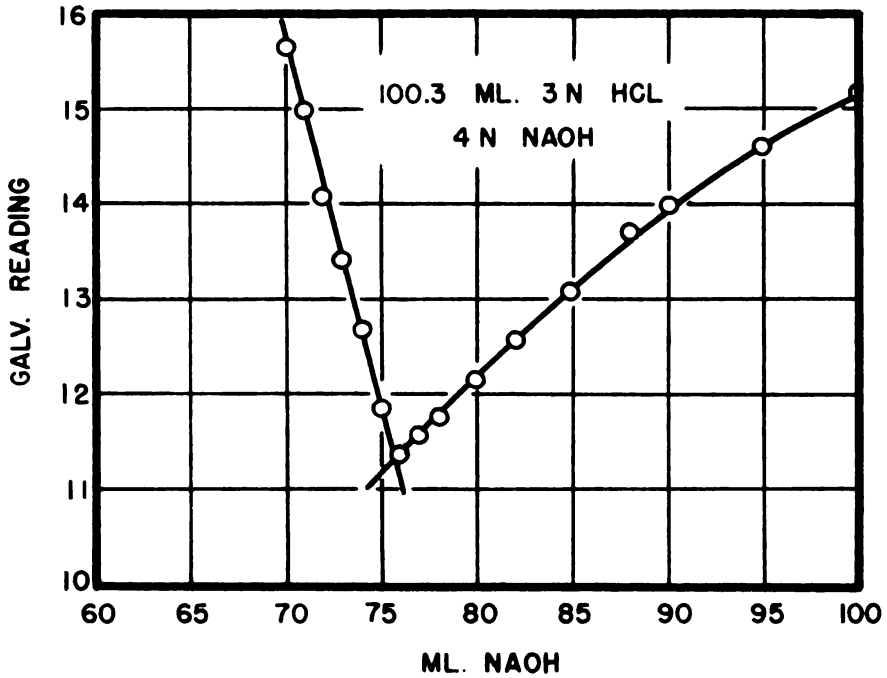

FIGURE 48. TITRATION OF HCL WITH NAOH.

The results of titrations of boric acid appear in Table X. The precision of the titrations was from zero to three parts per thousand. Figure 49 shows a typical boric acid titration curve.

In another series of boric acid titrations, the titration was continued through the theoretical monobasic equivalence points for possible neutralization of the second and third replaceable hydrogen ions. A slight break was obtained in the curves corresponding to these points. The angles between the titration curve lines at these points were approximately 175 and 178 degrees respectively for the second and third equivalence points in contrast to an angle of approximately 150 degrees between the lines at the first equivalence point. In view of the small angles, the evidence for polybasic neutralization was considered to be inconclusive. A titration curve from the series is reproduced in Figure 50. In obtaining the titration curve, three separate but identical samples were used and the titrimeter adjusted for each sample so that individual breaks would fall on the straightest portion of the titrimeter sensitivity curve. The resulting curve is really a composite of three titrations, one for each equivalence point. The results of the titrations in this series are given in Table XI.

Solutions of hydrogen peroxide were titrated with sodium hydroxide. Two mild breaks in the titration curve were observed. The initial and final portions of the curves were essentially straight lines, with an intermediate portion showing a slight curvature. Typical curves are shown in Figure 51, and the results compiled in Table XII.

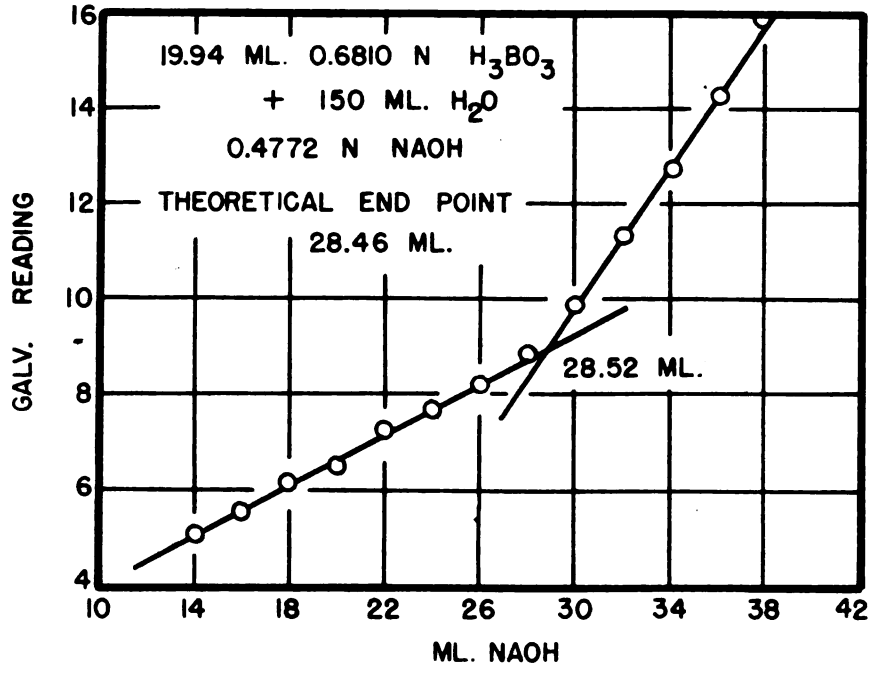

FIGURE 49. TITRATION OF H_3BO_3 WITH NAOH.

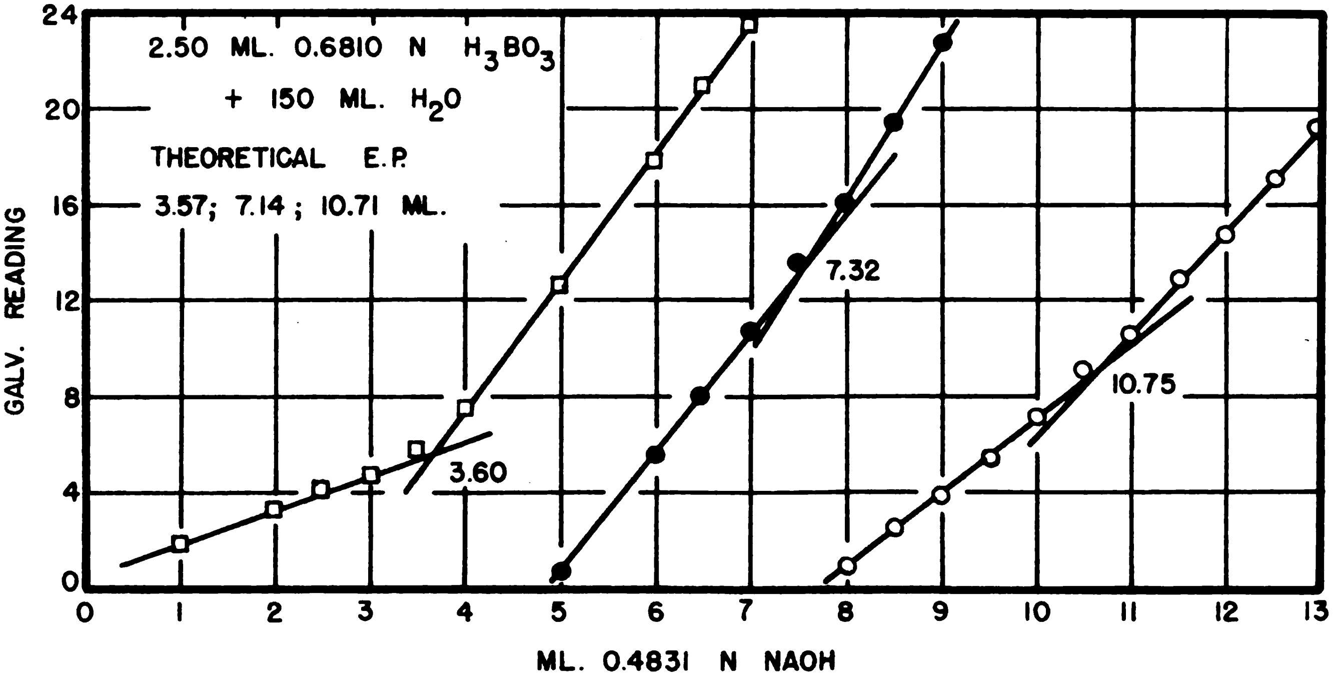

FIGURE 50. TITRATION OF H_3BO_3 WITH NAOH SHOWING EVIDENCE OF NEUTRALIZATION OF SECOND AND THIRD REPLACEABLE HYDROGEN IONS.

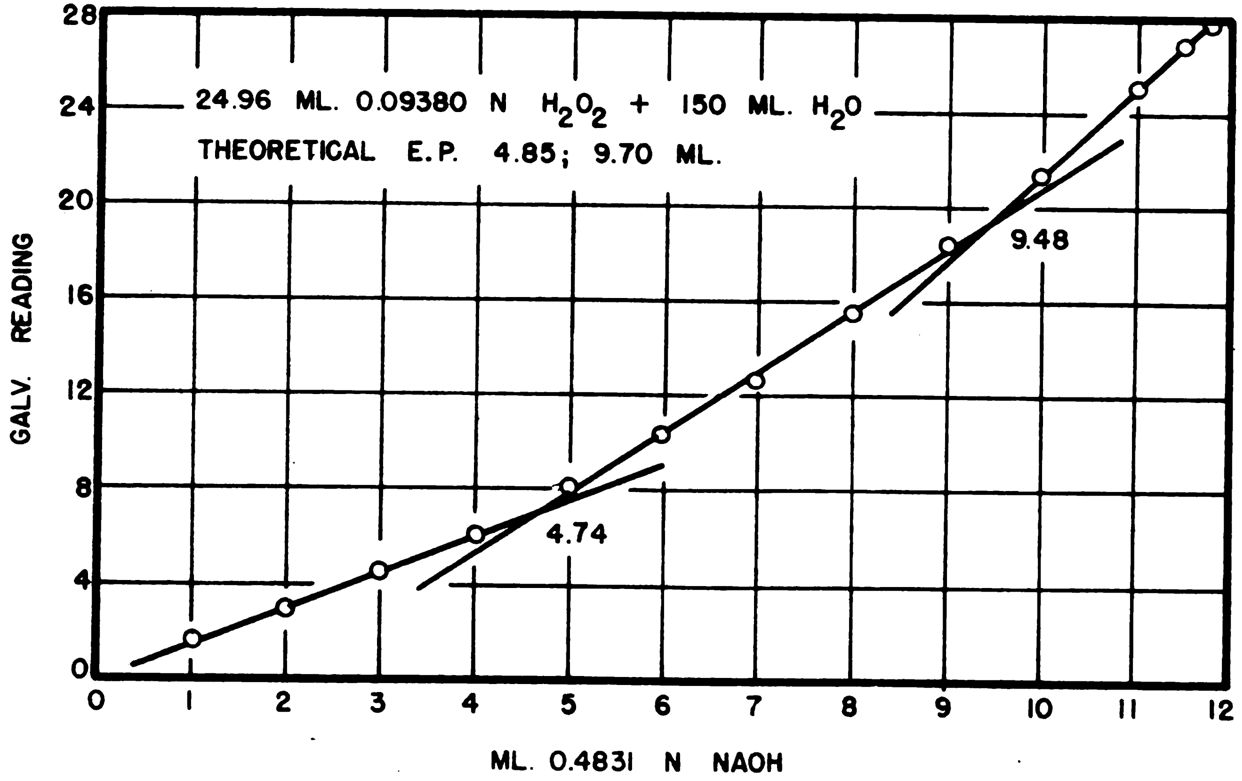

FIGURE 51. TITRATION OF H_2O_2 WITH NAOH.

TABLE VIII

TITRATIONS OF H_2SO_4 WITH NaOH

Ml. Taken	Normality H_2SO_4	Normality NaOH	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
49.96	0.4072	0.4772	21.32	21.30	- 0.47
			42.63	42.65	- 0.24
49.96	0.4072	0.4772	21.32	21.30	- 0.47
			42.63	42.62	0.12
24.96	0.4072	0.4772	10.65	10.60	- 4.69
			21.30	21.42	+ 5.63
49.96	0.4072	0.4772	21.32	21.28	- 0.94
			42.63	42.55	- 0.96
10.00	0.4072	0.4772	4.26	4.26	0.00
			8.53	8.53	0.00
9.98	2.049	0.6343	16.12	16.16	+ 2.48
			32.23	32.42	+ 5.90
4.96	2.049	0.6343	8.01	8.00	- 1.25
			16.03	6.11	+ 4.99
49.96	0.4072	0.4772	21.32	21.30	- 0.47
			42.63	42.58	- .60

TABLE IX

TITRATIONS OF HCl WITH NaOH

Ml. Taken	Normality HCl	Normality NaOH	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
24.96	0.7949	0.4772	41.58	41.65	+ 1.68
19.94	0.7949	0.4772	33.22	33.28	+ 1.80
19.94	0.7949	0.4772	33.22	33.30	+ 2.41
100.03	3	4	75.90*	75.80	- 1.32

* E.P. determined by comparison of solutions using Methyl-Red indicator.

TABLE X

TITRATIONS OF H_3BO_3 WITH NaOH

Ml. Taken	Normality H_3BO_3	Normality NaOH	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
24.96	0.6810	0.4772	35.62	35.73	+ 3.09
19.94	0.6810	0.4772	28.46	28.54	+ 2.81
19.94	0.6810	0.4772	28.46	28.52	+ 2.11
49.96	0.6810	0.4772	71.30	71.28	- 0.28
10.00	0.6810	0.4772	14.27	14.27	0.00
10.00	0.6810	0.4772	14.27	14.27	0.00

TABLE XI

TITRATIONS OF H_3BO_3 WITH NaOH

Ml. Taken	Normality* H_3BO_3	Normality NaOH	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
4.98	0.6810	0.4831	7.02	7.10	+ 11.4
			14.04	14.25	+ 15.0
			21.06	21.50	+ 20.9
4.98	0.6810	0.4831	7.02	7.07	+ 7.1
			14.04	14.23	+ 13.5
			21.06	21.50	+ 20.9
2.50	0.6810	0.4831	3.57	3.65	+ 22.4
			7.14	7.33	+ 26.6
			10.71	10.90	+ 17.7
2.50	0.6810	0.4831	3.57	3.60	+ 8.4
			7.14	7.32	+ 25.2
			10.71	10.75	+ 3.7

* H_3BO_3 0.6810 normal as a monobasic acid.

TABLE XII

TITRATIONS OF H_3PO_4 WITH NaOH

Ml. Taken	Normality H_3PO_4	Normality NaOH	Theor. E.P.	H.F.E.P.	Dev. P.P.T.
24.96	0.09380	0.4831	4.85 9.70	4.82 9.65	- 6.2 - 5.2
24.96	0.09380	0.4831	4.85 9.70	4.74 9.48	-22.7 -22.7
24.96	0.09380	0.4831	4.85 9.70	4.80 9.50	-10.3 -20.6

Deviations in titrations carried out with the wide range titrimeter are considerably less than those obtained in titrations performed with the frequency measuring instrument. In the results of neutralization reactions, listed in Table X, the deviations fall in the range of zero to five parts per thousand. The higher deviations in the results listed in Table XI are probably due to the technique employed.

The most noteworthy accomplishment in the performance of the wide range titrimeter is that three normal hydrochloric acid was titrated with sodium hydroxide. This is a sensitivity range heretofore not reported. The maximum limit of concentration range has not been reached. The use of a larger loop, longer lengths of C_1 and C_2 and higher cell position will extend the concentration range in which response is still noticeable.

CONCLUSIONS

CONCLUSIONS

In developing the frequency measuring instrument a stable and relatively simple 120 mc. oscillator was constructed as well as a practical titration cell.

The design is such that the instrument was converted to the wide range titrimeter without any fundamental change in the circuit. The only change was the insertion of a 100 ohm resistor in series with the 15,000 ohm grid-leak resistor which does not have to be removed if the instrument is to be reconverted to the frequency measuring type. The course of a titration may be followed by simultaneous observation of changes in the grid current of the oscillator and frequency changes with either the wide range cell or the capacity type cell. The instrument is constructed so that it may be converted to either the wide range type or the conventional type used by others (1,2,3,4,7), without breaking a single soldered connection. The operating frequency of the oscillator may be adjusted to any frequency between one mc. and 120 mc. by use of the appropriate coil, half wave line, or loop.

Therefore, the instrument is a universal high frequency titrimeter, and may be used to demonstrate the characteristics and limitations of practically every type of high frequency titrimeter that has been developed.

Certain improvements in the mechanical arrangement of the circuit components can be made which may improve the performance of the wide range titrimeter. The layout of the present instrument is essentially that of the original frequency measuring instrument and is not necessarily the most desirable one for the wide range titrimeter.

From the performance tests carried out with the wide range titrimeter it is apparent that: (1) in high frequency titrations the sensitivity concentration range has been extended to at least three molar hydrochloric acid, a level not heretofore attained; (2) the loading of the resonant circuit in the oscillator by the solution in the titration cell is purely resistive and truely representative of changes in the concentrations of ions in the solution. Substantiation of claim (2) is based on the agreement between the angle of titration curve lines at the equivalence point obtained in this study to that obtained by Kolthoff (11) in his original conductometric titration of boric acid solutions.

The reproduction of the boric acid titration curve obtained by Kolthoff (11) using the wide range titrimeter constructed in this study proves that the instrument responds only to changes in solution conductivity and its response is identical to the response obtained with the use of immersion type electrodes at a frequency of 1000 c.p.s. in the ordinary conductometric titration. The shape of the titration curves obtained using every other type of high frequency titrimeter indicate that their response is a complicated function of many variables from which the response due to changes in conductivity cannot be separated with any degree of certainty. A titration carried out on any instrument other than the wide range titrimeter developed in the present work is not a conductometric titration in the classical sense.

The extended range of the wide range titrimeter up to three molar hydrochloric acid is a distinct advantage attained over the conventional conductometric apparatus employing immersion type electrodes.

No exhaustive study of titrations was carried out in the present work. Titrations were confined to aqueous media and as a rule to systems titrated by others to permit necessary comparisons to be made. It is believed that the titrations of boric acid reported here are the first successful titrations of boric acid using high frequency titration apparatus.

The development of a truly conductometric high frequency titrimeter is a study complete in itself and obviously must come first. The applications of the instrument are to be the subject of continued work in this field.

LITERATURE CITED

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1. Anderson, K., Bettis, E. S., and Revinson, D., Anal. Chem., 22, 743-6 (1950).

2. Blaedel, W. J., and Malmstadt, H. V., Anal. Chem., 22, 734-42 (1950).

3. Blaedel, W. J., and Malmstadt, H. V., Anal. Chem., 22, 1413-17 (1950).

4. Blaedel, W. J., Malmstadt, H. V., Petitjean, D. L., Anal. Chem. 24, 1240-44 (1952).

5. Fujiwara, S., and Hayashi, S., Anal. Chem., 26, 239-41 (1954).

6. Hall, J. L., and Gibson, J. A., Anal. Chem., 23, 966-70 (1951).

7. Hall, J. L., Anal. Chem., 24, 1236-40 (1952).

8. Hall, J. L., Anal. Chem., 22, 1244-47 (1952).

9. Jankowski, C. M., unpublished master's thesis, Michigan State College of Agriculture and Applied Science, (1954).

10. Jensen, F. W., and Parrack, A. L., Ind. Eng. Chem., Anal. Ed., 18, 595-9 (1946).

11. Kolthoff, I. M., Z. anorg. Chem., 111, 18 (1920).

12. Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Third Ed., p. 534-5, The Macmillan Company, New York, N. Y. (1952).

13. Ibid., p. 600.

14. Lingane, J. J., "Electroanalytical Chemistry," p. 161, Interscience Publishers, Inc., New York, N. Y. (1953).

15. Llewellyn, F. B., Proc. I. R. E., 19, 2063 (1931).

16. Milner, O. I., Anal. Chem., 24, 1247-49 (1952).

17. Mizushima, S., Bull. Chem. Soc. Japan, 1, 47 (1926).

18. "Radio's Master," Fifteenth Ed., p. T9, United Catalog Publishers, Inc., New York, N. Y. (1950).

19. Reilley, C. N., and McCurdy, W. H., Jr., Anal. Chem., *25*, 86-93 (1953).

20. Sarbacher, R. I., and Edson, W. A., "Hyper and Ultrahigh Frequency Engineering," First Ed., p. 337-341, John Wiley and Sons, Inc., New York, N. Y. (1944).

21. Terman, F. E., and Pettit, J. M., "Electronic Measurements," Second Ed., p. 92-97, McGraw-Hill Book Co., Inc., New York, N. Y. (1952).

22. Terman, F. E., "Radio Engineering," chap. III, p. 48-69, McGraw-Hill Book Co., Inc., New York, N. Y. (1932).

23. *Ibid.*, chap. VII, p. 228-278.

24. West, P. W., Burkhalter, T. S., and Broussard, L., Anal. Chem., *22*, 469-71 (1950).

APPENDIX

APPENDIX

Parts List

Frequency Measuring Instrument, Figure 8

C_1, C_2, - 100 mmfd mica
R_1, R_3 - 15,000 ohm, 1 watt
R_2 - 100 ohm, 2 watts
L_1 - 12.2 mc; 45 turns #30 close wound 1/2" dia.
34.8 mc; 15 turns #24 close wound 1/2" dia.
60.0 mc; 8 turns #24 close wound 1/2" dia.
L_2 - 10 turns #22 wire wound around R_2
V_1 - 955

Power Supply, Figure 9

C_1,C_2 - 20 mfd., 450 V.
L_1 - Filter choke, Gracoil 200925
R_1 - 5000 ohms, 10 watts
SW_1 - SPST Toggle switch
T_1 - 350-0-350, 70 ma.; 5 v., 3 a.; 6.3 v., 3 a.
V_2 - 5Y3
V_3 - VR 150/30

Wide Range Titrimeter, Figure 29

C_1, C_2 - RG8/U Coaxial Cable of varying lengths
C_3, C_4, C_5, C_6, C_7 - 100 mmfd, mica
R_1, R_4 - 15,000 ohm, 1 watt
R_2 - 1000 ohm, 1 watt
R_3 - 100 ohm, 2 watts
L_2 - 10 turns #22 wound around R_3
V_1 - 955
L_1 - Loop #1 3/16" copper tubing 4" dia., silver plated
Loop #2 3/16" copper tubing 3 1/8" dia., silver plated
Coop #3 3/10" copper tubing 2 3/4" dia., silver plated