ELECTRONIC INSTRUMENTATION IN CHEMISTRY

A THESIS

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BY

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(Cornelius A. Menezes)

C O N T E N T S

S Y N O P S I S

Pt. 1: Measurement of E.M.F.

Previous work on the precision measurement of E.M.F. of electrode potentials has been given. New and modified circuits have been developed to measure the electrode potentials of various types of electrodes such as gas electrodes, metal electrodes and glass electrodes, using readily available electronic components. The application of these circuits to pH measurements, potentiometric titration and for recording small currents, has been described.

Pt. 2: Conductivity Measurements

a) A precision conductivity apparatus has been built for the measurement of conductivity at different frequencies using sign wave oscillator, shielded bridge and high gain amplifier. The application of this apparatus for anomalous dispersion of conductivity of strong electrolytes and for the determination of the freezing point by using thermistors have been described.

b) H.F. titration: A new type of cell has been designed for H.F. titration, using V.T.V.M. method and crystal oscillator with electron eye detector. A detailed analysis of the electrical circuit has been made to bring out the anamolous dispersion of strong electrolytes and in particular, the differential conductivity of hydrogen and hydroxyl ions and other ions.

Pt. 3 Various types of electrical power supplies of high stability, useful for precision measurements, have been described, using valves and transistors to eliminate the need of using batteries.

PART - 1

PART - 1

CHAPTER - I

Historical Survey.

Early attempts to measure pH with glass electrodes were made by using the quadrant electrometer. The high sensitivity, ease of handing, and lower cost of electronic devices have now displaced the cumbersome quadrant electrometer. By making use of the principle of electron tube operation, that a small change in grid voltage produces a large change in plate current, Goode (1922) pioneered the use of vacuum tube amplifiers for sensitive potential measurements.

Grid current in d-c amplifiers:

The existence of grid current is a serious limitation on an amplifier designed for measurement of glass electrode potential because of the very high internal resistance. The observed potential would be reduced by an amount equal to the drop determined by the resistance and grid current.

The factors affecting grid current are as follows: (1) Ions are formed by the ionisation of residual gases at potentials higher than the ionisation potential of the gases. Positive ions thus formed are attracted to the negative grid, (2) Thermionic emission from the grid due to heating of the grid. The emission of electrons due to heating can be controlled by choice of high work function metals for the grid and by ensuring that the grid temperature does not rise appreciably, (3) Positive ions emitted from the cathode surface; disintegration of the cathode due to thermal effects or due to bombardment by ions could result in positive ions being emitted, (4) Photoelectrons emitted by the grid under the action of radiation from the filament or external radiation, (5) photoemission from the grid under the influence of soft X-rays produced by the anode current. This phenomenon is dependent on the electrode potentials employed, and could be reduced to a negligible value if anode voltage and anode current are kept low.

Surface leakage external to the electron tube must be minimised by the use of high insulation materials like porcelain, lucite perspex or polyethylene. The leakage path between grid and other electrodes should preferably be kept as large as possible.

Electrometer valve circuits

The problem of reducing grid current may be solved by the use of specially constructed electrometer valves which are designed to operate at a low anode voltage and current and thus maintain a low grid current by the elimination of ionisation currents and heating effects.

Metcalf and Thompson[2] have described a very low grid current electrometer the FP-54; the grid current is brought down to the low value of 10^{-15} A by the use of an open grid structure and special attention to insulation. The electrode voltages are kept below 8 volts, thus practically eliminating ionisation. These electrometer valves are very expensive due to the stringent requirements of manufacture.

A high input resistance amplifier using the special electrometer FP-54 is described by Turner and Siegelin.[3] It is a single stage d.c. amplifier using a very sensitive galvanometer (sensitivity 10^{-10} μA/div.) as the indicator since the transconductance of the valve is low.

DuBridge and Brown[4] describe an improved electrometer circuit using the FP-54 valve. This circuit uses a plate-screen balancing bridge arrangement in which the galvanometer is placed across the plate load resistor and the screen resistor, thus compensating for changes in emission characteristics, and giving a higher stability.

A balanced electrometer circuit using the ET1 electrometer has been described by Hardy.[5] This circuit also requires the use of galvanometer of high sensitivity. The balanced circuit is similar to that of DuBridge and Brown (locus cit).

A two stage circuit using the Ferranti BM 4A electrometer is described by Brewer.[6] The higher gain of a two stage amplifier enables the sensitive galvanometer to be dispensed with. The electrometer input stage is directly coupled to a cathode follower output stage; a floating H.T.Supply is used in order to maintain the high cathode to HT -ve potential in the case of a cathode follower.

Vibrating Reed and Dynamic Capacitor Electrometers.

In applications of electronic circuits where extremely low drift is essential over a long period of time together with a very high input resistance, the vibrating reed or dynamic capacitor amplifier is most suitable.

A typical dynamic capacitor amplifier is described by Palevsky, Swank and Greenlink (1947).[7] The input stage consists of a resistance-capacitance network, the capacitance being modulated at an audiofrequency. The variation in the capacitance is necessarily small leading to a very small signal (a fraction of the applied signal) being available for further amplification. The changes in contact potential due to contamination of the surfaces of the vibrating reed or capacitor are the main causes of instability or noise voltages and become a limiting factor to the ultimate voltage sensitivity attainable with such a system. The vibrating reed is normally protected by being enclosed in a sealed system, which helps to stabilise the contact potential. The output of the amplifier after being used for indication, is returned to the input stage giving a negative feedback loop with high degeneration.

Circuits using receiving tubes

The disadvantages of grid current when using receiving tube types, and the low gain in single stage amplifiers, led to the design of a four stage cascaded amplifier with a condenser input, described by Ellis and Kiehl.[8] In this circuit the sensitive galvanometer is replaced by a sturdy microammeter. A condenser is used to enable a charge to be transferred from the potential source to the amplifier; this prevents the flow of direct current through the glass electrode or other source and condenser, which in turn, is discharged into the grid circuit of the amplifier. This impulse is amplified and is observed on an indicating meter. The disadvantages of this method are (i) the output current is subject to drift (where direct coupling is used), (ii) the deflections - produced by the charge only give a rough indication of the degree of unbalance, it can therefore only be used as a null indicator together with a potentiometer.

Another circuit using the condenser charging technique is described by Chun-Yu Lin.[9] This circuit is a modification of the Ellis and Kiehl circuit; it uses a three stage d-c amplifier with a condenser in the input stage. By using type 32 valves, a reduction in filament current is obtained (0.18 amp. vs. 1.04 amp. for the Ellis and Kiehl circuit), overcoming a drawback of the earlier circuit.

Working[10] has described a two stage cascaded d-c amplifier in which all the electrode and filament potentials and currents are obtained from a high voltage (340 V) potential divider; a constant voltage regulator supplies the H.T. to the potential divider to reduce fluctuations. This circuit has two major drawbacks (i) Drift is quite high in such a cascaded arrangement (2) A large amount of power is dissipated, as the entire filament current flows through the potential divider at the full voltage across it; the good voltage sensitivity obtainable with this circuit, is perhaps its only merit.

McFarlane[11] describes a pH meter based on the parallel balanced or differential d-c amplifier; the lower drift obtainable with this type of circuit makes it suitable for direct reading pH meters where zero stability and constant gain (by negative feedback) are more important than voltage sensitivity. The instrument is battery operated and uses a 100 volt supply for H.T.

A mains operated circuit, also based on the use of a parallel balanced twin triode 6A6, is described by Garman and Droz.[12] Although no voltage stabiliser is used, the stability is quite good due to the bridge balance inherent in this circuit.

A line operated pH meter, based on the Roberts[13] feedback amplifier, uses commercial receiver tubes in a two stage push pull arrangement. The input valves are

6SJ7 R.f pentodes operated at reduced (50 %) filament voltage, when a grid current of 10^{-12} A is obtainable. However it would appear that the high anode and screen potentials used would increase grid current by ionisation.

An excellent review of d-c amplifiers has been made by Artzt.[14] in which the principal types of d-c amplifiers have been classified as follows:

1) Bleeder cascaded amplifier. This circuit has a very high drift although it is capable of high gain.

2) Potentiometer coupling: This arrangement is characterised by high drift and is unbalanced for changes in E_f (filament voltage), R_p (dynamic plate resistance) or E_b (plate supply voltage).

3) Cathode compensation: This type of circuit has medium drift characteristics and is compensated for E_f.

4) Parallel balance: This has a low drift and is zero balanced for E_b, R_p.

5) Electrometer tube circuit: Characterised by low drift and accurate balance for E_b and R_p.

6) Emission compensation.

7) Cathode and B supply compensation.

8) Series balance (Cascade amplifier).

The most common draw back of the first two amplifier circuits is their susceptibility to change in anode voltage, heater current and variation in valve characteristics.

The most serious type of drift is experienced with cascaded stages operating from a bleeder supply or with interstage coupling batteries.

Series balanced amplifiers are compensated for changes in E_f and have high gain and good stability.

D-C amplifiers of the types classified above have been described by Brubaker[15], Mezger[16], Williams,[17] and Goldberg.[18] The use of multielectrode tubes as electrometers has been discussed by Johnson and Neitzert,[19] Maconald,[20] Gabus and Poole[21] and Nielsen.[22]

A differential amplifier suitable for use in pH measurements is described by Morton.[23] This amplifier uses negative feedback and the gain control varies the amount of negative feedback from 0 to 100 %. This use of negative feedback in instruments represents an advance over previous circuits as it enables a high degree of linearity of output with regard to input, and a higher input impedance, provided the negative feedback is large; this also means that the sensitivity of the amplifier is reduced.

A high sensitivity d-c amplifier with a stabilised power supply is described by Anker.[24] The amplifier is said to be suitable for measuring small voltages or currents from high impedance sources. The input stage is a 12BE6 pentagrid converter run at an anode potential of 12 V, and a reduced filament current of 105 Ma instead of 150 Ma; under these conditions the valve has a input current as low as 10^{-13} A. The cascaded amplifier requires rigorous stabilisation of filament current and electrode voltages, which are provided by an elaborate electronic stabiliser. The large dissipation of heat in bleeder resistances and the additional components required are among the disadvantages of such a circuit.

Drift compensation

Drift in d.c. amplifiers is most severe in cascaded stages where a small drift in the input stage is amplified and passed on to the output. The design of high gain d-c amplifiers, therefore, requires the use of compensation techniques by which the individual drifts are cancelled out by common mode rejection.

Artzt[14] in a review of circuits, notes that parallel balance and series balance types of amplifiers have lower drift than most other types, and are compensated for changes in supply voltage and mutual conductance.

Well regulated filament and plate supply voltage has the effect of reducing drift to a low value and is used in some makes of pH meters, particularly the direct reading types, where zero stability is very important.

Rapid or erratic fluctuations in the filament supply can give rise to a 'noise' voltage of about 2 to 3 mv, reducing the useful sensitivity of the amplifier.

Considerable attention has to be paid in design to maintain a high signal to noise ratio in d-c amplifiers for small signals. A d-c amplifier for use with low level signals is described by Aiken and Welz.[25]

The changes in cathode to grid voltage caused by a change in heater voltage are the same for a triode and a diode and hence a diode may be used to cancell the effects of heater voltage variation which causes drift in d-c amplifiers.

The same function of the diode is used in a circuit described by Terman[26] using a twin triode in which one grid is returned to a point on the common cathode resistor.

In transistor d-c circuits, drift is strongly temperature dependent, since temperature influences the important parameters of a transistor:

i) The base to emitter voltage V_{be}

ii) The forward current gain h_{fe}

iii) The collector leakage current I_{co}

Of the three parameters above, the collector leakage current I_{co} can be minimised by using silicon transistors rather than germanium transistors, which have much higher leakage currents at normal ambient temperatures. The relation between I_{co} and temperature is given by

$$I_{co} = I_{co}(T_o) \exp (b(T - T_o))$$

Reducing the operating collector current, decreases the change of base current required, to keep the collector current constant as the current gain changes (with temperature).

The change of base to emitter bias voltage is approximately linearly proportional to temperature drift in the emitter-base voltage V_{BE} is more pronounced at lower temperatures, while changes in I_{co} are prominent at high temperatures. By balancing the changes in V_{BE} as in d-c difference amplifiers, and by using transistors with matched characteristics, the drift may be substantially controlled.

High input impedance circuits using transistors:

The application of transistors to high input impedance electrometer circuits is severely limited by the inherently low input impedance of a typical transistor, the parameters of which are given below:

Typical Transistor Characteristics

	Grounded base	Grounded emiter	Grounded collector
Input resistance (ohms)	64	625	10.000
Voltage gain	14	14	0.94
Power gain	127	1240	9.2

The low input impedance of the transistor in the common emitter configuration may be increased to a higher value by using it in the common collector configuration (or the emitter follower, as it is called, in analogy with the cathode follower electronic amplifier).

The design of high input impedance transistor amplifiers has been discussed by Bell and Venning[27] who give a few a-c amplifier circuits having input impedances of the order of a few hundred to a thousand megohms. However, these circuits, which are based on cascaded emitter followers with large negative feedback, cannot be used for d-c measurements, as the noise level then reaches several hundred millivolts.

A simple circuit for a portable electrometer voltmeter designed for field work has been described by Gibbs.[28] This circuit has a two stage transistor amplifier driven by an ME1401 electrometer. Silicon transistors OC420 are used in the output stage to lower the drift due to thermal effects. This circuit has the drawback of requiring an expensive electrometer valve. The circuit is essentially an anode follower but suffers from a reduction in gain, as the input impedance of the transistor is much lower than the valve impedance which is in series with the output signal to the transistor. An additional transistor has been introduced for providing temperature compensation of the collector current. The output is single ended and is therefore more liable to drift than a push-pull circuit would be.

Yet another circuit using a high input impedance valve in conjunction with transistors is described by Jones.[29] It is a high input impedance converter for operating a digital voltmeter and has two balancedd anode follower stages using electrometer valves.

The use of a constant current device as a stabilising element is well known. The application of this principle to transistor output stages enables a high degree of stability to be obtained. An adequate current gain can be obtained to drive a rugged milliammeter and the large current feeback enables negative feedback stabilisation of gain to be achieved.

A transistor differential amplifier, analogous to the electronic cathode follower differential amplifier, has been described by Slaughter.[30]

The complementary symmetry possessed by a combination of p-n-p and n-p-n transistors enables d-c amplifiers of high gain to be designed with a minimum of components. Lohman[31] discusses the properties of complementary symmetry transistor circuits.

The use of a n-p-n transistor enables a hybrid circuit using a cathode follower and a transistor to be designed; such an aplifier is discussed in a later section of this work.

The properties and advantages of emitter follower transistor stages are dealt with by Shea,[32] Greiner,[33] Bell and Venning[34] and by Cattermole.[35] Their chief characteristic is the relatively high input and low output impedance possible which contrasts with the very low input impedance in the common emitter configuration. It has the disadvantages of providing a voltage gain less than unity. This is offset by the high linearity of output voltage with respect to input voltage, due to the negative current feedback introduced by the emitter resistance.

A family of low voltage hybrid amplifier circuits has recently been dewcribed by Laishley.[36] The input valve used is a double triode which can be operated at a low anode voltage. Both anode followed and cathode followed circuits are analysed, and expressions have been obtained for the voltage gain and impedance for these circuits.

C H A P T E R - II

A Survey of Representative Commercial pH Meters

Several problems encountered in the design and operation of practical pH meters are best understood by an analysis of actual instruments used in the laboratory. The following types of instruments may be regarded as fairly representative of pH instruments used in research and analytical laboratories. Details are discussed here as they are not easily available.

The Beckman model G pH meter

This instrument features compensation and null point indication. The instrument will be considered in two parts: (1) The potentiometer, with the details of temperature compensation, assymetry potential adjustment, standardisation and conversion of scale from pH to mv. (2) The amplifier circuit, with the operational features and mode of indication.

The potentiometer P is in the form of a precision slide wire bearing divisions from 0 to 13. In series with this potentiometer, is another small potentiometer which is calibrated to read temperature from 10° to 40°. The current flowing in the potentiometer circuit from the battery B is controlled by a variable resistance R_s which serves as the standardising adjustment. (STD).

A parallel resistance network with a potentiometer and fixed resistances R5, R7 enables the electrical zero point of the potentiometer to be shifted arbitrarily along the pH scale so as to constitute an adjustment for the assymetry potential (A.P.).

The signal applied E_1 (the potential developed between the glass and calomel electrodes for example) is balanced by the equal and opposite signal E_1 developed across the potentiometer and the nett difference of potential between the two sources is fed to the amplifier which will indicate a null point on the indicator.

The A.P.Adjustment

In a continuous pH scale from 0 to 14, the sign of the input EMP developed by the glass-calomel cell changes in sign according to the table below**

pH	EMF	pH	EMF
0	- 0.4142	8	+ 0.0592
1	- 0.3550	9	+ 0.1183
2	- 0.2958	10	+ 0.1775
3	- 0.2366	11	+ 0.2366
4	- 0.1775	12	+ 0.2958
5	- 0.1183	13	+ 0.3550
6	- 0.0592	14	± 0.4142
7	0.0		

** Bates: Electrometric pH determinations.

Thus it is necessary to be able to shift the center point of the pH indicating potentiometer scale so that at the midpoint (pH 7), the potential is zero with respect to the amplifier ground potential (against which the signal is measured).

In addition to this, the small variations in the e.m.f. developed by glass electrodes due to their assymetry effect can be compensated for by the same adjustment.

The assymetry effect, first recognized by Cremer, is due to both sides of the glass membrane not behaving exactly alike. If identical solutions are placed inside and outside the bulb of the electrode, there is a small potential difference built up between identical electrodes placed in these two solutions. This assymetry potential is of the order of a few millivolts. In most direct reading pH meters the A.P. is compensated for, by adjustment of the buffer standardising knob or zero adjuster, when the instrument is standardised on a standard buffer solution.

During standardisation, a standard cell opposes the potential developed across the standard resistor R. The amplifier is thus used as a null indicator. Once the potentiometer is standardized by adjusting the series resistance in the B supply, the adjustment will not change, as long as the batteries are in good condition and maintain a constant E.M.F.

The standardisation can be carried out to a precision which is limited by

1) the drift stability of the amplifier
2) the stability of the potential source B
3) the sensitivity of the amplifier.

It is assumed that the potentiometer elements are all of low temperature coefficient materials like magnanin wire.

Beckman Model G Amplifier

Having discussed the features and functions of the potentiometric compensation circuit, we now turn to the amplifier, which in the model G operates as a high impedance detector. (fig.1.)

The amplifier consists of a two stage direct coupled amplifier. The first valve V_1 is a selected 32 valve which operates as an electrometer. Potential changes across the load resistor R_1 due to the changes in plate current in V_1 are coupled through the Battery B_3, in order to maintain the required negative grid bias on V_2, the expedient of using a battery to bring the d-c level down from the anode to following grid has to be used. This in itself is a possible cause of drift, besides being inconvenient in use, if the batteries are stacked together. The grid of V_2 now follows the amplified signal applied to V_1 and thus the current in V_2 swings through a large range. The current amplification of V_2 is large, since it has a high value of g_m i.e. a large transconductance.

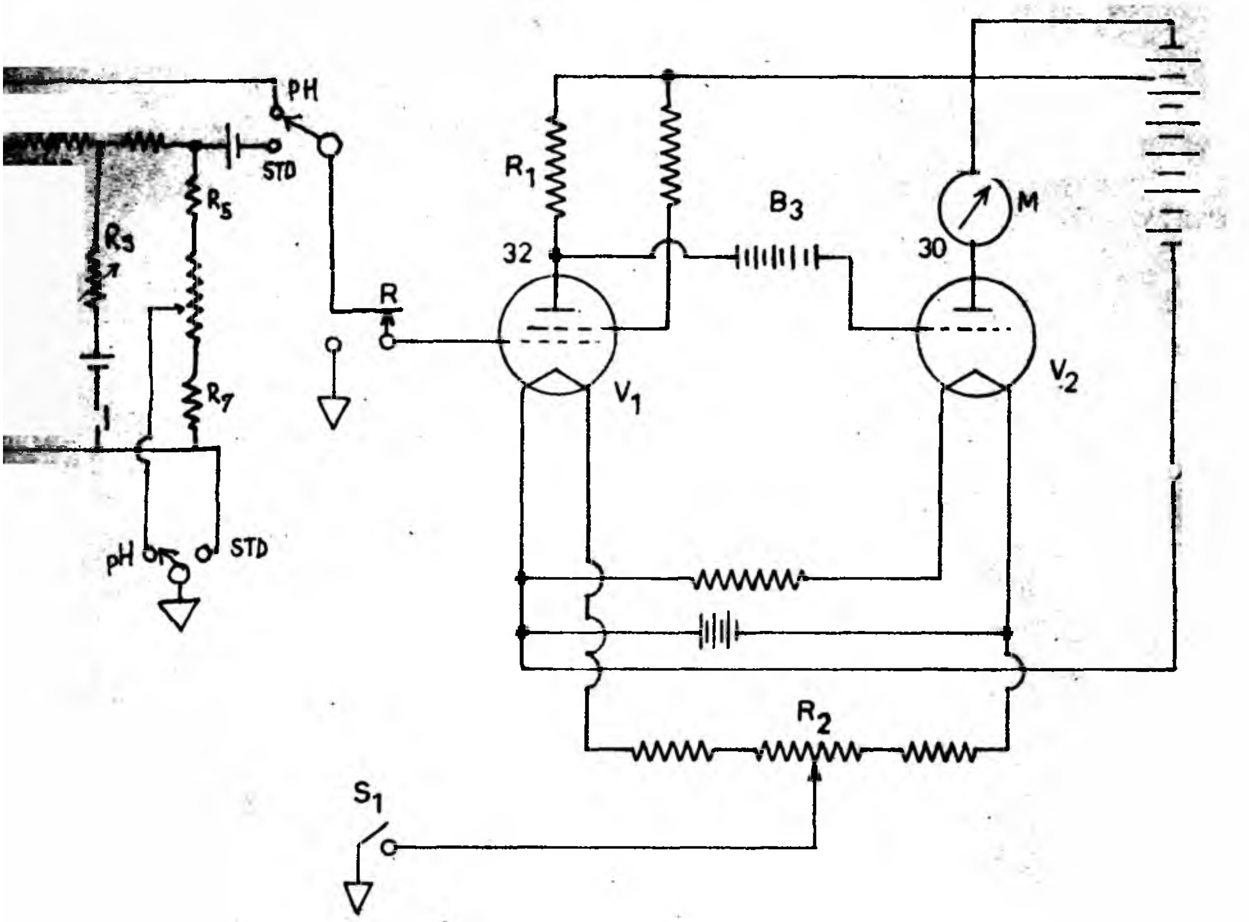
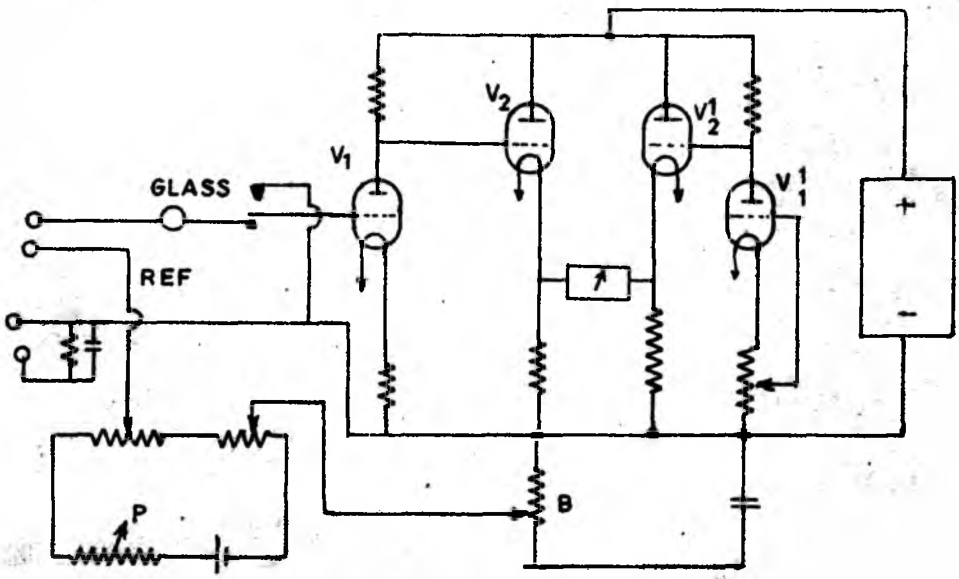


FIG 1(a) SCHEMATIC CIRCUIT : AMPLIFIER MODEL G



1(b) RADIOMETER pHM4 pH METER

The amplifier is operated as follows:

After the initial warm up period, and with the grid grounded, (Switch S_1) the bias is adjusted (by varying R_2), until the meter in series with V_2 shows an arbitrary "zero" deflection. This is nearly half the full scale deflection on the meter, but this serves as a reference point. The switches are then turned to standardize, in which position the amplifier acts as a null detector. The series resistance R_{STD} is then adjusted, till the deflection of the needle reaches the reference ("zero") point. This indicates that the out of balance signal from the potentiometer is actually zero.

This amplifier is inherently subject to a high rate of drift (c.f. Artzt[14]) as it is cascaded and requires more than one potential source for operation. However in the application above, this amplifier fulfills the need for a null detecting device of high input impedance.

Temperature compensation

The change of pH with temperature is given by the slope of the graph of E.M.F. against pH i.e. 2.302 RT/nF. This change in pH amounts to 0.020 pH units per degree centigrade, and must be compensated for in taking pH measurements.

The problem of compensating for the temperature in a potentiometric compensating instrument is solved by interposing a variable resistance in series with the main potentiometer. Thus the value of the current flowing through the potentiometer and hence the value of potential per pH unit (i.e. the value of 0.059) can be adjusted to give the theoretical slope at that temperature. Automatic compensation is also possible by the use of a resistance thermometer or thermistor in the pH measuring circuit.

Standardization

Standardization is carried out in the model G potentiometer by incorporating a resistor in series with the potentiometer and switching the amplifier so that the potential of the standard cell is compared with the pontential drop across the standard resistance in series with the potentiometer.

The Radiometer PHM 4 type pH meter

The circuit consists principally of a two stage push pull direct coupled amplifier and a precision potentiometer.

The input signal from the glass electrode is fed to the grid of the input electrometer V_1. The calomel electrode is connected to the precision potentiometer P; this potentiometer is biased with respect to the amplifier by the auxiliary potentiometer B which serves as a buffer adjustment.

The meter is a null type center zero instrument with a full scale deflection of 90 μA. It is connected across the cathode follower stages V_2 V_2' during measurements of potential. For the initial operational checks, the meter is connected by a multiple contact switch to the various battery power units shown in the figure.

The features of the instrument as detailed by the manufacturers are: (1) It is a battery operated universal pH and MV meter, (2) The input resistance is 10^{12} ohms and grid current is low (less than 3×10^{-12} A), (3) The design is based on the compensation principle. The compensation voltage is applied through a stepped potentiometer (14 steps) in series with a variable slide-wire (272 mm length), (4) The total readability is 0.001 pH or 0.1MV all over the range from 0 to 14 pH.

Power Unit

One of the features that is interesting, is the use of a transistorised d-c to d-c converter. This enables the use of one type of cell (1.5 volt, high capacity) throughout the instrument.

The d-c to d-c converter is effectively a power oscillator operating at 4 kcs. The output of this oscillator is rectified by semiconductor diodes (OA81) and used as an HT supply for the amplifier. The output voltage is 47 V d-c at the filter. The converter also supplies an AC filament voltage to the output valves V_2V_2', while the input valves V_1V_1' are supplied the filament current from the dry cells B.

The amplifier: The use of electrometer valves of the subminiature type with matched characteristics solves the problem of grid current; a grid current as low as 10^{-12} A can be easily attained with these valves.

The balanced amplifier which is symmetrical about the input and output serves to eliminate the common mode drift signal. Drift due to changes in plate or screen potentials affect both halves of the amplifier to the same extent and are cancelled out in the output. This arises from the fact that in a push pull amplifier the signals to the valves in push pull are out of phase with each other. The amplifier is then a straight forward null detector with negative current feeback in the output stage. The biasing potential for the input is obtained by an auxiliary potentiometer and the main precision potentiometer gives the input potential in terms of the compensating voltage applied by the potentiometer.

The Beckman Model H2-pH Meter

The model H_2-pH meter is a widely used direct reading pH meter featuring mains operation, power stabilisation high amplification, and negative feed back.

This circuit will be discussed in detail, as it has formed a basis for several other designs. It may be sectioned into 1) the power supppy, 2) the pH sensing and indicating circuit and 3) the negative feed back circuit.

A transformer with mains voltage tappings (selected on the fuse holder) feeds a 6X5 (or 6X4) rectifier. This valve is rated at 800 v. (p.i.v) and 81 ma i_k. The output voltage at the cathode at the valve is nearly 300 volts d-c. This is filtered by a π filter formed by two 32 m.f.d. capacitors and a 2000 ohm resistance. This d-c supply voltage is fed to the electronic regulator section.

A fairly elaborate regulator is used here which has to provide a stabilised voltage, low output impedance source for the amplifier and maintain a constant potential for the biasing circuit.

A regulator of this type has three functional components: 1) the series element, 2) the voltage reference and 3) the error signal amplifier. These are connected together to form a closed feed back loop so that any changes in the output voltage are automatically compensated for.

This is achieved by having the amplifier control the series valve by feeding the amplified difference between the voltage reference and an arbitrary pre set voltage which is a fraction of the total output voltage. This is the sampling circuit.

The out of the voltage stabiliser is then fed to a potential dividing chain $R_1R_2R_3R_4R_5R_6$. This chain includes the filaments of the first two valves, the electrometer 932 and the following pentode (DAF91). Since the potential across this chain is maintained constant at 108 volts (the operating voltage of the V.R.tube) the filaments obtain a constant current and this contributes to the d-c stability of the circuit. The ground point (0 volts d-c) is the negative end of the VR tube and the negative end of the potential divider is maintained at a constant value by the electronic regulator. (Fig. 2.) This potential can be adjusted by altering the resistance R_B in the circuit, which changes the grid bias of the amplifier tube V with respect to its cathode.

We now consider how the circuit responds to electrode potentials from very high impedance sources, typically, the glass electrode.

The important feature of this circuit is the use of negative feedback to give an indication (on a meter) that is exactly proportional to the input signal, and which will be independent of variations in tube characteristics or small fluctuations in voltage.

Essentially, a feed back circuit which provides negative feedback must ensure that the phase of the feedback signal is out of phase with the input. In d-c amplifiers the frequency dependence does not arise, as there are no reactive coupling elements to produce a phase shift from input to output which is frequency dependent.

The design of the circuit is based on the well known Loftin-White d-c amplifier in which each stage is succeeded

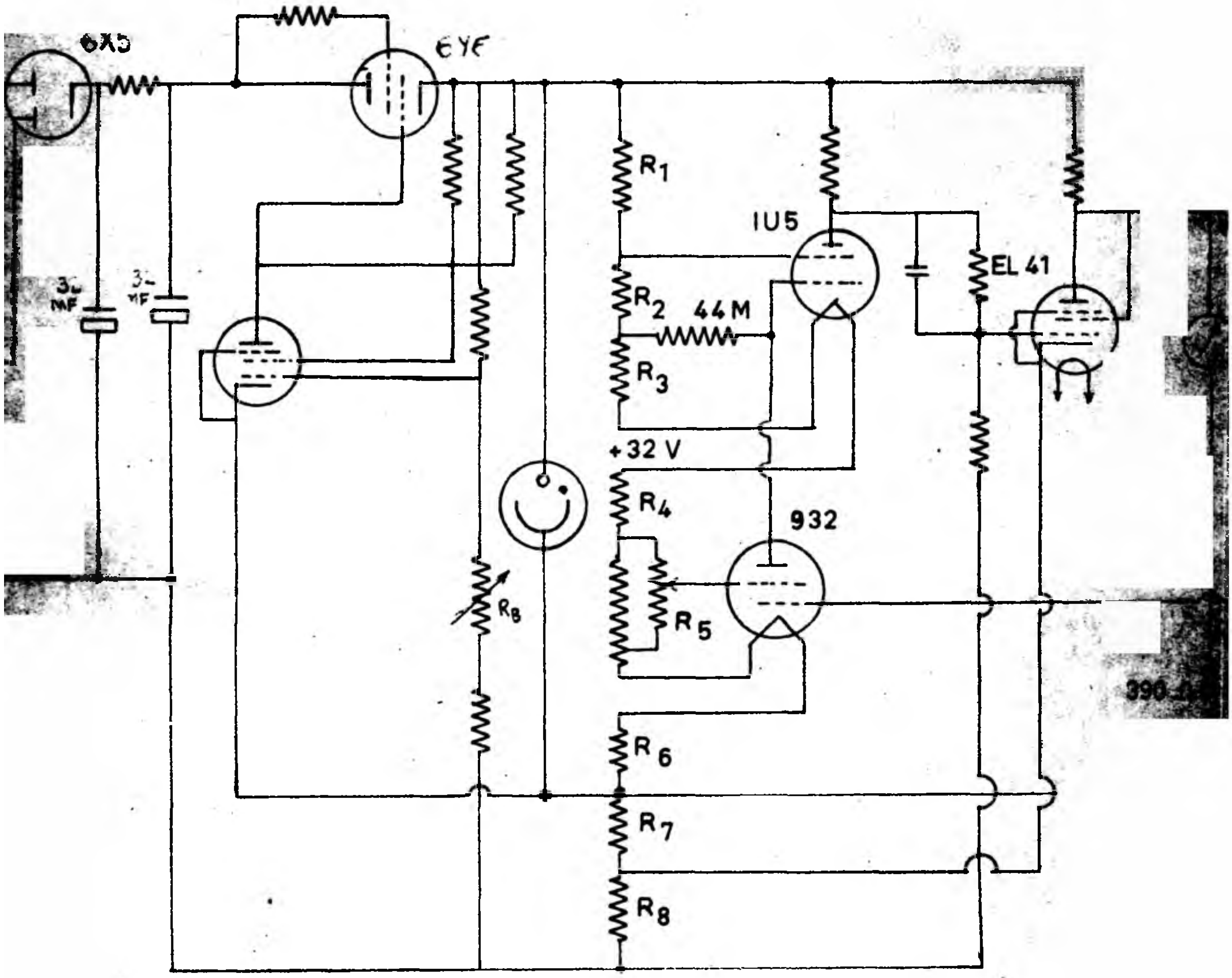


FIG.2. SCHEMATIC MODEL- H-2 pH METER

by another at a higher potential with respect to the first. Sich circuits have been described by Arzt[14] and have the advantage of eliminating interstage battery supplies to maintain d-c levels from one stage to another. The 932 input electrometer is a type 32 valve selected on the basis of low grid current, low noise and low ionisation (due to residual gas) from a very large number of 32 valves. The 932 has a directly heated filament. The characteristics of a typical 32 valve are given below*

V_f d-c	I_f	Plate volts	Grid_1 volts	Gride current	r_p	I_p	g_m
2.0	0.06A	180 (max)	- 2	.4 ma	1 m	1.7 ma	650 mhos

* Data from RCA receiving-tube manual.

For electrometer operation this filament current is cut down to 50 ma from the normal rating of 60 ma. The anode potential is fed through a load resistor of 22 meg ohms from the potential divider R_1 . . . R_6 (at 30 V d-c with respect to ground). The 932 is directly coupled to the next stage, a high gain pentode (1U5 / DAF91). The filament of this valve is also in series with the potential divider R_1 .... R_6 and so the mean cathode potential is at +32 volt with respect to ground.

Thus the potential drop across the load resistor of the 932 provides a negative grid bias for the 1U5. A very small change in anode current of the 932 would cause a large voltage swing across the 22 meg ohm load resistor, which would swing the grid of the 1U5. It would be well to remember that this swing is out of phase (of opposite polarity) with the signal applied to the grid of the 932. The 1U5 high gain pentode stage drives the power output stage EL41 again, by a direct coupling network.

The interesting part of the circuit design is provided by the output stage. The power pentode EL41 has two important functions.

1) It provides a large current output (because of its high transconductance) to drive the indicating milliammeter. This enables a rugged instrument to be used in place of fragile microammeters. A rugged milliammeter has a better zero stability and greater shock absorbing capabilities.

2) The current output is proportional to the signal voltage produced by the glass electrode; by allowing the voltage drop provided by the output signal current in a fixed resistance to be applied to the cathode of the input valve (in antiphase with the original signal) a very large negative feedback is applied to the amplifier.

The large negative feedback is effective in making the gain independent of valve characteristics and variation in voltage. The feedback also increases the input impedance of the amplifier considerably.

Critical review - Having outlined the design and operation of this instrument, it is worth considering some aspects of the instrument design from the viewpoint of reliability and performance.

The input stage circuit is based on a valve that is selected and hence not replaceable by a readily available equivalent. The valve provides a grid current level of 10^{-12} Amps. under the operating conditions. This is not a very low grid current level but may be tolerable for routine work with low resistance glass electrodes.

The use of a cascaded bleeder type of d-c amplifier has two important disadvantages.

1) There is an excessive dissipation of heat in the bleeder due to the full filament current flowing through it. This leads to damage to temperature sensitive components including capacitors and resistors. Such a breakdown is no fiction, but was actually detected in two models examined by this author.

2) The bleeder cascade arrangement is inherently subject to a high rate of drift because any drift in the first stage is amplified and passed on to the output without any effective compensation being possible. The drawbacks observed in this circuit have probably led to the new circuits seen in the "Zeromatic" instrument.

The Coleman pH meter (using condenser charging)

This commercially developed pH meter embodies the principle of charging a condenser from a high impedance potential source and discharing it into a comparatively low impedance detector.

It has a potentiometric compensation circuit for pH/MV measurements, and a standard cell for calibration of the pH/MV scale.

The detector is connected to the potentiometer by a micro switch. The capacitor is allowed to charge on depressing the switch, and on release the discharge to ground occurs. Since the other end of the condenser is directly connected to the grid, the grid follows the charging and discharging cycles.

The detector is a three stage resistance capacitance coupled amplifier with a milliammeter in the anode circuit of the third stage output valve.

The distinct disadvantage in this circuit is that the pulse obtained is differentiated at each stage and the resultant differentiated pulse is difficult to follow on an indicating instrument.

The Coleman "Compax"

This portable model pH meter has a novel device for indication of the null point on the compensated pH scale.

The pH measuring potentiometer is supplied directly from a mercury cell which has a fairly constant EMF. The standard cell has been eliminated together with all the elaborate switching that the standardizing procedure entails.

The two stage direct coupled amplifier incorporates the subminiature electrometer CK 721 in conjunction with a subminiature pentode CK 722. The null indication is the flashing on of a neon tube T_1 in a relaxation oscillator which is triggered by the change in the anode potentials when the input signal is zero. The pH scale is a disc mounted on a small (2") wire wound potentiometer. The smallest division on the scale reads 0.1 pH from 0 to 12 pH.

This circuit uses a large number of dry cell batteries which are difficult to maintain in good condition in tropical conditions.

CHAPTER - III

Experimental

Studies of electrode potentials, particularly the E.M.F. of the glass electrode as a pH measuring electrode, require an amplifier with a high input impedance. Conventional circuits using multistage d-c amplifiers tend to be unstable or elaborate.

The amplifiers discussed here are designed to have the following features: 1) high input impedance (10^{13} ohms), 2) low grid current (10^{-12} A), 3) fairly good drift stability. In amplifiers used for null measurements drift is not a serious problem, 4) operation from conventional dry battery packs, 5) use of solid state devices where practicable, and 6) a voltage sensitivity of 0.1 MV at an input impedance of 10^{13} ohms.

CIRCUIT No.1

The circuit (fig. 3) was designed around the ME1400 electrometer (Mullard). The inherent linearity of the cathode follower stage due to the large current feedback makes this high impedance amplifier suitable for direct measurements of electrode potentials and pH measurements. No voltage feedback is used in this amplifier as the voltage gain is less than unity for both the stages. The

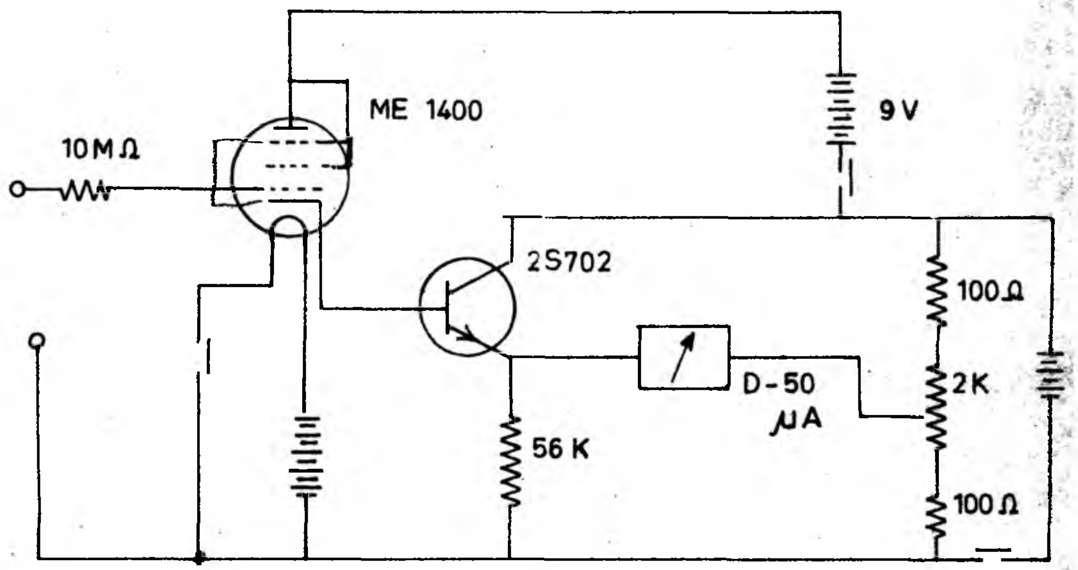


FIG. 3. 2 STAGE HYBRID DC. AMPLIFIER USING ME 1400 ELECTROMETER

CHARACTERISTICS

VOLTAGE GAIN	0·9
SINGLE TRANSCONDUDTANCE	0·5 mA/V
INPUT RESISTANCE	10^{12} Ω
FILAMENT CURRENT	150 mA
DRIFT	5 MV/ hr.

ME1400 is triode operated, with screen tied to the plate and supressor to cathode. Operating characteristics of the ME1400 are given below:

TABLE - 1

ME 1400

V_f	I_f	V_a	I_{g_2}	$-V_{g_1}$	I_a (μA)	I_{g_1}	g_m μA/V
4.5	0.16	45	45	2	80	10^{-11}	240

The cathode follower ME1400 is coupled directly to the base of the n.p.n. transistor 2S702 (Texas Instruments). The main difficulty in using a transistor in conjunction with a cathode follower stage is its base bias with respect to ground. A p.n.p. transistor must be operated with the base negative with respect to emitter, while an n.p.n. type requires its base to be positive with regard to the emitter. The design therefore justifies the use of an n.p.n. transistor, as the cathode is at a positive potential with respect to ground.

The emitter follower configuration is used as it provides an input resistance (T-parameters):

$$r_i = r_b + r_c \frac{r_e + r_p}{r_c(1-a) + r_1}$$

which is much greater than the corresponding value of resistance in the other two configurations.

The emitter follower has the advantage of providing high input impedance and low output resistance and a higher degree of linearity than the common base or common emitter configuration.

The current gain is nearly equal to h_{fe} (forward current gain) while the voltage amplification is unity.

The 2S702 has a high value of forward current gain ($h_{fe} = 100$) which does not fall very much at lower collector currents. The electrometer was operated at a bias of minus one volt. This required that a potential drop of one volt in the emitter load resistor be obtained at an anode current of a few microampers. The load resistor of 56K ohms (high stability, cracked carbon $\frac{1}{2}$ watt) was therefore introduced. A simple zero balancing circuit and 0-50 μA meter complete the set up.

The use of a cathode follower-emitter follower enabled the use of a low current 9 volt battery for the electrometer tube and two series connected 1.5 volt torch cells for the transistor. The emitter to collector voltage was nearly 2 volts. The transistor is thus very conservatively rated as far as operating voltages go.

Amplifier using EF37 as input valve.

The preceding amplifier was based on the commercial electrometer ME1400 (Mullard). It has a rated grid current or 1×10^{-12} A under normal conditions. The circuit now described uses commercially available receiver tubes EF37 or EF37A which have been tested for 'starvation' operation at reduced anode and filament voltage. The suitability of these low noise pentodes for such an application was investigated by studying their behaviour at low anode voltage.

Valve characteristics of EF37, EF37A

The valve characteristics (plate current grid voltage curves) were determined for EF 37 valves at low filament and anode voltages. (fig.4)

The anode voltage was kept low to reduce ionisation in the tube which could lead to a positive grid current. The use of lower filament voltage also helps in reducing grid current by lowering the cathode temperature and thus electron emission . Filament voltage was 4.5 volts d-c, obtained from three heavy duty dry cells of 1.5 volts each.

The magnitude of grid current was estimated by the change in anode current caused by the introduction of a precision "Welvyn" 10 Kilo megohm resistance in series with the grid.

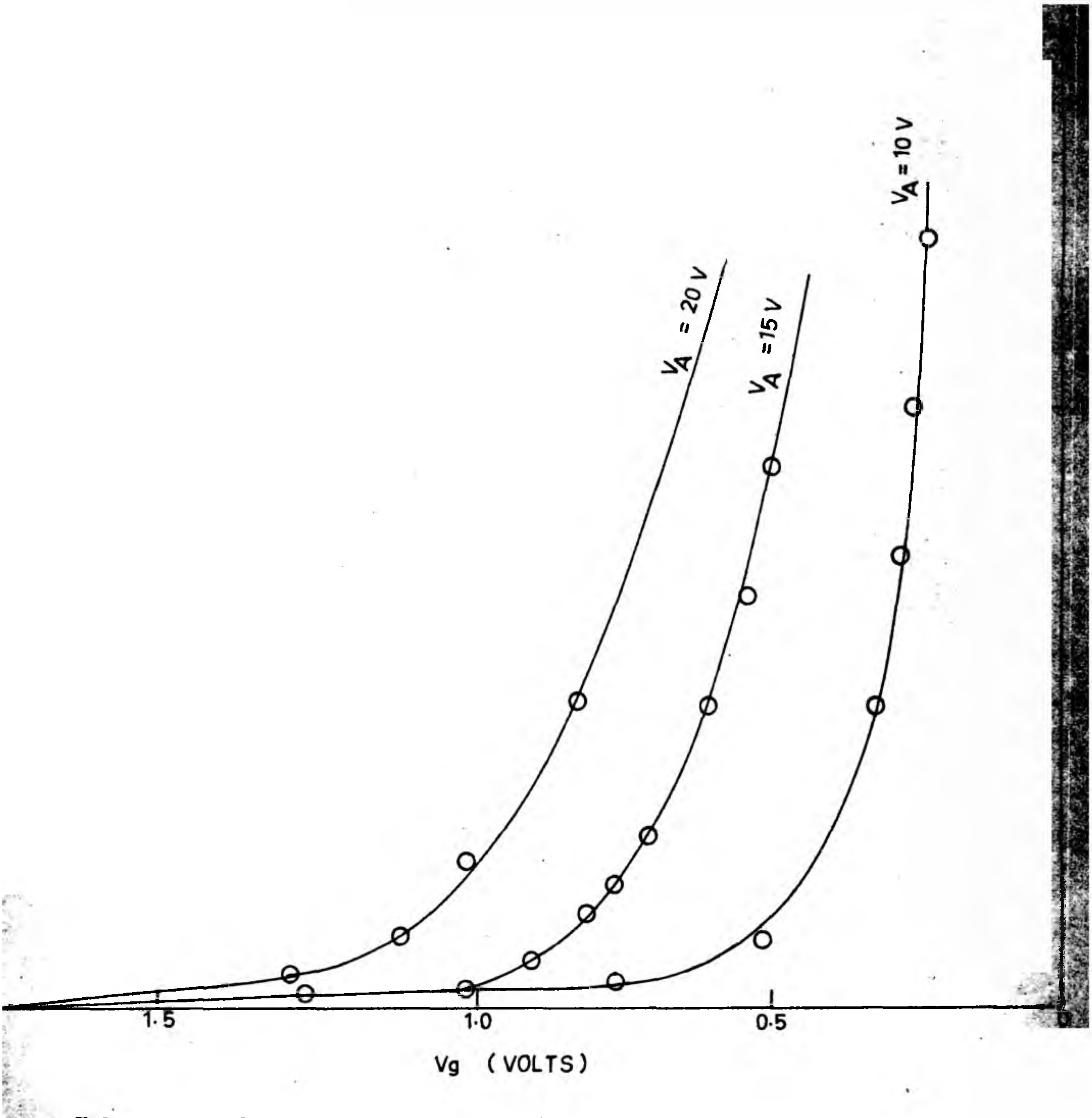


FIG. 4. ANODE CHARACTERISTS EF 37A

TABLE - 2

Operating conditions

EF37A (low noise A.F.Pentode)

Low anode voltage operation

V_f	I_f	V_A	V_{g2}	$-V_{g1}$	I_a (μA)	I_{g1}
4.5v	0.160A	9v	9v	1v	3	1×10^{-13}A

Characteristics

2S702 (n.p.n. transistor)

h_{fe}	V_{CB}	V_{CE}	P_{MAX}	I_{CO}
100 (average) at $I_C = 1_{MA}$	25 volts	25 volts	0.10 watts	1 μA

2-OC72 (matched pair)

V_c	I_c(MA)	$h_f(\alpha^1)$	I_{co} UA	P_c(max) m.w	V_c(max) volts	I_c (max)
-5.4	-1.0	45-120	-125	100	-16	-50

C I R C U I T No.2

(A three stage d-c amplifier)

The input circuit is based on the use of receiving tube type EF37-A (Mullard, low noise A.F.pentode) operated under conditions that ensure a grid current of less than 10^{-12}A.

The cathode follower EF37-A is directly coupled to the base of the following emitter follower; (fig. 5) this is an n.p.n. transistor (2S702, Texas instruments). This transistor has a forward current gain (α^1) of 100, and can be used at low collector currents. The emitter follower thus constitutes the second stage of the three stage amplifier. The load resistance for the cathode follower is the input resistance of the transistor 2S702 which in the emitter follower configuration is given by (approximate formula) $r_1(h_{fe} + 1)$.

Using a value of r_1 = 50K ohms and h_{fe} = 50

$$R_L = 50 \times 10^3 \times 51$$

$$= 255{,}000\,\Omega$$

This is effectively the cathode load for the input valve and the input resistance of a cathode follower is commonly of the order of a million times the cathode load resistance.

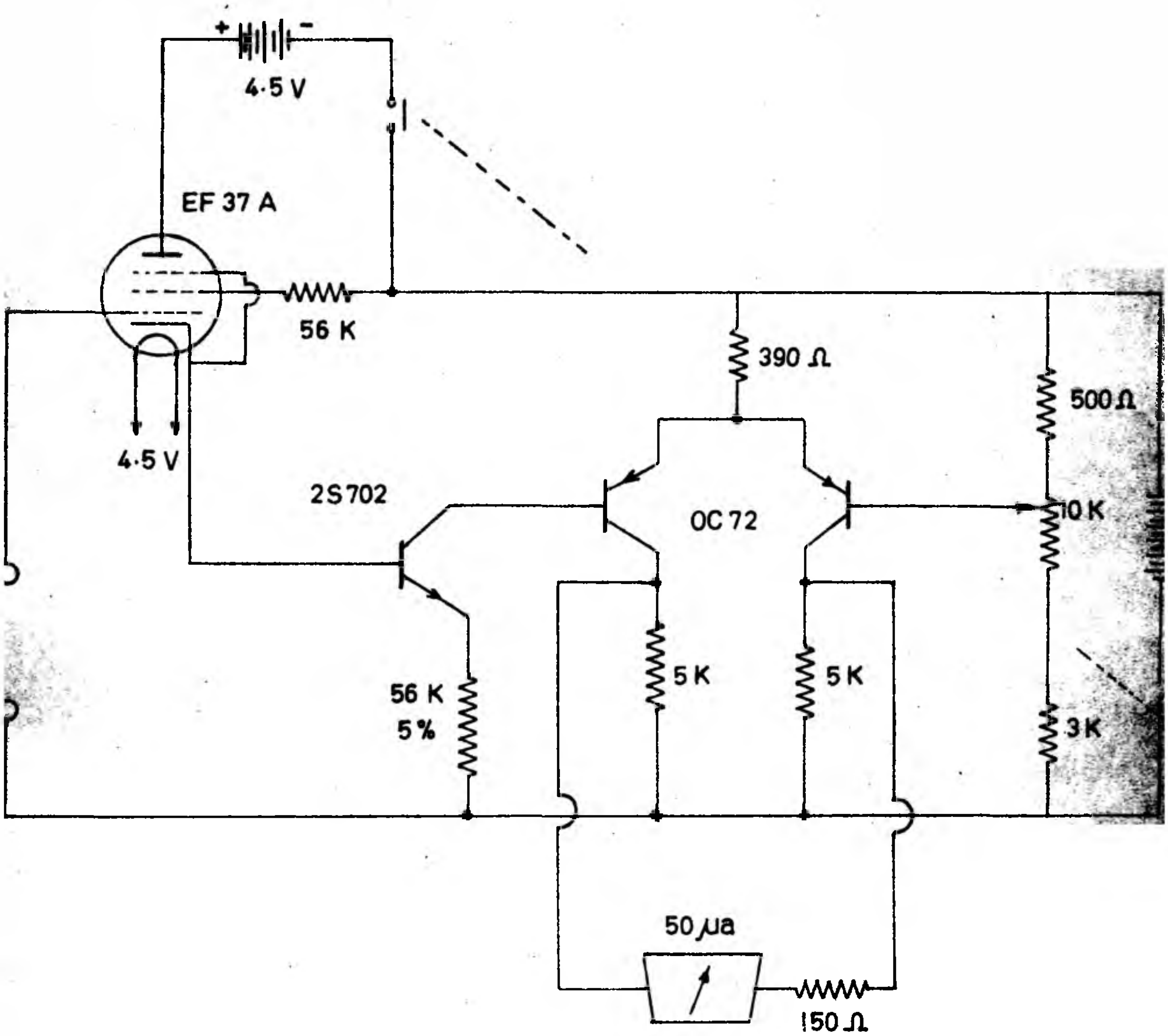


FIG. 5. THREE - STAGE D.C. AMPLIFIER

The collector current of the 2S702 is given by $I_C = h_{fe} I_b + I_{cbo}$. This is the base signal to the transistor following in the next stage.

The output stage (3rd stage) is a balanced transistor amplifier using two OC72 transistors in push-pull. The collector load is designed to drop 0.55 E_{bb} at the Q point. This is in line with the half supply voltage principle which prevents thermal runaway. The low collector current contributes to thermal stability which is further increased by the degenerative emitter resistor introduced.

The collector of the 2S702 is directly coupled to the base of one OC72, while the other OC72 has its base connected to the variable point of a wirewound potentiometer; this constitutes the zero setting circuit. Care is taken that the base of the transistor (T) cannot be connected to a negative potential which would cause a disastrously high collector current by inserting resistance R, in series with the potentiometer. Placing the transistors together in an aluminium block which acted as a heat sink resulted in a lower rate of drift.

The 0-50 μA meter with a suitable shunt is connected across the collector load resistors. A variable meter sensitivity control take the form of a wire wound variable resistor in series with the meter.

The power requirements are met from a 9 volt battery for H.T. supply to both the electrometer and transistor amplifier. The filament current of 100 UA is supplied by three 1.5 volt torch cells in series. A d.p - d.t toggle switch controls both the H.T. and L.T. circuits.

TABLE - 3

Amplifier Test Data

Input Resistance	10^{12} ohms
Grid current	10^{-13} A
Voltage gain	0.9
H.T. (Volts)	9 V Common to triode and transistors.
L.T. (Volts)	4.5 V
Drift	0.5 mv/hr (referred to the input)
Signal transconductance	5 (MA/V)
Input sensitivity	0.5 mv.

Circuit Discussion

The circuit II described above is characterized by the use of a hybrid combination of an electron tube and d-c transistor amplifier. The electrometer ME1400 used in the circuit I has been conveniently replaced by the EF37-A operated under "starvation conditions". The conditions for operation were determined by the experimentally plotted low anode voltage curves.(fig.4) The curves show a sharp cut off and a high slope which is maintained even at low anode voltages of 8 to 10 volts. The operation of the tube under a combined reduction of low anode voltage and reduced cathode emission is the essential modification of normal characteristics which leads to a high input resistance and low grid current.

The low cathode temperature attained by the reduced (150 ma Vs 250 ma) cathode current is effective in reducing the noise due to (i) shot effect, (2) partition noise, (3) gas noise (caused by ionisation), (4) flicker noise (random fluctuations in cathode emission). The lower anode and screen voltages are also contributory to the lowering of tube noise.

The input transistor is a critical stage of the amplifier. A particularly interesting problem arises from the "starved" operation of the electron input tube, limiting the cathode current to a few micro amps. The output resistance of the cathode follower is effectively the equivalent generator resistance for the input signal to the transistor. The low value of transconductance of the input valve under "starved" conditions leads to a value of output resistance of the order of 50K ohms. The effect of this in aiding the stability of gain of the transistor amplifier is seen from the relation:

$$G = \frac{A_i^2 \, r_1}{r_g + r_i} \qquad (1)$$

where

G = power gain of the stage

A_i = current gain

r_g = generator resistance

r_i = transistor input resistance.

Since r_g is very much greater than r_i the gain is stabilised for small changes in r_i which is temperature dependent (r_i increases with increase in temperature)

The third stage (output stage) of the circuit is balanced difference amplifier using matched OC72 power transistors. These transistors have a current gain h_{fe} 100 at I_c = 10 ma. The use of a difference amplifier helps to solve the drift problem to a large extent. The circuit has a high common mode rejection ratio which is improved further by the use of a degenerative emitter resistance.

The various temperature dependent terms tend to cancell; any changes in V_{BE} of both the transistors will not give an output signal. The drift referred to the input is given by

$$V_1 - V_2 = V_{BE_1} - V_{BE_2} + (R_g + R_E + r'_{bb}) \frac{I_{Co_1} - I_{Co_2}}{\alpha\beta} + I_{B\alpha_1} - I_{B\alpha_2} \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

Where V_1 V_2 are the signals applied to the amplifier,

V_{BE_1}, V_{BE_2} are the emitter to base potentials,

R_E = Emitter resistance,

I_{Co_1}, I_{Co_2} are the collector leakage currents of I_1,I_2.

The above requirements of stability are met if $V_{BE_1} = V_{BE_2}$ which would be so for two identical matched transistors.

Silicon transistors have a controlled I_{Co} of the order of 1 μA compared to 4 μA for typical germanium devices.

<u>D-C Stability and current feedback</u>

In the course of the design, one factor contributing to the low drift obtained is the low current condition existing in the input transistor. It is desirable to make the current in the input transistor as small as possible so that variations of h_{fe} with temperature have a reduced effect.

The use of a constant current source as the emitter supply contributes heavily to the stability of the amplifier; by doing so the collector current changes for large symmetrical signal voltages are reduced.

The first transistor stage following the cathode follower uses an n.p.n. silicon plan or transistor which has a high current gain at low collector current. This ensures a large current gain in the common collector (emitter follower) configuration and the use of large current feed back through the emitter resistor.

The importance of using transistors with large current gain has been stressed by Shea[45] in describing transistor d-c amplifiers.

The negative feedback employed in the common collector configuration can be evaluated from the relation for ($1-A\beta$) where β is the feedback factor.

$$1-A\beta \quad = \quad 1 - \frac{\alpha^1\beta^1}{Y^1 Z} \qquad (3)$$

where α^1, β^1 are the current gain and internal feedback respectively.

Y^1 = output conductance

Z^1 = input resistance

For the circuit under discussion the following values are substituted in the equation (3) which approximates to $F = \frac{\alpha^1}{Y^1 Z^1}$

Z^1 = 50 K

Y^1 = 100 micromhos.

α^1 = 100

Then

$$F = \frac{100}{10^3 \times 100 \times 10^{-6}} = 1{,}000$$

indicating very heavy negative feedback.

The circuit thus relies on heavy negative feedback to rigidly stabilise the gain and operating point. The very heavy negative feedback may also be considered from the aspect of providing a constant current generator of high internal impedance to the transistor amplifier which leads to higher stability.

CIRCUIT No.3

A negative feedback hybrid amplifier is now presented incorporating the basic features of the two amplifiers described previously. (fig.6(a))

The amplifier is specifically designed for direct potential measurements, and hence the use of negative voltage feedback has been made in order to obtain high linearity and stability of gain.

The EF37A input cathode follower is directly coupled to an n.p.n - p.n.p combination high gain d-c amplifier. Heavy negative current feedback gives it a high inherent stability as previously discussed.

Circuit analysis

The simplified equivalent circuit (fig. 6(b)) reduces the current and voltage amplifying stages into an equivalent current generator. Negative voltage feedback is applied from the collector load of the output stage in series with the input signal v_i.

The input signal v_i gives rise to an output voltage. V_o which is (approximately) equal to the product of the transconductance (g_m) of the valve and the current gain of the two d-c transistor stages into the load resistance

$$R_L = R_A + R_B \tag{4}$$

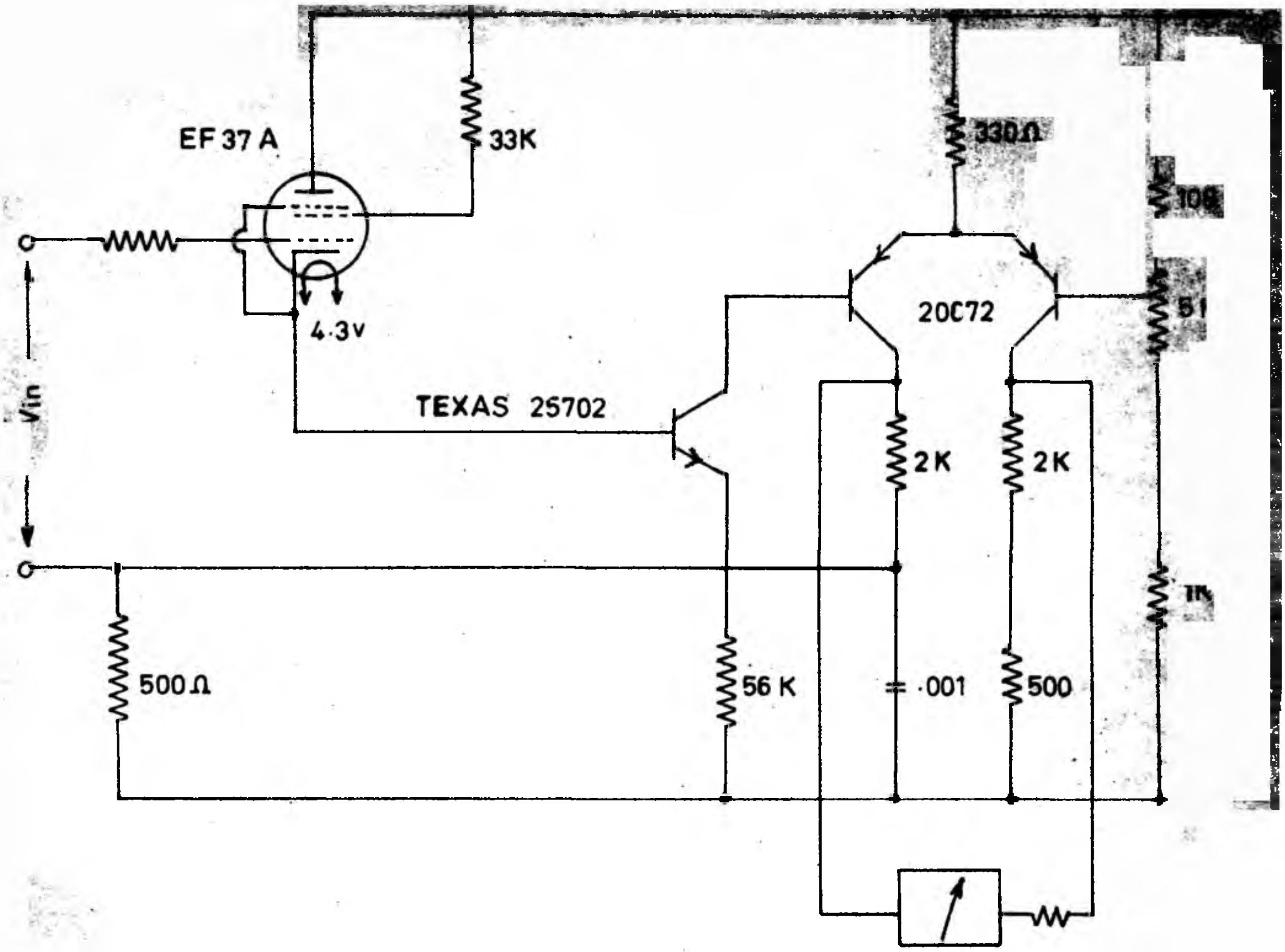
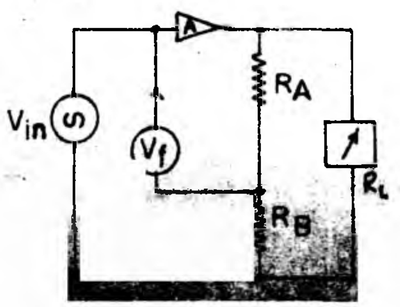


FIG. 6 (a) CIRCUIT : HYBRID FEEDBACK AMPLIFIER

DATA

INPUT IMPEDANCE	$> 10^{12}\ \Omega$
GRID CURRENT	$< 10^{-13}$ A
HEATER CURRENT	150 ma @ 4·5 V
H. T. VOLTAGE	9 V
SIGNAL TRANSCONDUCTANCE	2 MA/V
DRIFT VOLTAGE REFERED TO V INPUT	0·5 MV
LINEARITY OUTPUT WRT INPUT	± 1%



$V_o = (gm \times h_{fe} \times h'_{fe})\, R_L$

Thus

$$V_o = (g_m \times \alpha_1' \times \alpha_2) R_L \qquad (5)$$

The feedback voltage taken across R_B is therefore BV_o where

$$B = \frac{R_B}{R_A + R_B} = \frac{R_B}{R_L} \qquad (6)$$

The voltage gain with feedback is therefore

$$\frac{V_o}{V_1} = \frac{A}{(1 + A\beta)} \qquad (7)$$

where A is the open circuit gain without feedback

$$\frac{V_o}{V_1} = \frac{G_M \times R \ (R_A + R_B)}{1+G_m(R_A+R_B) \ \times \ R_B(R_A+R_B)} \qquad (8)$$

i.e. voltage gain $= \dfrac{G_M(R_A+R_B)}{1 + G_m.R_B}$ (9)

if G_m is large $1+G_m \simeq G_m$ and hence stabilised voltage gain $= (R_A+R_B)/RB$ which is independent of tube and transistor parameters.

The condition of large gain is satisfied by the use of a high current gain planor transistor in the second stage followed by a high gain output stage.

The circuit thus provides both a heavy current feedback with rigid stabilization of the operating conditions and negative voltage feedback to provide a high linearity of output with regard to input signals of both polarities.

Applications of the hybrid amplifiers to pH measurements

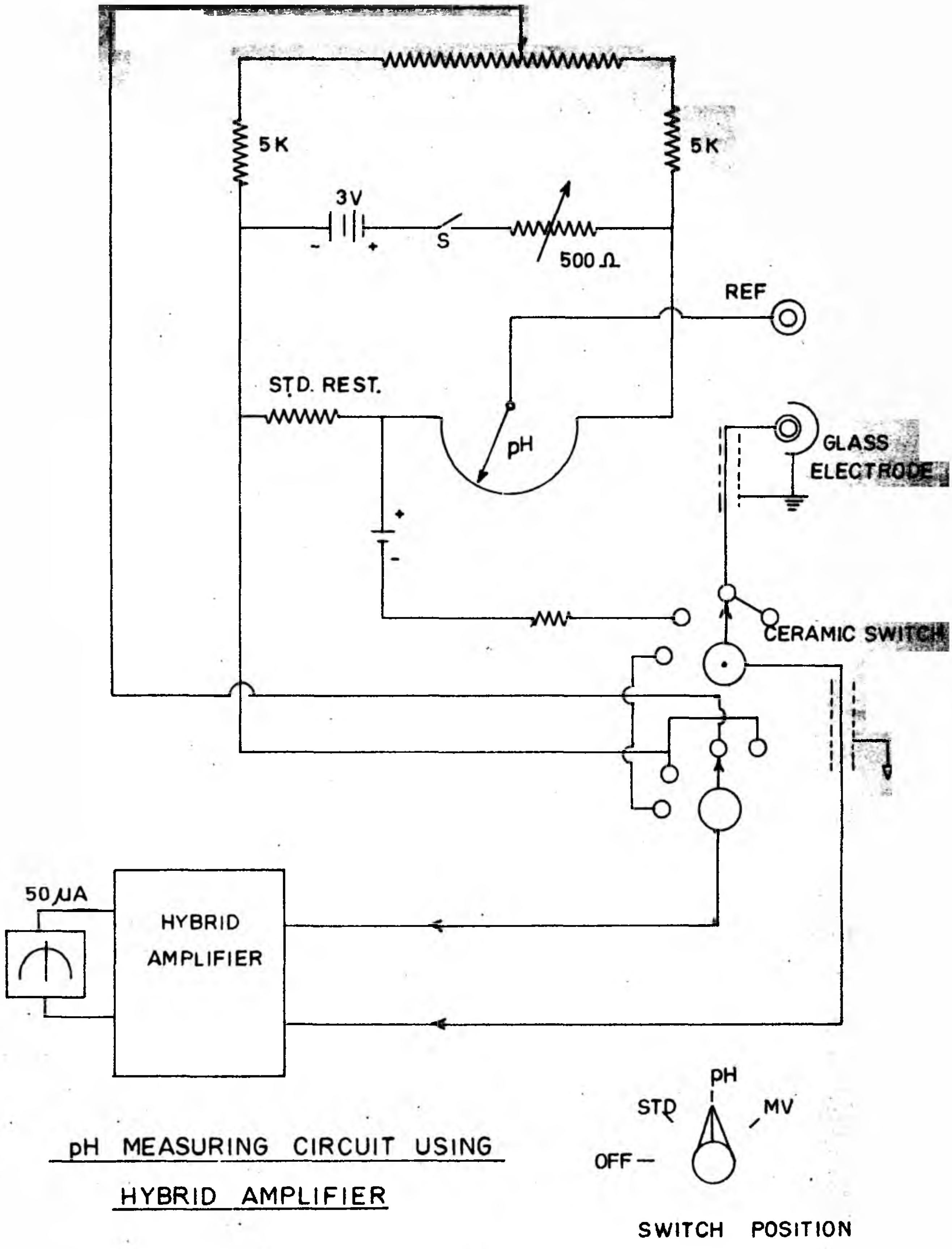
The circuit No. II described earlier was used in a potentiometric pH meter using the amplifier as a high input resistance null detector. A detailed circuit is given herewith (fig. 7). The instrument uses a standard Weston cell for standardisation of the pH scale reading pH units from 0 to 14. The divisions on the pH scale enabled pH to be read to ± 0.05 pH unit.

The sensitivity of the amplifier was fully adequate to reach this value of measuring precision.

The pH scale was adjusted so that the current through the potentiometer produced a potential drop of 59.16 mv per pH unit (at 25°C). This could be increased to 60 mv/°C at higher ambients by the temperature compensator in the potentiometric circuit.

The response of the pH meter using a set of glass and calomel reference electrodes (Jena glass works - W. Germany) was tested using standard (N.B.S.Standards) buffer solutions:

		pH (25°)
1.	Potassium hydrogen tartarate (satd)	3.55
2.	Potassium hydrogen phthalate (0.05M)	4.01
3.	Potassium dihydrogen phosphate (0.025M)	6.86
4.	Borax (0.01M)	9.18



pH MEASURING CIRCUIT USING
HYBRID AMPLIFIER

FIG. 7.

The glass electrode was stabilized according to standard procedures, before use. The calomel electrode when not in use was kept immersed in a saturated solution of pure KCl.

All pH measurements were reproducible within .1 % and no errors attributable to polarization of the glass electrode were observed.

C I R C U I T No.4

(A circuit using the 4067 semielectrometer)

The problem of evolving a more compact electrometer amplifier that would also operate on a greatly reduced power supply requirements led to the development of the circuit to be described. (fig.8).

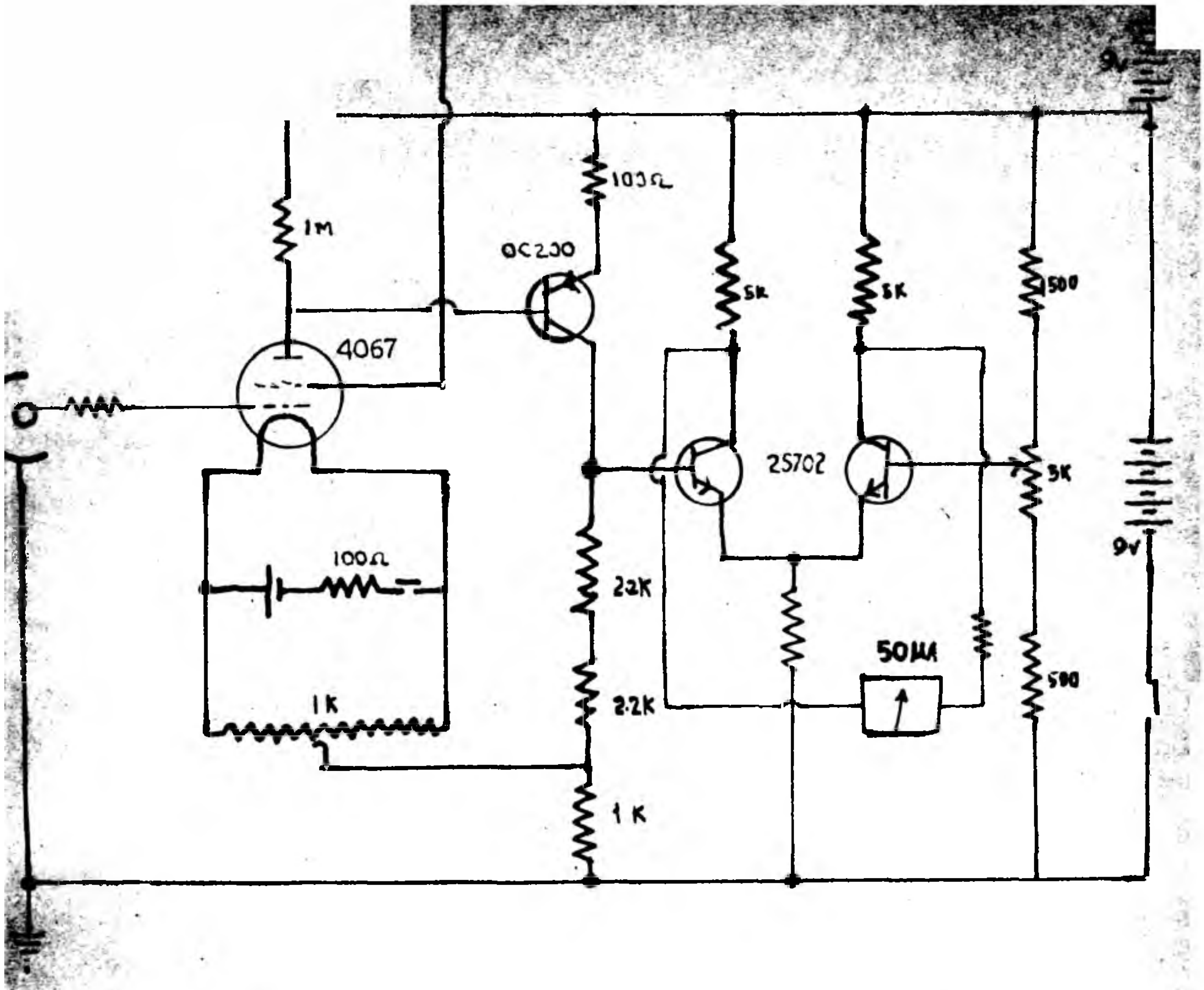
The input resistance was required to be greater than 10^{12} . This figure, though not as high as that attainable with the very best electrometers, is nevertheless quite acceptable for normal pH measurements with glass electrodes.

The input valve used was the subminiature Phillips 4067. This is a low cost semielectrometer valve with the following characteristics:

4067:

V	V_{g_2}	V_{g_1}	I_a	I_S (μA)	I_{g_1}
5 v	21 v	-0.75 v	50 μA	75 μA	10^{-11}A

Its outstanding advantage is its low filament current and voltage which make the problem of battery power much easier to solve. The rated grid current is 10^{-11}A, but a selected valve gives a much better value (10^{-12} A). The



4067 HYBRID AMPLIFIER

FIG. 8

directly heated filament supply provides a ready means of maintaining the required grid bias and enables a potentiometer to be connected across the filament to adjust the grid bias.

The requirement of high sensitivity dictated the form of coupling employed in the hybrid circuit. The anode of the 4067 (triode connected) is connected to the base of the transistor OC200; the low leakage current ($1\mu A$), and high gain (h_{fe} 100) at low collector current making it the ideal choice for this application. The anode current swing of the 4067 is thus amplified by the large value of h_{fe} (current gain) in the first transistor amplifier.

The use of an p.n.p - n.p.n combination was made in the following stage, where the OC200 drives a 2S702 n.p.n transistor so that a high current gain results. The first as well as the second transistors are both connected in the emitter follower configuration, which results in large current gain, negative feedback and low output impedance. Compensation is provided by the balanced push pull output stage using 2S702 n.p.n. transistors.

A UNIVERSAL pH METER

The construction of a precision null reading pH meter incorporating the hybrid amplifier circuits described in the previous section is now described. The instrument has been designed to make use of the recently developed silicon and germanium transistors in a null reading potentiometric pH meter. The high current gain of the n.p.n transistors (2S702 Texas Instruments) used in conjunction with a semielectrometer tetrode (4067) enables a sensitivity sufficient to detect pH changes of the order of 0.005 pH unit. The use of null measurement has the following advantages over the direct dial reading of pH:

(i) The null method gives the highest accuracy.

(ii) All measurements are made against a standard reference potential supplied by a Weston Standard cell.

(iii) The linearity of the indicating instrument is inconsequential to the accuracy of measurements.

(iv) The amplifier design is greatly simplified with regard to the following:

(a) The deviations from linearity of the amplifier do not vitiate the observations as they would in the case of a direct reading instrument.

(b) The drift problem in a null instrument is not so severe as in a direct reading instrument, because a ready check against a present zero can be made intermittently.

(c) Rigorous stabilisation of filament and anode voltages is not necessary.

The design of a compensation type precision pH meter can therefore be conveniently described under two heads.

(1) The compensation circuit.

(2) The detector and amplifier with power supply.

The heart of any compensation circuit is the precision potential divider from which accurately known and calibrated potentials can be applied to oppose the unknown. The compensation circuit used in this instrument consists of a stepped switch with 13 steps in series with a continuous slide wire. The temperature compensation has been incorporated in the form of a wire wound precision linear potentiometer. The stepped switch is fitted with 13 precision resistors, each step representing a unit of pH on the pH range from 0 to 14 and a unit of 100 mv on the MV scale from 0 to 1400 millivolts. The continuously variable slidewire, divided into 100 divisions on a scale attached, enables measurements to 0.01 pH directly with interpolation to 0.005 pH using the null meter. The 13 steps in series with the slidewire gives a total range of 14 pH units or 1400 m.v. The temperature compensator provides a temperature range of 0 to 40°C, the slope provided agrees with that specified by Du Mond and Cohen. The rest of the circuit comprises the Assymetry potential adjustment (referred to as A.P.) and the potentiometer standardising circuit. The A.P. adjustment is a potentiometer circuit in parallel with the main potential divider. The A.P. adjustment enables the electrical zero point of the potentiometer to be moved along the measuring potentiometer, and this also serves for making adjustments of the Assymetry potential arising out of the glass electrodes. This adjustment is electrically equivalent to the usual "Buffer Adjust" control.

The standardising circuit incorporates a standard Weston cell whose e.m.f. at 25° is 1.0186 volts. The instrument features independent standardising which is not affected by the position of the potentiometer. The potential of the standard cell is compared by the electronic amplifier with the potential developed by the potentiometer current across the precision resistor of 1018.6 Ω. This current in the potentiometer is adjusted by means of the standardising control R which is a wirewound potentiometer in series with the potentiometer potential source. The use of the amplifier with its high sensitivity and high input impedance is of great advantage as it enables the standardisation of the potentiometer with great precision. (The Cambridge Model - pH meter uses a galvanometer directly to effect the standardisation).

CIRCUIT DIAGRAM UNIVERSAL pH METER

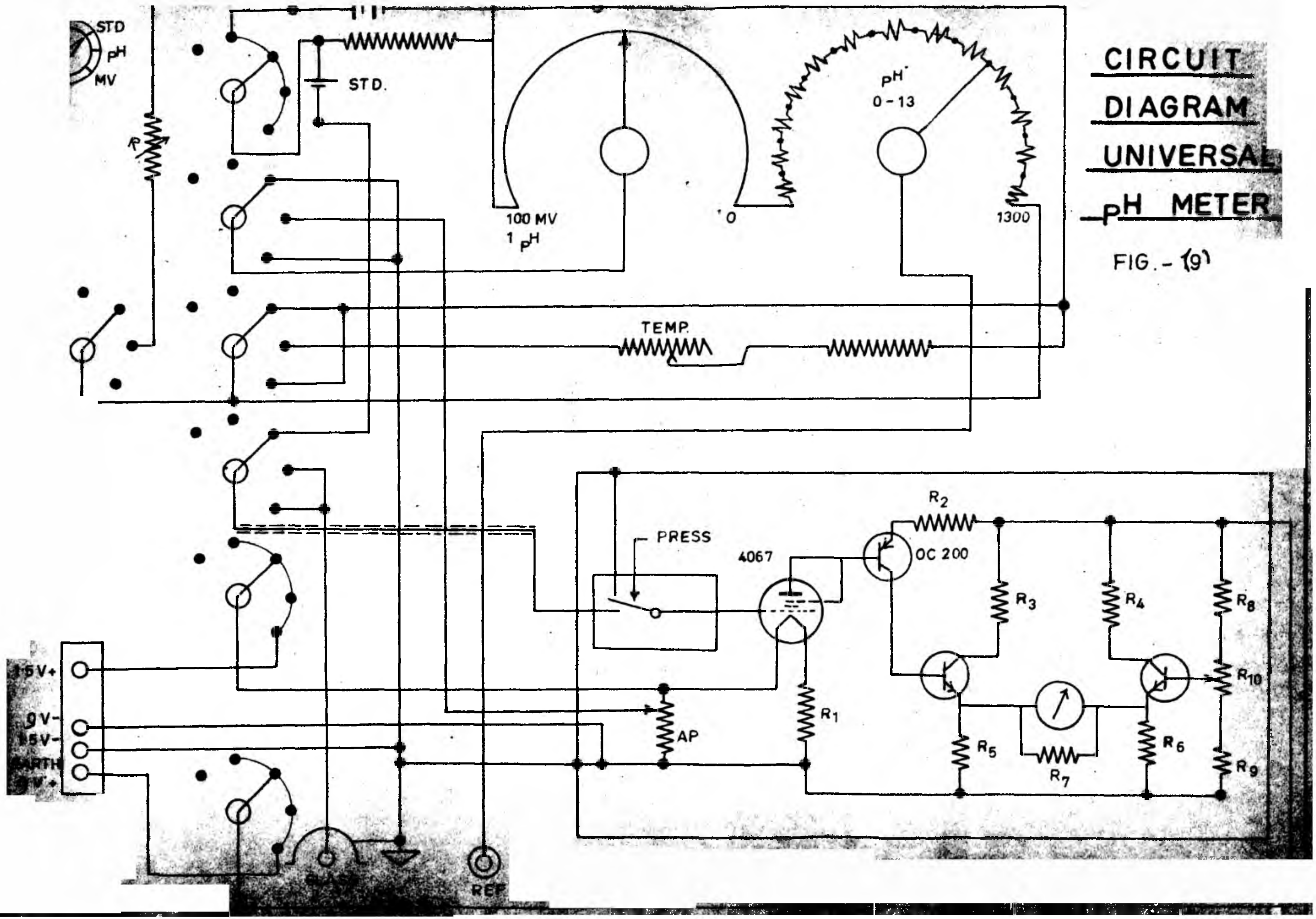


FIG. - (9)

The switching sequence which is best understood from the (fig.9) provides the proper earthing and zero potential points for the various parts of the circuits. The switching is elaborated by the necessity for incorporating 3 functions: pH measurement, standardisation, M.V. measurement. The grid of the amplifier can be connected to the external circuit only by depressing the push button on the panel. This helps to minimize grid current flow which would take place in a high impedance source directly connected.

SPECIFICATIONS

1. Measuring potentiometer:

The potentiometer consists of a multicontact switch integrally moulded in bakelite with bronze studs. 14 studs are fitted with lugs for soldering, on which the 13 precision resistors are mounted. The rotor is of the concentric ring contactor type and the movement is spring loaded. The contact resistance is less than 0.001 ohms, Insulation resistance of the order of 10^{14} ohms. Triple spring leave of phosphor bronze provide contact between the studs and rings.

2. Slidewire

The slidewire is a non inductive unit consisting of a 100 ohms coiled coil of manganin circumferentially mounted on an 8" diameter Paxolin disc which forms the base of the potentiometer. The rotor is a triple leaved phosphor bronze spring mounted on a moving arm concentric with the potentiometer axis.

Temperature Compensator: The temperature compensator is a 100 ohm wire wound linear potentiometer in series with the main potentiometer.

The Standardizing Potentiometer: This is a wire wound 500 ohm potentiometer of 10 watts rating. The standardizing range is 0.5 volts.

The Standard Resistor: The standardizing resistor develops a potential equal and opposite to that of the standard cell. It therefore has to be of high precision and accuracy. It was specially wound from high grade cotton covered manganin wire on a bakelite former.

The resistance was adjusted on a precision vernier potentiometer "Cambridge Model IV". It was finally incapsulated in an epoxy resin compound. The resistance measured was 1018.60 ohms at 25°C.

The Selector Switch: The selector switch is a 5 way six pole rotary switch. It is constructed from high grade low loss high insulation resistance bakelite sheets with silver plated contacts. The selector switch is triply ganged to allow synchronised switching in 6 different circuits.

The amplifier input switch: This is a vital component of the instrument. The insulation resistance requirement is 10^{15} ohms. The high quality microswitch used here has been found to be satisfactory from all aspects including size, switching pressure and switching program.

It is of the normally shorted type, the grid being kept at a ground potential except during measurements, when it is depressed. The switch is mounted on a bracket and is operated by an ebonite knob moving in a metal bush before the switch arm.

Amplifier Unit: The amplifier is constructed in a miniature aluminium casing measurement 10 cm x 6 cm x 5 cm. The case provides additional protection from dust, insects and adverse weather conditions experienced in tropical countries. (India). The amplifier is fed with H.T.L.T. and grid potential through ceramic bushed terminals. The zero adjustment potentiometer is fitted integrally with the amplifier making it a demountable unit.

Operational Principles. The operational principles are based on the use of a null sensing high impedance amplifier to detect and measure cell potentials by comparison with the standardized potentiometer.

The first operation that has to be carried out in use is the standardization of the potentiometer. The potential drop across a standard resistance caused by the potentiometer current flowing through it is compared with the potential developed by a saturated Weston cell in the instrument described. This operation is performed by switching the selector switch to STD. (Standardize) and adjusting the series resistor (STD Standardize Potentiometer) on the panel, until the amplifier output meter shows a null.

Once the standardization has been done, the instrument is now ready to use for measurement of any external potentials e.g. the pH measuring cell comprising of a glass electrode together with a calomel reference electrode.

If measured potentials are to be referred to a pH scale (0 to 14) the selector is switched to pH (position 4 on the switch panel) and the potential (pH) dials are manipulated till a null is obtained the position at the pointers.

<u>Electronic Amplifier</u>:

The instrument is based on the high impedance high sensitivity d-c amplifier described in section

The design of the amplifier features the use of an electrometer stage followed by a solid state amplifier incorporating the recent developments in transistor circuitry. The silicon transistor used has the exceptional advantages of high h_{fe} and low temperature sensitivity at the ambient temperatures encountered in use. The amplifier has been tested for use between 18°C to 32°C. The drift is maintained at a low value by the use of emitter degeneration. The electrometer used is a Philips 4067 which has been especially chosen for its low filament and anode voltage, and the very low filament current. This valve, incidentally, has been designed for use exclusively in pH measuring circuits. The design of the amplifier includes a potentiometric circuit for adjusting the Assymetry potential arising at the electrodes. This is a novel feature in comparison with other precision type pH meters which use an elaborate separate potentiometer for the same function.

The Glass Electrode:

Glass electrodes can be designed for special purposes, requirements based on either pH range or temperature being considered.

The instrument described can accommodate glass electrodes having an internal resistance of one thousand meg ohms or a little more. (The glass electrodes have a resistance range from 100 meg ohms to a thousand megohms.)

Recommended glass electrodes for the instrument are those made by: 1) Beckman Inc. USA; 2) Central Glass and Ceramic Research Institute, Calcutta; 3) Jena Glass Works, Schott and Gen. Germany.

A high insulation (10^{15} ohm) plug and coaxial cable must be used in this application, or else the glass electrode will be shorted.

The calomel electrodd is connected to the terminal post provided below the high impedance jack.

General Applications:

The pH measuring instrument has a very wide application in chemical research and industry, laboratories, biological studies, agricultural research.

The millivolt scale provided on the instrument enables the response of my electrodes to be measured accurately with respect to the calibrated potentiometer.

The pH scale used in conjunction with a glass electrode system is of wide application to pH measurements in general.

Specific applications

The instrument can be used with suitable electrode systems for the measurement of concentration of lithium, sodium, ammonium, potassium, silver chloride ions, redox potentials and concentration of O_2 and CO_2.

The instrument can also be used for carrying out electrometric titrations and could be used with a recorder.

Operating Instructions

The operation of the instrument will be outlined in the following steps:

1. Check the batteries periodically. The H.T.battery (9 v) should not read below 8 volts. The two L.T. batteries should be replaced when the voltage goes below 1.3 volts.

2. Put the instrument on by rotating the selector switch (second from right) on the lower panel from OFF to ON.

The instrument will now warm up. During a three minute wait, observe that the indicator microammeter needle moves across the scale first to the right and then to left.

An arbitrary zero may be set for the instrument by rotating the zero adjustment knot at the top center.

3. The scale may now be standardized by switching the selector to STD. (Standardize). The standardization is checked against the internal reference Weston cell by depressing the PRESS switch (at lower left) and the STD control is adjusted till a null is restored.

4. <u>pH measurement:</u> pH is measured by connecting the glass and calomel electrodes to the terminals provided on the panel.

The calomel is connected to the (REF). red terminal while the glass electrode is connected to the high impedance 1 jack above the reference terminal.

The selector is switched on to pH position.

Use standard buffer solutions such as 4.01 pH, 6.88 pH or 9.0 pH for calibration. Set the pH of the buffer on the dials and rotate the A.P. control till a balance is reached.

Millivolts measurement:

The unknown potential is applied between the two input jacks. The millivolt scale reads from 0 to 1300 mv on the unit dial and 0 to 100 mv on the large dial. The millivolt scale is adjusted till a null point is reached on the meter. The corresponding reading on the two dials read together gives the required Mv of the unknown.

For measurements of potential from high impedance sources, shileded leads should be used to minimize stray signals.

The glass electrode input jack has a grounded collar which engages with a sleeve on the input plug. This enables earthed shields to be used with the cables.

Component specifications:

1. Cabinet: M.S. integral type with offset panel. made from 18 SWG M.S. sheets Wrinkle finished in light grey.

2. Panel: M.S. 18 SWG. bolted to blange on the cabinet by 4 self tapping plated screws.

3. Dials: (1) Unit Dial.
Made from Opal perspex 1/8" thick. turned and engine divided. Fitted to panel.
(2) M.V. x 100 dial.
Made from Opal perspex (ICI) 1/3" thick fitted on moving spindle by plated brass bushing.

4. Knobs: Function knobs (A.P., STD., Temp., SWITCH)
Moulded from P.V.C., light grey
1" diameter.
Dial knobs: Black, serrated, made from bakelite.

5. Microswitch: Best quality, low contact resistance,
2 gms. pressure. 1" x 3/4" out diameter.

6. Meter: 0-25 MA. movement. 3" diameter.
Inst. Resistance 100.

7. Potentiometers (1) A.P. Adjust. 5000 "colvern" linear w/w 3 watts.
(2) STD. Adjust. "colvern" linear w/w 3 watts.
(3) Temp. °C set: 100 "colvern" linear w/w 3 watts.

8. Terminal Jack modified phonojack.
Glass, High impedance - Insulation resistance 10^{15}
made from perspex sheet
1/4" thick.

SUMMARY

A study of previous pH measuring circuits has shown that critical components constitute a major drawback in operation and maintenance. Simple circuits using readily available components have been designed and constructed which meet the requirements of pH measuring instruments and other applications.

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PART - 2

PART - 2
CHAPTER - I
HIGH FREQUENCY TITRATION.

Historical Survey

Instruments

High frequency titrations and conductance studies have attracted considerable attention.

Blake[1,3] studied the leading effect of an electrolyte when it was inserted in the tuned circuit of a valve oscillator. Jensen and Parrack[2] developed an H.F.titrimeter based on a tuned grid tuned plate oscillator. The changes in grid current, due to the introduction of a cell (containing an electrolyte) into the anode tuned circuit, were measured by a galvanometer. This circuit is reported[4,5] to have a poor stability at high sensitivity.

A review of instruments developed for high frequency titrations has been made by Blaedel and Malmstadt.[4] Among the instruments described are the titrimeters of Anderson[5] and Diehl.[6] West and Broussard[7] describe a hetrodyne titrimeter in which a coil type of circuit element is loaded by the tiration cell.

Since instruments developed before 1950 have already been reviewed,[4] a discussion of circuits and instruments that have been developed since is now presented. Hall[8] has described a simple high frequency titration apparatus for general laboratory use. The circuit is very similar to one[9] described for measurement of dielectric constants. A 6E5 magic eye tube acts as an oscillator and visual detector. The oscillator is a Pierce crystal oscillator with a shunt fed tuned circuit. An arrangement is made for monitoring changes in grid current by an external vacuum tube voltmeter. (V.T.V.M.). The tiration cell forms part of the tuned LC circuit. The frequency used is 2 mcs/sec. At this frequency the concentrations that could be studied were of the order of 0.01 m in NaCl. The change in V.T.V.M. volts, which is the means of following the titration, shows a total change (from an initial value of 12 v) of three volts, from 12 v to 15 volts for a complete titration of several ccs. This was an obvious case for designing an improved instrument with increased resolution.

A high frequency titrimeter based on the use of beat frequency oscillators has been designed by Blaedel and Malmstadt.[3] The circuit consists of two identical oscillators operating at 30 mcs. One of the oscillators has a titration vessel attached to the tuned grid circuit. A crystal mixer unit is used to produce a beat frequency note which is fed to the frequency measuring circuit. An oscilloscope and variable frequency oscillator constitute the frequency measuring circuit.

The cell used in this apparatus is fairly representative of high frequency titration cells described so far, and consists of a pyrex beaker which is fitted inside a hollow metal vessel. A ring electrode is fitted around the wall of the beaker while a flat disc electrode contacts its base. The sensitivity reported is 0.003N for HCl. The admitted defect of this instrument is the necessity of working in a limited, rather dilute, concentration region.

An important review of the principles of high frequency Titrimeters has been given by Reilley and McCurdy.[10] This paper describes the various types of instruments and the parameters measured, it also deals extensively with the design of cells for high frequency titrations. A twin-T impedance bridge was used in making quantitative measurements of both conductance and capacitance components. An attempt was made by these workers to study very thin cells but this was not possible because the measurements were out of the range of the bridge.

A tuned plate tuned grid circuit with an arrangement for recording the grid current changes is described by Flom and Elving.[11] The jacketed solution cell loads an inductance coil which forms the anode tuned circuit. Good results for acid base titrations were obtained at concentrations of 0.0063N. This circuit does not appear to have any special frequency stabilising elements; this would limit its suitability for recorded work, as described by these workers.

An oscillator of the tuned grid type is described by Anderson, Bettis, and Revinson.[12] The circuit is based on an acorn tube, 955. The grid current is measured with a galvanometer and zero suppression circuit. This instrument has the drawback that an end point can be obtained in the case of 0.1M NaOH only at 6 and 40 mcs, and not at 8 and 22 mcs. The application of this instrument to the volumetric determination of beryllium has been described.[13]

A 350 megacycle titrimeter has been described by Blaedel and Malmstadt.[14] Quarter wavelength concentric line oscillators are used. This instrument, though possessing good stability, is rather cumbersome and requires the use of V.H.F. techniques and components. In this instrument the differential method of titration could not be followed and the change in beat frequency after addition of solution was noted. The sensitivity was adjustable by varying the coupling to the Invar rod used in the quarter wavelength oscillator. The sensitivity reported is at a maximum for a concentration of 0.1 to 0.5N HCl.

Milner's circuit for a titrimeter[15] is similar to that of Jensen and Parrack[2] and has been applied to the titration of sodium sulphate with Barium Chloride. The total electrolyte concentration tolerable is reported to be 0.03m.

A study of the theoretical aspects of high frequency titrations is reported by Fujiwara and Hayashi.[16] The circuit is basically a 'Q' meter. A test tube containing electrolyte is placed within a coil coupled to an R.F. generator. The voltage across the coil, which varies with the 'Q' of the circuit is measured by a sensitive voltmeter amplifier. The plot of maximum resonance as a function of concentration for HCl shows an optimum sensitivity of 10^{-4}m HCl and again at 10^{-2}m HCl at a frequency of 6 mcs. In all the titrations reported the value of the change is only 0.2 to 0.3 units over a complete titration. Though sensitivity is reported at a concentration of 0.1 m the curve is not quite sharp at the end point.

Applications of H.F. titrations are described by Hall et alia[17] and by Bien.[18]

The application of a H.F. titrimeter to the titration of typical metal ions with E.D.T.A. has been described by Blaedel and Knight.[19] These measurements were restricted to a concentration of 0.1 m metal ion concentration although the frequency used is 30 megacycles.

A high frequency apparatus for the determination of moisture in solids (salts) has been described by Jensen, Kelly, and Barton.[20] The instrument consists of an oscillator which feeds an R.F. signal through a sample tube containing a mixed solvent. The solvent extracts moisture from the salt and thus affects the loading of the oscillator. The current flowing through the tube is rectified and fed to a meter system.

A titration apparatus operating at 100 mcs is described by Johnson and Timnick.[21] The unit uses a coaxial half wave line with a 955 acorn tube as the oscillator. A Sargent polarograph is the detecting instrument by which grid current changes are recorded. Sensitivity is attained for a conductance range corresponding to 0.005 to 0.08 m NaCl in aqueous solution. The instrument was found to be susceptible to temperature variations and an increased stability was felt to be desirable.

Johnson and Timnick[22] in a later paper, describe a modified circuit operating at 120 mcs in which the titration cell is placed within a loop of 3/16" copper tubing forming the anode tuned circuit. By placing the cell within the loop, the changes in conductivity have the maximum loading effect. It was possible to titrate 3N HCl with 4N NaOH though the relative sensitivity is not high.

An apparatus based on the Franklin oscillator in which the voltage developed across a tuned circuit containing the cell is fed to an high impedance detector is described by Ishii, Hayashi and Fujiwara.[23]

An H.F. titrimeter suitable for titrations involving colloidal electrolytes is described by Kupka and Slabaugh.[24] The circuit consists of a Pierce crystal oscillator with a clamping tube to ensure a constant amplitude and low impedance source. The oscillator applies a constant voltage to the conductance cell and the r.f. current though it is rectified and fed to a microammeter circuit, with arrangements for zero suppression.

An unbalanced twin-T bridge has been used by Walker (et alia)[25] for performing high frequency titrations.

<u>Physico-chemical principles</u>

The nature of the response of H.F. titrimeters has been discussed, with particular reference to the mechanism of the loading effect, by Blaedel, Malmstadt, Petitjean and Anderson.[26] The response of two typical titrimeters has been explained by Blaedel (et alia)[26] on the basis of an equivalent circuit involving the capacitance of cell and solution, the resistance of the solution and the inductance introduced in the circuit of the oscillator. It is pointed out that the maxima and points of inflection observed depend upon the operating frequency, and the electrolyte concentration, in the case of a grid dip oscillator, while the frequency measuring instrument shows only one region of high sensitivity. The circuit parameters which are involved in the response of a titration cell are L, the inductance (which is fixed); C_1, the capacitance in series with the solution, essentially the capacitance of the cell walls, from the outside electrodes to the electrolyte through glass; C_2, the capacitance of the solution which depends on its dielectric conatant, and $1/R$ the ohmic conductance.

Hall[27] discusses the electrical characteristics of cells and the response of high frequency titrimeters. An equivalent circuit has been described which enables experimental results to be explained on the basis of maximum power dissipation at a critical value of resistance.

An equivalent circuit for an H.F. conductance cell placed within a coil of the oscillator has been described by Anderson, Bettis and Revinson.[12]

In principle, high frequency conductance phenomena are characterized by the existence of a capacitance component and a resistive component of the total radio frequency current carried by the cell. The high frequency conductance has been a subject of investigation by Debye and Falkenhagen.[28] At very high frequencies which are comparable in period with the relaxation time of the ionic atmosphere, an increase in conductance was predicted and experimentally verified.

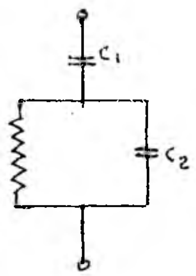
The relaxation time of a typical 1:1 electrolyte has been calculated to be of the order of 10^{-10} sec for a molar solution so that for a solution of 0.001 m this would be increased to 10^{-7} sec.

However, this effect, according to Blaedel and Malmstadt, has only a second order effect on high frequency titrations. This would be the case, if the capacitance effects were predominant in the response of the instrument.

A detailed analysis substantiated by experimental measurements has been made by Reilley and McCurdy.[10] The co-relation between the low frequency conductance and high frequency (5 to 30 mcs) conductance has been given by the relation (reproduced here) :-

$$G_p = \frac{1}{R_p} = \frac{K^2 C_1^2}{K^2 + 4\pi^2 f^2 (C_2 + C_1)^2}$$

The above relation gives the value of the high frequency conductance Gp in terms of the parameters of the equivalent circuit below:



from the above relation, the condition that Gp should be zero (giving a peak at a particular frequency) is obtained by differentiation and equating to zero:

$$G\ \text{peak} = 2\pi f(C_1 + C_2)$$

for a thick walled cell, C_1 is negligible in comparison so that

$$f\ \text{peak} = \frac{1.8 \times 10^{12} K}{D}$$

where K is the low frequency conductivity and D the dielectric constant. This expression is the same as that obtained by Forman and Crisp who studied the absorption of radio frequency power in electrolyte solutions by measuring the temperature rise in the solution.

The relation between electrolyte concentrations and frequency of maximum sensitivity has been given in the form of a table from data by Blaedel and Malmstadt, and Forman and Crisp:

Osc. frequency mcs	Con. of max sensitivity		
	NaCl	$CaCl_2$	HCl
5	0.0025M	0.0013	0.006M
30	0.014	0.008	0.003
57	0.032	0.015	0.005
100	0.05	0.027	0.01
375	0.2	0.1	0.036

This table, based on the equation of Forman and Crisp

$$f\ \text{peak} = \frac{1.8 \times 10^{12}\ K}{D}$$

shows that very high frequencies must be used if concentrated solutions are to be studied.

Reilley and McCurdy state that an increase in C_1 (the cell capacitance) would lead to oscillations stopping eventually. Thus it was apparent that the possibilities of increasing the concentration region to higher concentrations had not been fully explored.

One of the objects of this study has been to investigate the possibility of extending the useful range of concentration to higher concentrations (0.5 m) at frequencies not exceeding 10 mcs. This frequency limit has been set by considerations of simplicity and stability of oscillators which would be built readily without the use of special components.

Recalling the equation described earlier

$$Gp = 2\pi f(C_1 + C_2)$$

It is apparent that the sensitivity maximum contains a parameter C_1 (capacitance at the cell walls) which is capable of adjustment. C_1 would be made comparable with C_2 (the solution capacitance), instead of being negligible in comparison, which is the basis of the equation:

$$fp = \frac{1.8 \times 10^{12} K}{D}$$

This led the present author to investigate the possibility of using a new type of cellwhich could be used at higher concentrations together with lower frequencies than were hitherto practicable and to develop the related circuitry.

The use of a thin walled glass cell has apparently not received the attention it merits.

Reilley and McCurdy measured the characteristics of different types of cells with a twin-T bridge.

They report that a cell design was tried in which a metal foil was attached to the inner wall of a beaker with airplane dope. This resulted in too high a conductance for measurement and no measurements were possible.

This method was tried by the present author using Araldite epoxy resin on a metal cylinder. The experiment failed, however, due to the presence of microscopic pinholes in the film, which caused a virtual short circuit.

A glass containing vessel with very thin (10^{-2} cm) glass walls would obviously not be a practical proposition. It would be too fragile to stand normal stresses imposed during routine work. The exceptional strength of thin shell structures led to the development of the new electrode system described in this work.

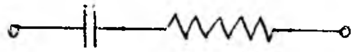
The electrodes, which retain their "electrodeless" character by being out of direct electrical contact with the solution, are in the form of probes which can be inserted into a liquid electrolyte without restriction on the volumes taken. The "electrodes" are very thin walled spheres, blown at the ends of a 0.5 cm soft glass tubing and are used in pairs at a fixed distance apart and inserted into the solution of the electrolyte. Electrically, the new electrodes are identical with the conventional external metal electrodes around a beaker or tube, with the important difference that the capacitance provided by the thin glass shell is very large in comparison with that of a metal sleeve around a glass beaker.

It is the large value of C_g obtained in this design that enables the high sensitivity of detection for concentrated (0.1 m) solutions to be achieved at frequencies as low as 5 mcs.

The new cell design has a lower effective impedance at lower frequencies, thus facilitating the use of simple transistor circuitry (described later) for a high sensitivity titrimeter.

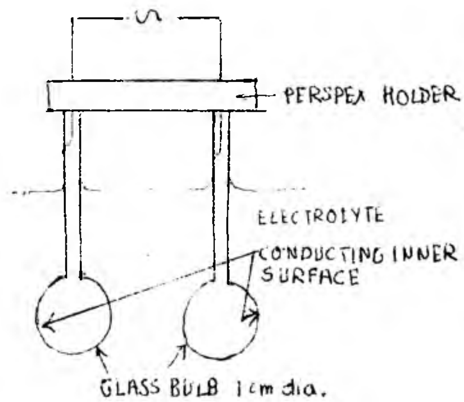
Analysis of the new conductance cell

The Conductance cell used in this work is of a novel design. It is based on the analysis of the behaviour of a composite dielectric such as that encountered in high frequency conductance studies. The simplified equivalent circuit for the cell is given below in terms of lumped parameters.

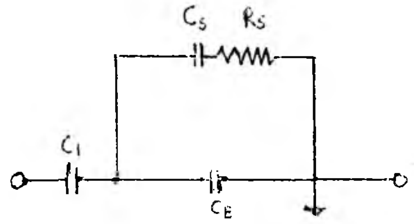


(A)

The above circuit represents the resistive and capacitive components of the impedance of a conductive cell of the general shape given below



To consider the current distribution in this network and the interaction of the various components on each other, consider a sinusoidal voltage E_s to be applied across the terminals of this two terminal network.



B.

Ignoring the capacitance to ground represented by CE in fig.(β), the circuit reduced to its essential form, is that of a capacitor C_1 in series with the electrode capacitance and conductance components C_{gs} and $1/R_s$ respectively.

The voltage vector therefore is given by

$$E_s = \frac{I}{jwC_1} + \frac{I}{jwC_s} + I \cdot R_s$$

In a conventional cell C_s is very small. Thus the impedance of the second term becomes very large and hence only comparable impedances in the third term (R_s) have any effect on the current in the circuit.

In the new cell, however, the value of C_s has been made so large that it is the conductive components that become the determinants for the high frequency response. A value of 130 pf is quite a reasonable average for a cell of the type used here; previously the capacitance was of the order of 10 pf to 22 pf. If it is possible to couple a reactive load such as a H.F.

conductance cell to a hypothetical generator having an internal impedance Zg, then if the load is turned to the generator or if the two impedances are matched, the system would become sensitive to small changes in the impedance of the load in this case, the conductivity cell. In conventional cells the coupling has been predominantly through a capacitance formed by a metal ring round a glass beaker, such a capacitance is commonly of the order of a few tens of picofarads; in the new cell described here the capacitance is of the order of 150 to 300 pf depending on the shell thickness and the spacing of the "electrodes". The reactance of the series capacitance of such an electrode system would thus be of the order of 10 to 100 ohms at a frequency of 5 megacycles, which is comparable with the conductance of salt solutions in range of 0.1 M. It is thus possible to make the impedance of the cell approximately equal to that of the components of the tuned circuit of the oscillator (acting as a generator) and thus fulfil the conditions for maximum sensitivity.

Analysis on basis of Impedance match

Consider the cell as an impedance Z_L forming a load on a generator producing in emf E and having its internal (Thévenin) impedance Zg

Then the current through the circuit can be expressed as

$$I = \frac{E}{Z_g + Z_l} = \frac{E}{R_g + R_L + j(X_g + X_L)}$$

where R_L , X_L and R_G, X_g are the ohmic and reactive components of the impedance of load and generator respectively.

To find the relative power dissipation in the load and generator, the voltage and current through the load is required. This is given by

$$V = Z_L \times I \text{ and hence}$$

power dissipation in load is given by

$$P = \frac{1}{2} R_L (V \times I) = \frac{\frac{1}{2} E_o^2 \quad R_L}{(R_g + R_1)^2 + (X_g + X_L)^2}$$

So far as the reactive component of the load X_L is concerned, as it can be both positive or negative the maximum power dissipation will be obtained with $X_L = X_g$ i.e. if the reactive component of the load is of opposite sign but equal in magnitude to that of the generator i.e. tuned to resonance with the generator.

TABLE - I

Comparative table showing the relation between frequency of operation and concentration region

Frequency	Concentration m	Author	Reference
2 mcs	0.01m(NaCl)	Hall	Anal.Chem.24,1244,1952.
18.5 mcs	0.03	Milner	Anal.Chem.,24,1247,1952.
1 to 30 mcs	-	Reilly & McCurdy	Anal.Chem.,25,86,1953.
15-20 mcs		Flom & Elving	Anal.Chem., 25,541,1953.
2.5-5.9 mcs	10^{-2}-10^{-4}	Fujiwara & Hayashi	Anal.Chem., 26,239,1954.
30 mcs		Hall (et alia)	Anal.Chem., 26,839,1954.
4.65		Bien	Anal.Chem., 26,909,1954.
30 mcs	0.01	Blaedel & Knight	Anal.Chem., 26,743,1954.
5-30 mcs		Blaedel & Knight	Anal.Chem., 26,743,1954.
5.45 mcs		Jensen (et alia)	Anal.Chem., 26,1716,1954.
4.89 mcs		Dean and Cain	Anal.Chem., 27,212,1955.
130 mcs	0.005 to	Johnson & Timnick	Anal.Chem., 28,889,1956.
130 mcs		Lipincott & Timnick	Anal.Chem., 28,1690,1956.
0.1 to 3		Kupka and Slanbough.	Anal.Chem., 29,848,1957.
120 mcs	3N(HCl)	Johnson	Anal.Chem., 30,1324,1958.

Table - 1

(... Contd.)

Frequency	Concentration m	Author	Reference
10-30 mcs		Walker (et alia)	Anal.Chem.,32,9,1960.
		Present author	This work
6.5 mcs	0.1 m	"	Transistorized circuit.
10 mcs	0.1 m	"	Crystal oscillator circuit.
5 mcs	0.1 m	"	Improved Titrimeter.
5.3 mcs	1 m	"	"
30 mcs	0.01 m	"	Beat frequency method (conventional cell)

E X P E R I M E N T A L

SECTION A:

A beat frequency type titrimeter

The first instrument to be described is based on the beat frequency method of detection of changes in the conductance cell.

A titration cell consisting of a pyrex 10 cc test tube with two circular copper straps (16 SWG, 1 cm wide) placed at a distance of 1 cm apart, was used as the titration vessel.

The sleeve electrode was made a part of the tuned circuit of a modified Colpitts oscillator (Fig. 10).

This modification due to Clapp, consists in using the inductance and capacitance in series instead of in parallel, as in the Colpitts circuit.

The frequency stability of the Clapp oscillator is inherently high due to the swamping effect of the capacitances placed in parallel with the interelectrode capacitances.

The valve used was the miniature pentode EF92 (6AM6); it has the following characteristics.

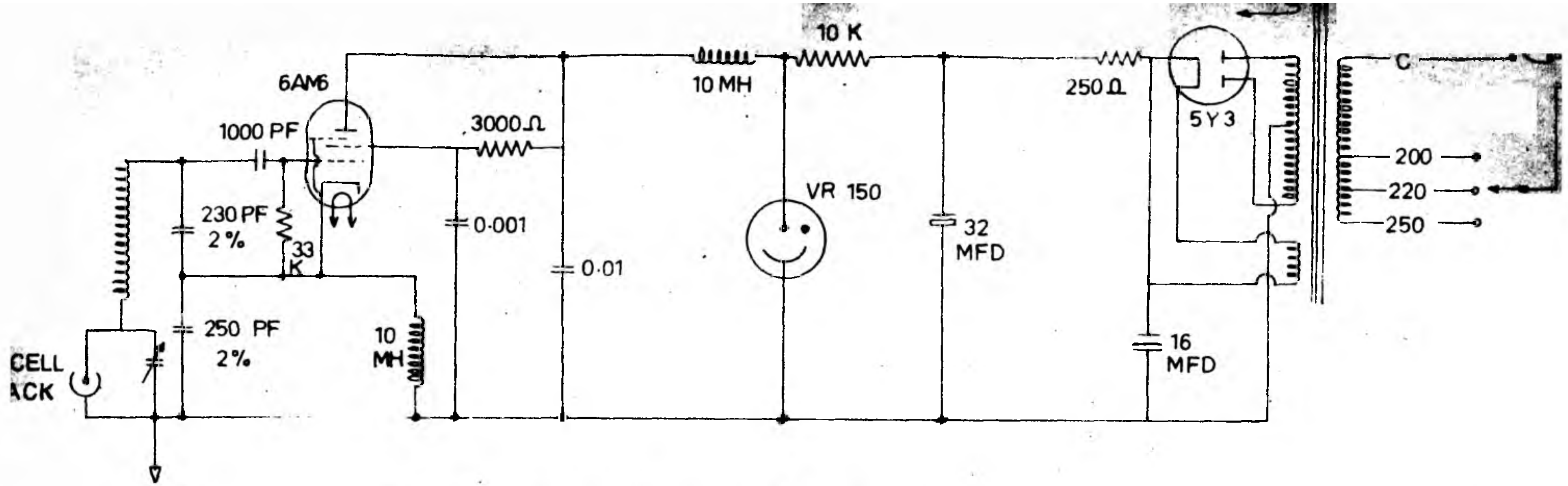
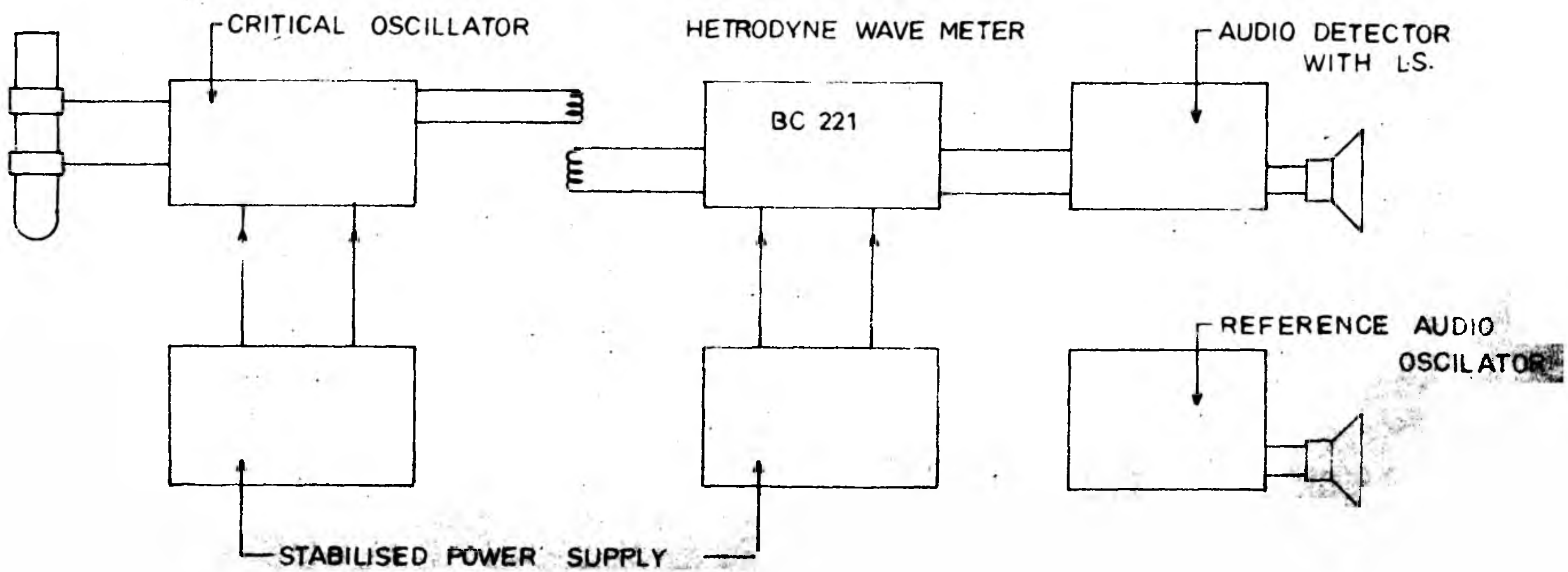


FIG. CIRCUIT DIAGRAM OF CRITICAL OSC...



<u>6AM6</u>

V_f	V_a	I_a	$-V_g$	G_M	R_a	C_{gP}	C_{gK}
6.3	100	5 ma	-4	3900 mho	150 MΩ	0.0035 pf	5.5 pf

The oscillator was capable of operating on a frequency range from 8 mcs to 30 mcs; tuning was accomplished by variation of a capacitor in parallel with the titration cell.

The oscillator was powered by a regulated power supply delivering 150 volts DC at 30 ma and 6V AC at 3 A.

The oscillator was loosely coupled to a BC-221 hetrodyne wavemeter which provided the reference r.f. signal for the hetrodyne beat note which was monitored by a loud speaker or oscilloscope. This oscillator had a good frequency stability and no difficulties due to frequency drift were experienced.

The arrangement described above dispenses with the use of the elaborate duplication of two oscillators and buffer amplifiers described by West[28], Thomas and Faegin, etc.

The hetrodyne wavemeter consists of an input r.f. amplifier which feeds on to a mixer stage and then to a detector audio stage. A one megacycle quartz crystal provides a reference signal to the mixer.

The parameter that is noted down for following the progress of the titration is the change in the beat note as the titrant is added to the solution in the cell.

The dial reading is then adjusted to give the original double hetrodyne beat with a 1000 cps audio oscillator.

The graphs accompanying this show the change in frequency of the critical oscillator as a function of the volume of titrant added.

The frequency is in cycles per second and the titrant volume in ccs. The graphs show a V shaped nature which enables the end point to be located with greater precision. S shaped curves have been obtained by Malmstadt using the beat frequency method

Sample titrations were performed with HCl-NaOH, NaOH-Acetic Acid, and Ca-E.D.T.A.

The change in frequency with addition of unit volume compares very favourably with that reported in the literature.

The drawback noticed early in the experiments was that the frequency showed a steady rise with increase in volume above the sleeve electrodes. This was eliminated by the use of a guard ring above the electrodes, which was connected to the electrical ground point. The stirring of the solution was accomplished by a thin glass stirrer which did not perturb the electrical signal.

The operation of the instrument can now be considered in some detail:

In a beat frequency type of titrimeter the response (frequency change) is sensitive to capacitance changes rather than to conductance changes. The series tuned circuit, with the cell capacitance in parallel with the tuning capacitor, is therefore most suitable as a small change in the cell capacitance has a large effect on the tuned circuit capacitance. The change in oscillator frequency for a small change in cell capacitance is thus optimised.

The tuned circuit thus comprises of an inductance L_1, a variable air capacitor C_1 and the titration cell which is in parallel with C_1; an isolating switch is provided in series with the cell. The capacitances C_3, C_4 are 2% silver mica capacitors. The stabilisation of frequency obtained in the Clapp oscillator is largely due to the e effect of these capacitances. The large value of C_3 and C_3 is effectively in parallel with the inter-electrode capacitances Cgk and Cgp and changes in these values due to thermal effects are minimised.

FIG. 11.

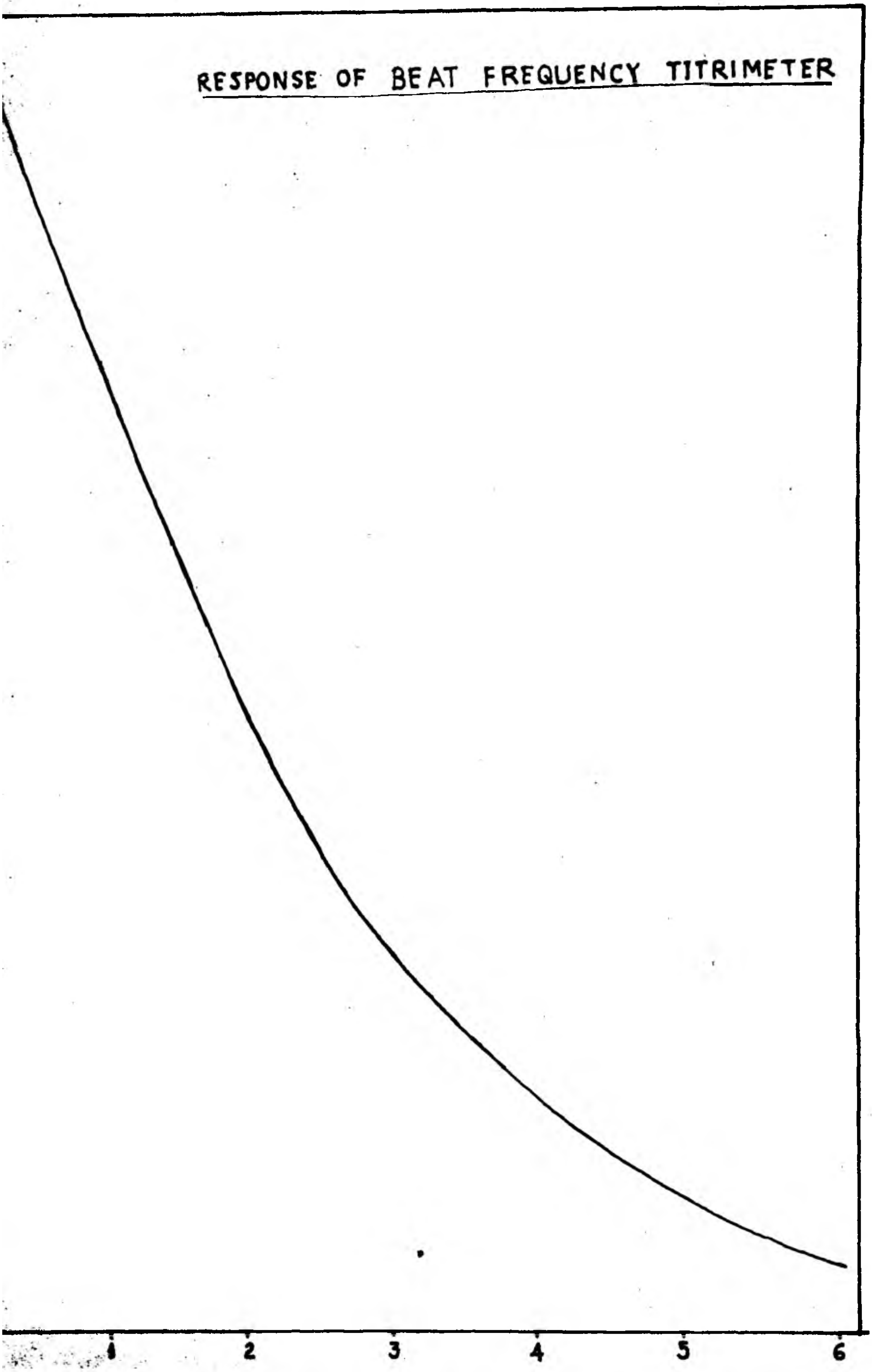
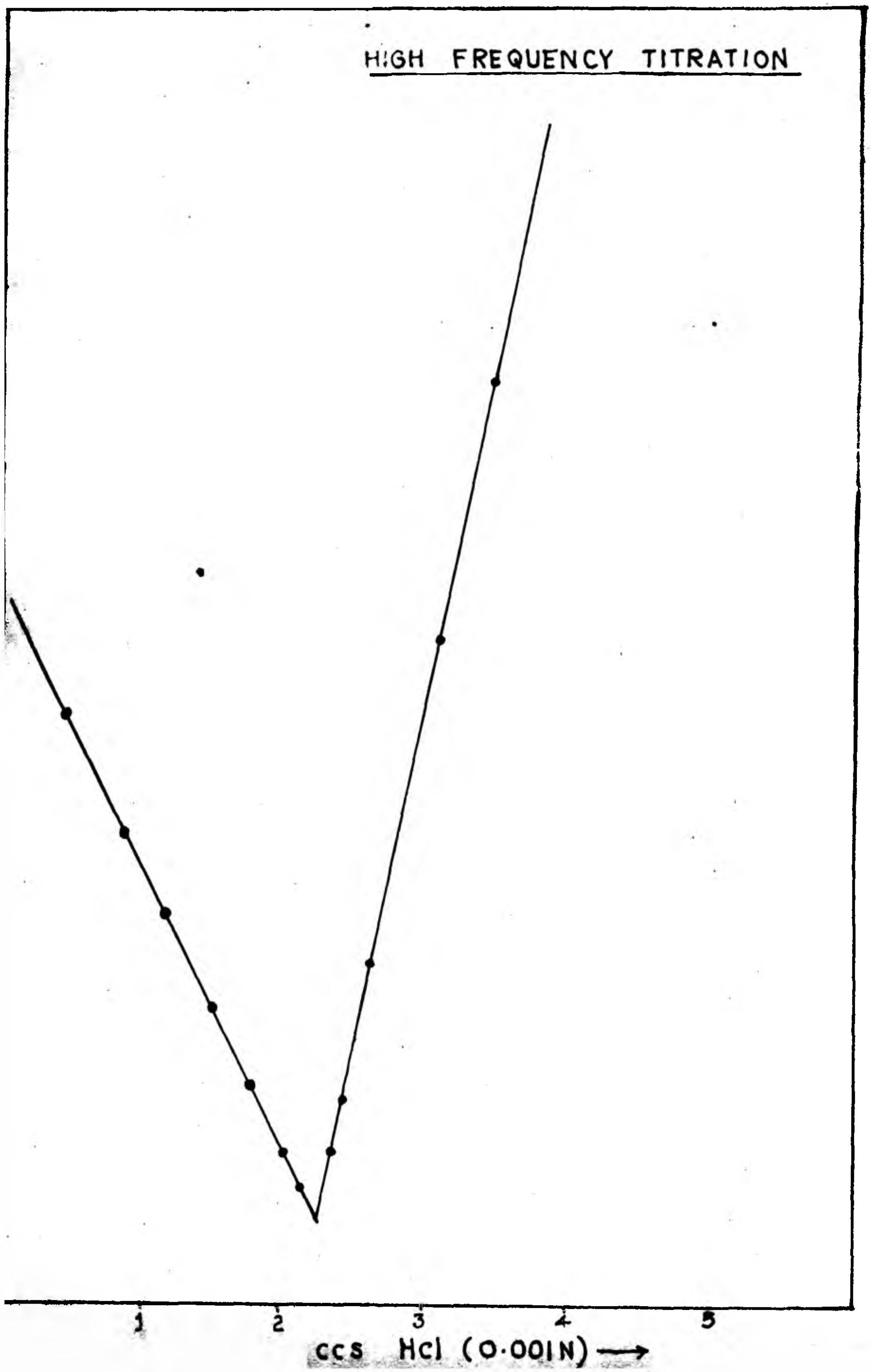


FIG. 12



A shielded cover protects the tube from electrical fields. The anode and screen were strapped together and the valve was triode operated.

Titrimeter A: (Hetrodyne-beat apparatus)

Fig.11 shows the response curve of the titrimeter to increasing concentration of KCl in distilled water.

A 0.10 m KCl solution was prepared from pure crystalline KCl (Analar, B.D.H.) and conductivity water. It was added from a 5 c.c. microburette to 10 c.c.s of conductivity water in the titration cell.

The frequency change observed was measured by adjusting the beat note to double beat with a 1000 cps audio oscillator fitted with a speaker. Dial divisions corresponding to zero double beat are plotted against the volume of titrant added.

Fig.12 gives the observations for the titration of HCl against NaOH.

The volume of acid added is recorded against the frequency change (represented by dial divisions on the frequency meter).

The V type titration plots give end points within 0.1% of the calculated end point in the case of titrations between strong acid - strong base (NaOH - HCl).

SECTION - B

Capacitance Measuring Titrimeter

The wellknown Pierce circuit with grid to cathode connection was used for the basic oscillator. In this circuit the frequency of oscillation is governed by the quartz crystal which takes the place of the grid tuned circuit. No external excitation is used for the crystal and oscillation depends on the internal feedback through the grid to anode capacitance.

The frequency of such a crystal oscillator is nearly independent of the capacitance in the tuned circuit e.g. a change in capacitance in the tuned circuit from 900 pf. to 1000 pf does not cause any appreciable frequency deviation.

Oscillation will cease abruptly when the tuned circuit capacitance exceeds the critical value required by the condition that the anode grid capacitance be less than the value which makes the frequency of the oscillatory circuit equal to the vibration frequency of the crystal.

Thus the cessation of oscillations becomes a reliable reference for capacitance measurements.

The Pierce oscillator oscillates at the crystal frequency if the anode tuned circuit resonates near the frequency of the crystal.

The inertia of the meter movement **which** is used to detect the changes in oscillation amplitude tends to introduce an uncertainty in the detection of the "kick off point".

The apparatus described here eliminates any uncertainty by making use of the illumination due to the electron beam of an electron ray tube as a sensitive detector.

The electron ray tube is connected (as in the fig.134 across the load resistor R_L in the plate supply lead.

When the oscillations build up there is a decrease in the plate current and a reduction in the light intensity of the electron ray tube due to the decreased potential applied across its anode and cathode.

When oscillations stop, there is an instantaneous illumination of the fluorescent screen.

This use of the electron tube purely as a detector is a useful modification of the circuit described by Hall for dielectric measurements.

In the Hall circuit small changes in the angle of the magic eye, cannot be definitely detected, and the magic eye tube does not have a good characteristic for an R.F. oscillator. This follows from a comparison of characteristics (given below) for the 6E5 and a typical oscillator valve the 6AG7.

6E5			
Plate and target supply	200	250	volts
Series Triode Plate resistor	1	1	meg ohms
Target current	3	4	ma
Triode plate current	0.19	0.24	ma
Triode grid voltage	-6.5	-8.0	volts

6AG7		
Plate volts	300	V., d-c
Grid No.2 volts	150	V., d-c
Grid No.1 volts	-3	
Transconductance	11000	mhos
Load resistance	10,000	
Max signal output	3 watts	

An efficient r.f. oscillator requires the use of a screened tube with a high transconductance such as the 6AG7 (above).

The operation of the circuit is as follows:(Fig.13a):-

V_1 is an indirectly heated rectifier which provides the H.T.Supply (300 VDC. 30 ma). The filter capacitors C_1 C_2 are 32 mfd each.

The load resistor R_L drops the H.T. anode voltage of V_3 to 150 volts and provides a "firing" voltage for the electron ray tube V_2.

V_2 is connected across the tapped load resistor. A large grid leak resistor biases the tube to give the required brightness when the oscillator is inoperative.

The parallel tuned LC circuit is shunt fed from the oscillator anode. This enables one side of the cell to be grounded and greatly simplifies earthing and handling.

The measuring capacitor C_M is in parallel with L_2 and the capacitance cell C which is connected to the circuit with coaxial cable.

The crystal is directly connected to the oscillator grid across the grid leak (Rg).

The H.F. titration was carried out by tuning the variable capacitor to a state of oscillation. Bringing the oscillator into oscillations has the effect of reducing the plate current (in a parallel tuned circuit). The decrease in plate current causes a reduction in the potential drop across the anode load resistor R_1. This reduction in voltage across the electron ray tube causes the target illumination to fall abruptly till oscillations stop, when there is a sharp illumination of the target.

Thus the visual effect is that of a quick change from a non-illuminated to an illuminated target.

If the "crevasse" of the drop of current is not steep, a gradual decrease in illumination is noticeable.

The reference point for purposes of measurement is the "kick off" point of the current-capacitance curve.

At this point the capacitance in the tuned circuit is critically exceeded, and the oscillators stop abruptly.

The capacitor dial reading at this point is noted for each observation:

This method has some advantages over circuits previously used:

(1) In circuits where a meter (usually a milliammeter) is used to follow changes in plate current, a lag in following the damped meter needle readily introduces an error in determining the reference point C_{MAX}.

(2) Because at the end point there is a reversal of direction of the indicator, the observed meter movement must take into account the inertia of the movement. In the circuit described, the indicator is essentially a "weightless" electron beam.

(3) The low cost of the components compared with an instrument using a robust meter movement (or a shunted microammeter) is a point in its favour.

(4) A separate oscillator and detector system is incorporated. This enables higher frequencies than can

be used with a magic eye tube (as in Hall's circuit) to be employed. There is no reaction of the detector on the oscillator.

(5) The detection of the end point can be readily followed without any strain. This compares favourably with the conventional circuit where small changes of shadow angle on the illuminated target have to be discriminated against.

However, the use of this circuit is critically dependent on the availability of a large number of quartz crystal oscillators to enable various concentrations to be studied with adequate sensitivity.

The operation of taking a capacitance reading is also a laborious one, involving the setting back of the capacitor dial before the next reading could be taken.

A variation of this circuit (fig.14) was tried in which a neon indicator lamp was used across the load resistor R_L in the plate circuit of the oscillator valve. This circuit functioned well although the illumination was not quite as good as in the previous circuit. This arrangement also has the disadvantage of an abrupt change in the anode load due to the low resistance offered by the neon lamp when in the 'on' condition. This effect is reduced by introducing a series resistor to counteract the negative resistance characteristic of the neon lamp.

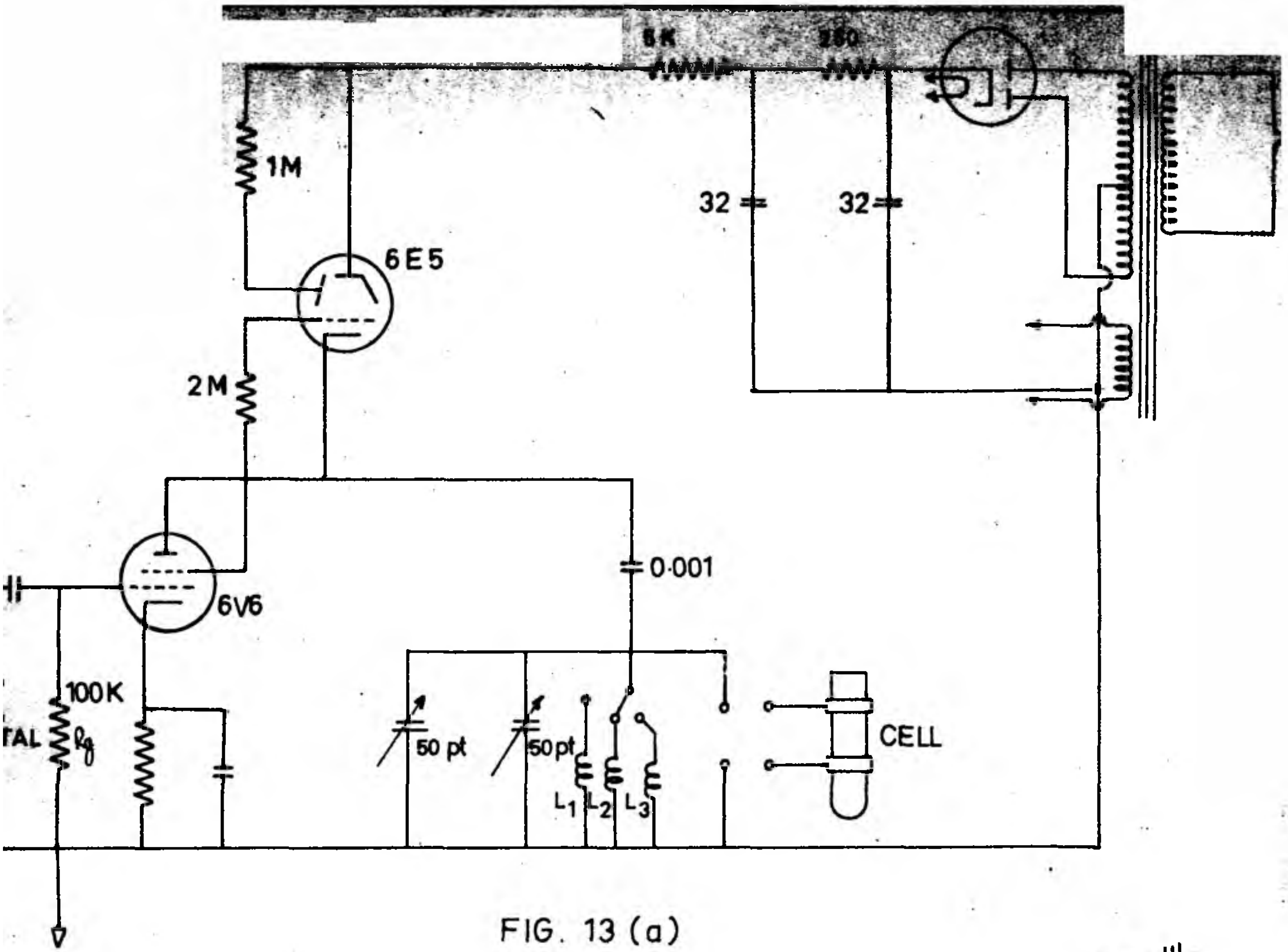


FIG. 13 (a)

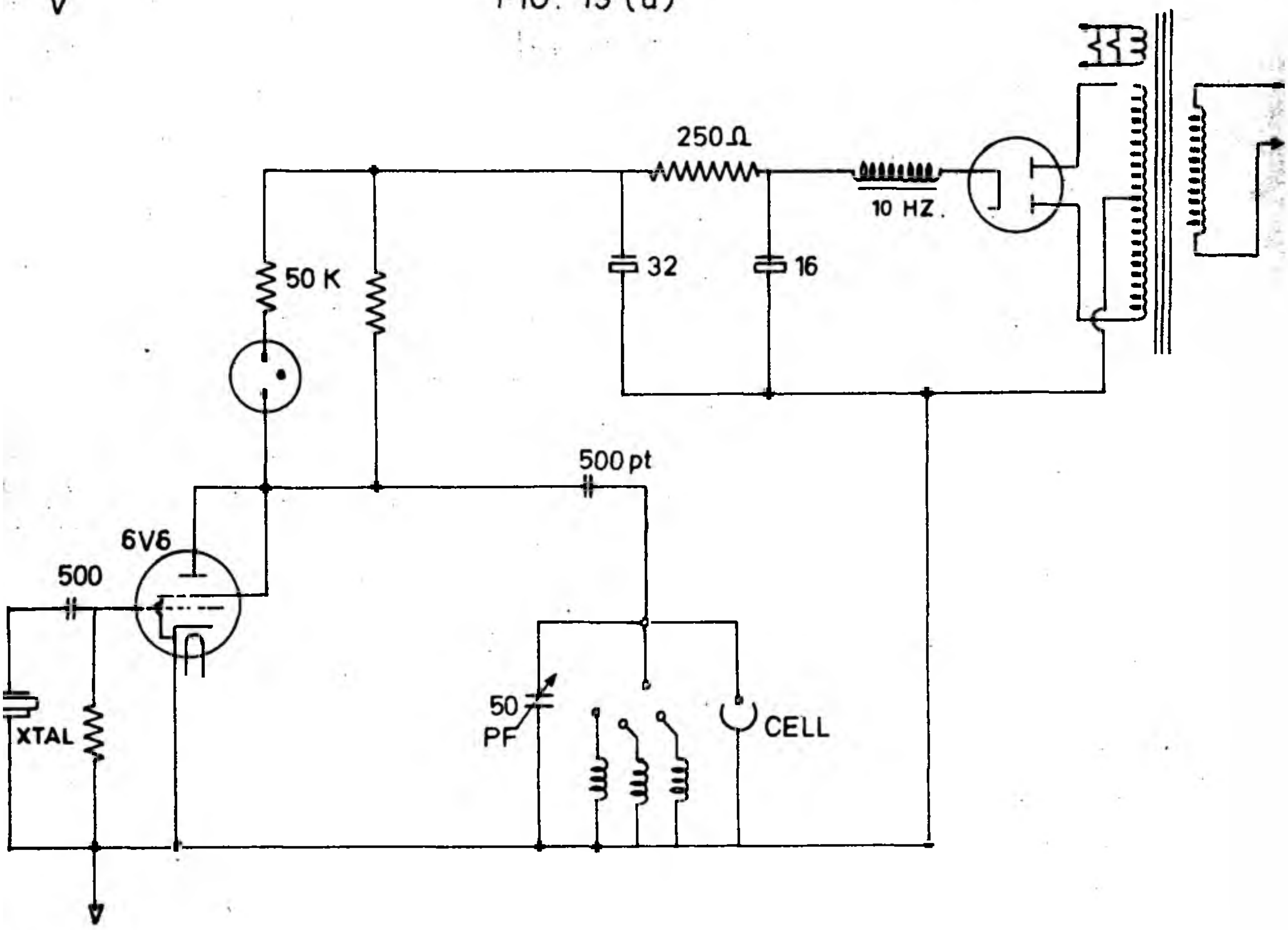


FIG. 13 (b).

In view of these drawbacks, it was decided to build a new instrument which would give stable direct observations, and would operate without the use of crystals.

Typical Titration Curves

Fig. 14 shows a high frequency titration plot of capacitance of the measuring capacitor against volume of titrant added. (frequency : 10 mcs)

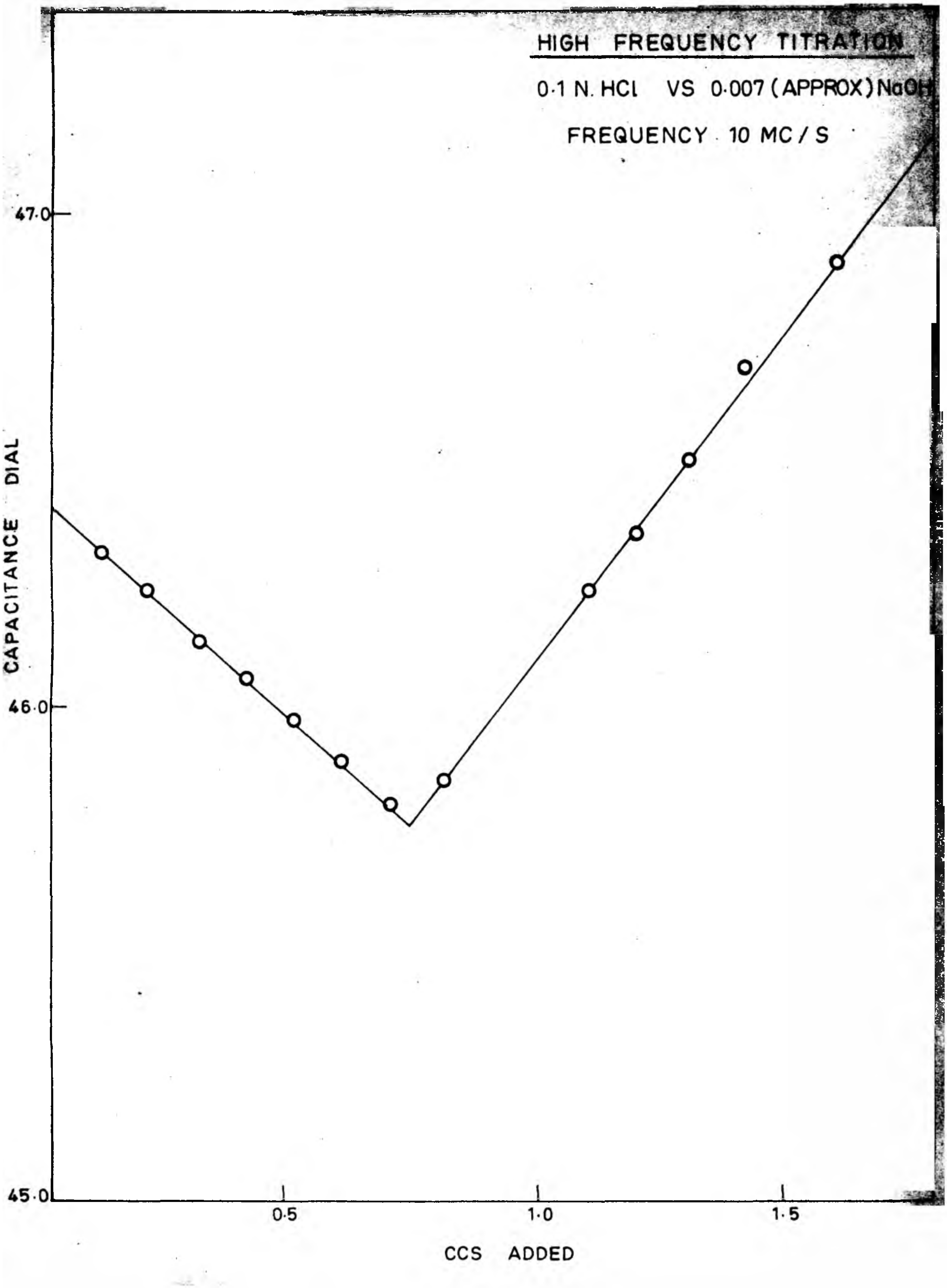
10 ccs of stock NaOH solution (0.007 N) were introduced into the titration cell which consisted of a pyrex test tube fitted with two copper straps of a distance of 1 cm.

HCl (0.1 N) was added from a micro-burette just above the titration cell. Stirring was effected by means of a glass stirring rod after each addition.

Fig.15 shows a titration graph for Acetic acid - NaOH at 10 mcs.

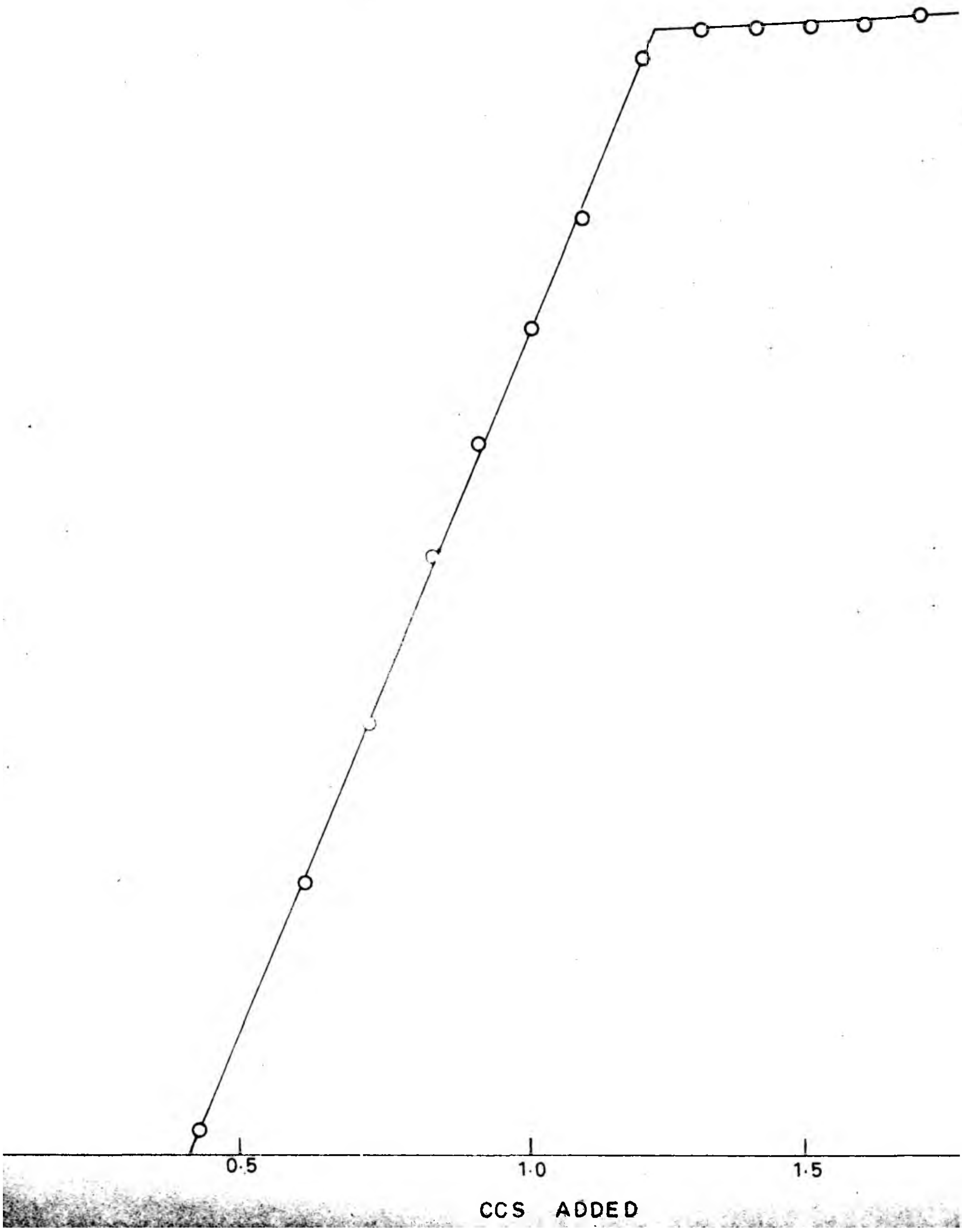
10 ccs of stock NaOH solution (0.007 N) were titrated against 0.057 N Acetic acid (frequency 10 mcs).

In both cases a sharp inflection point is observed with a sensitivity of better than 0.1 % of the total volume titrated.


HIGH FREQUENCY TITRATION
0·1 N. HCl VS 0·007 (APPROX) NaOH
FREQUENCY 10 MC/S
47·0
46·0
45·0
CAPACITANCE DIAL
0·5
1·0
1·5
CCS ADDED

HIGH FREQUENCY TITRATION

PLOT OF CAPACITANCE CHANGE
CCS ADDED OF 0.05 N
ACETIC ACID
FREQUENCY - 10.0 MC/S



SECTION - C

A high sensitivity grid current measuring titrimeter:

The beat frequency type of titrimeter described in the previous section had the drawback of requiring the use of auxiliary equipment like a BC-221 frequency meter in order to record changes in frequency as a titration was carried out. The capacitance measuring titrimeter (also described previously) though self contained, depended on the use of a number of quartz crystals and could only be operated at these fixed frequencies.

The titrimeter circuit (fig. 16) uses the Colpitt-clapp oscillator, chosen for its high frequency stability. The tank circuit consists of inductances L_1, L_2 chosen by a switch S_1 in series with the tuning condenser C_1. The conductance cell for titrations is connected through a coaxial connector to the points AA. The cathode of the oscillator is returned to the capacitative voltage divider C_2C_3 and is grounded through an r.f. choke of 3 mh. The grid resistor of the oscillator tube is connected in series with an r-f choke to the grid resistor R of one section of the difference amplifier.

The changes in grid current are thereby converted into voltage signals, amplified by the difference amplifier and read out on the indicating microammeter. A zero adjustment is provided by the wire wound potentiometer in the anode circuit of the d-c amplifier; this allows the

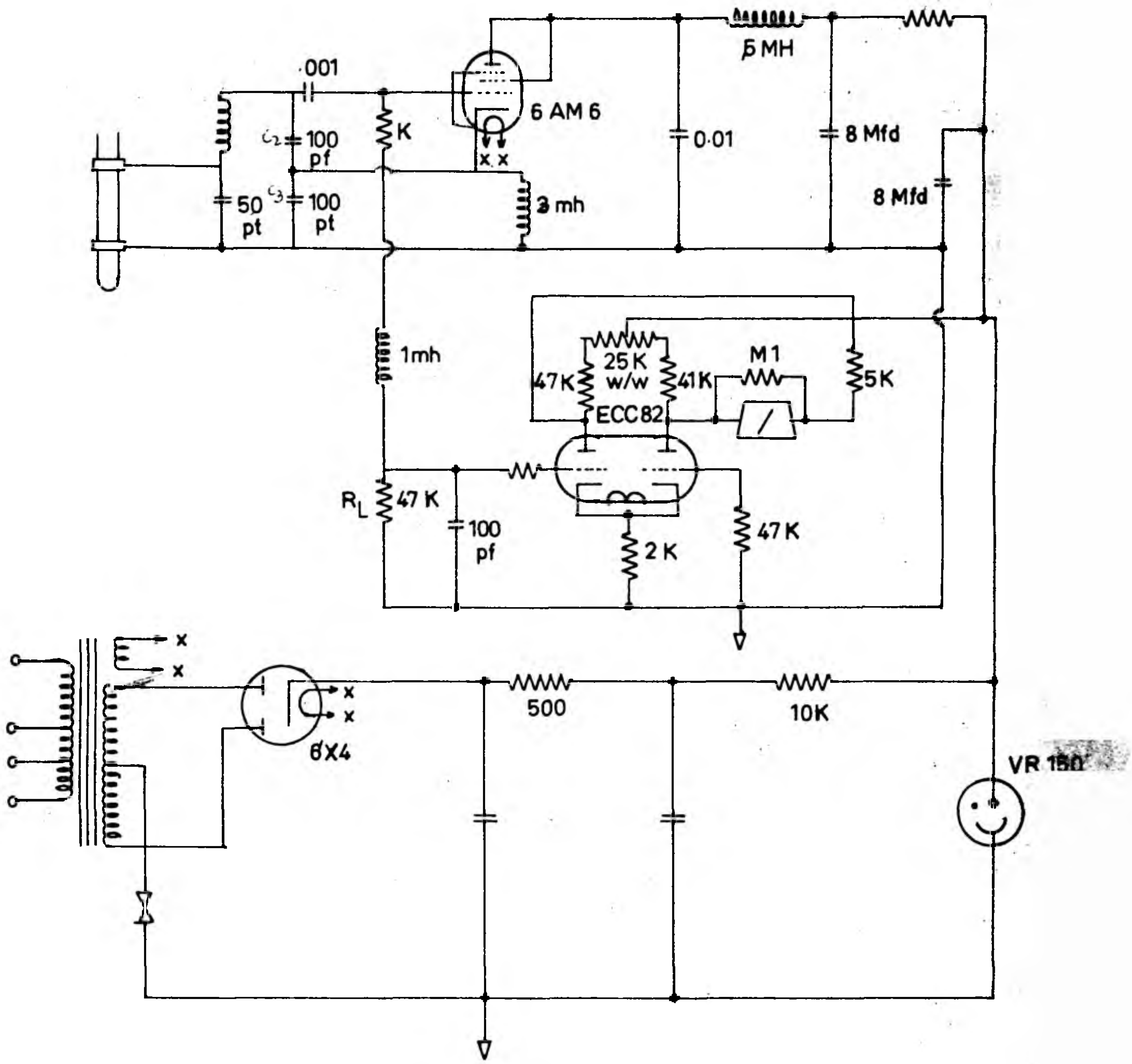


FIG.16. GRID CURRENT MEASURING TITRIMETER

initial readings for a titration to be set at a convenient point on the scale so that no overshoot of the end point takes place as the titration proceeds.

An attenuator in the meter circuit allows two values of sensitivity to be chosen depending on the concentration of the electrolytes used in the titration. Stability of frequency, amplitude and low drift in the d-c amplifier are improved by the voltage stabilizer provided. The voltage stabilizer uses a high slope high transconductance pentode EF80 as the voltage amplifier together with an EL-84 power output pentode as the series tube control.

The resulting voltage stabilizer has a stability of 0.5 % for mains variation of 10 % and a ripple of 1 to 2 mv under rated load currents. The reference tube is the Mullard 85A2 operated under constant current conditions by the use of a large dropping resistance, thus giving very high stability of voltage.

The titrimeter circuit has proved to be stable, easy to operated and found to give reproducible end points for normal titrations.

Typical titration curves for acid-base systems are given along side (figs 17,18).

Typical titration graphs at frequencies of 9.5, 9.0 9.5 and 10.4 megacycles/sec. are shown in fig.19.

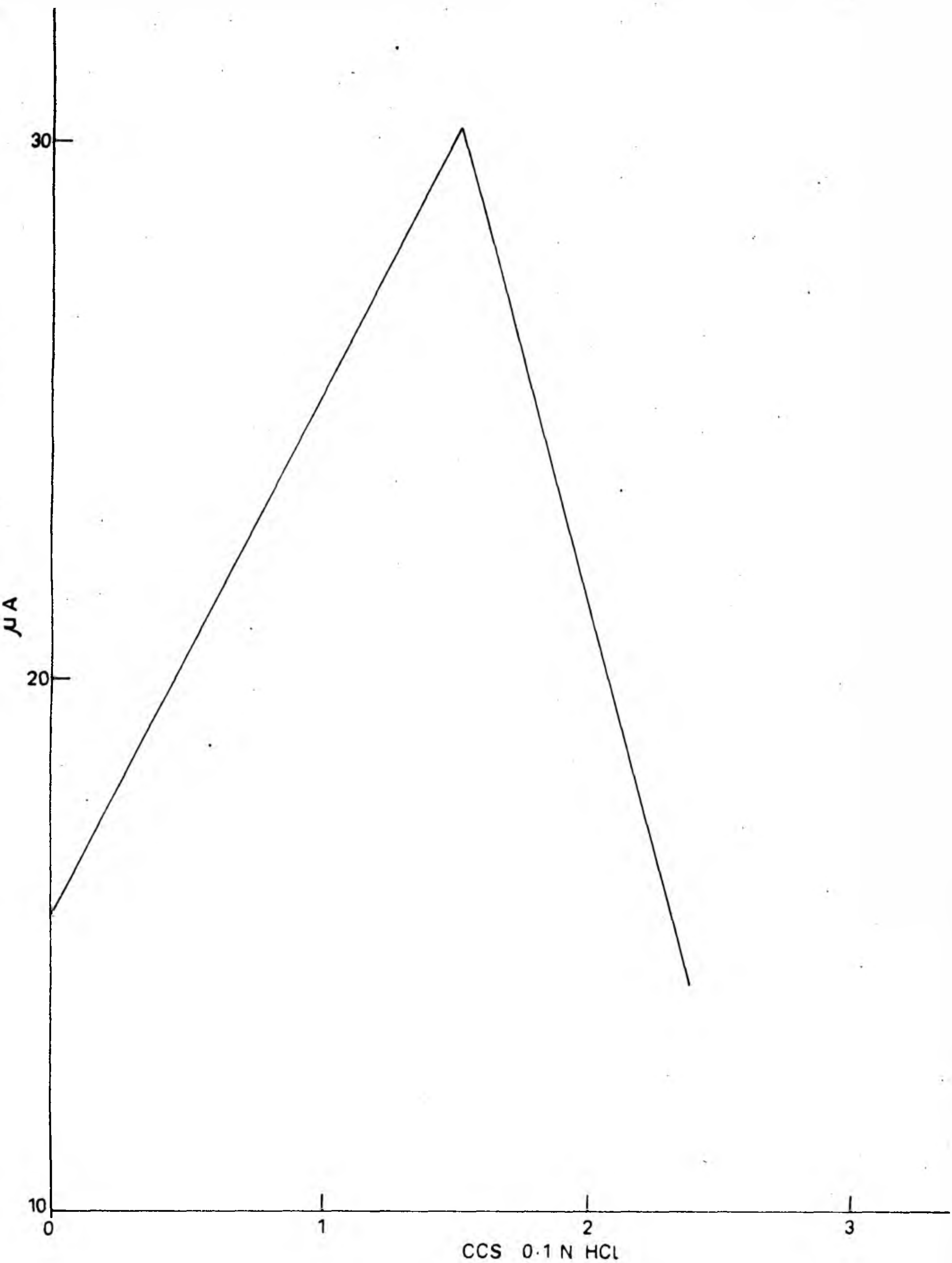


FIG.17. HIGH FREQUENCY TITRATION PLOT AT 11·8 MCS GRID CURRENT MEASURING TITRIMETER

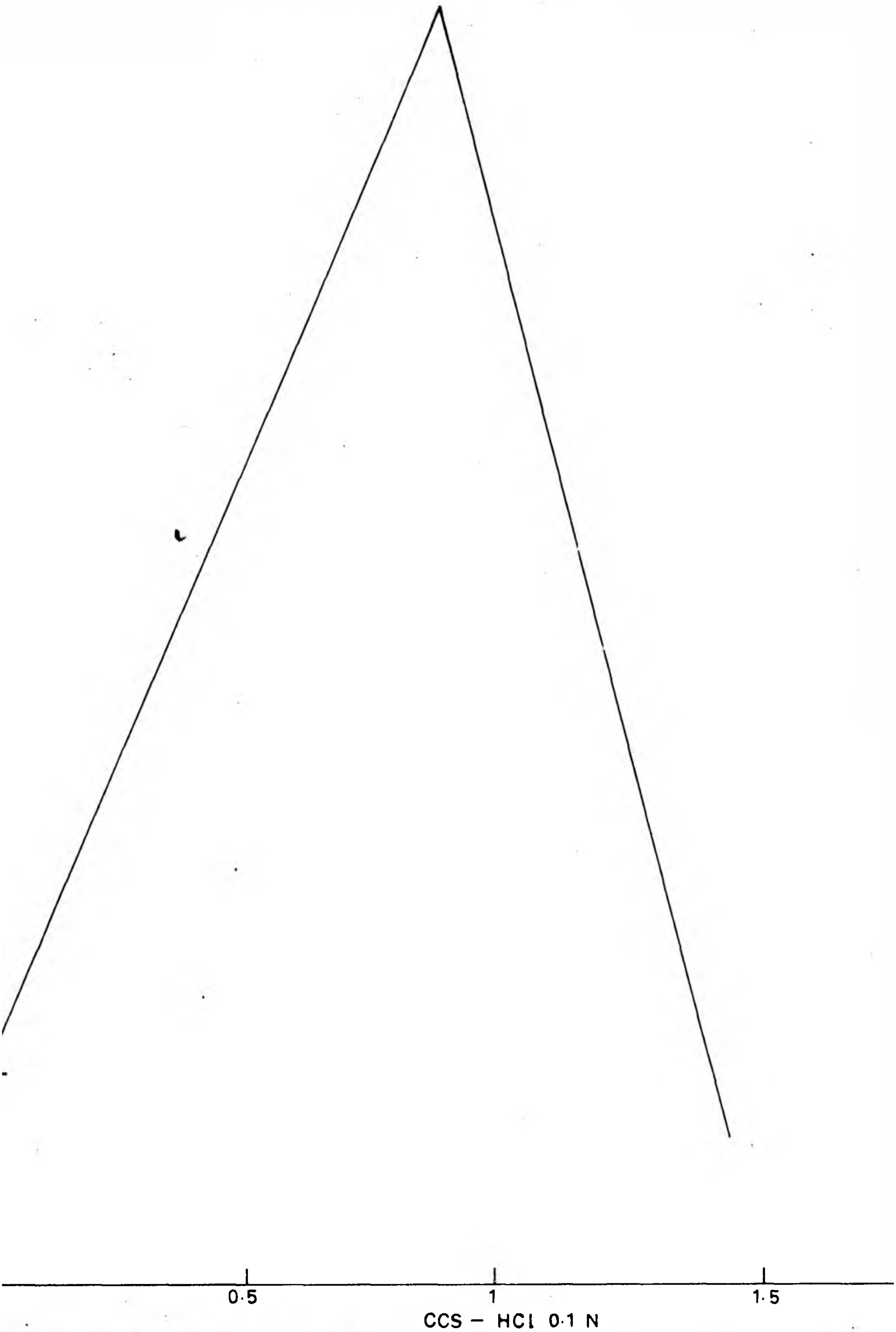


FIG. 18 H.F. TITRATION PLOT AT 8 MCS / SEC HCl – NaOH

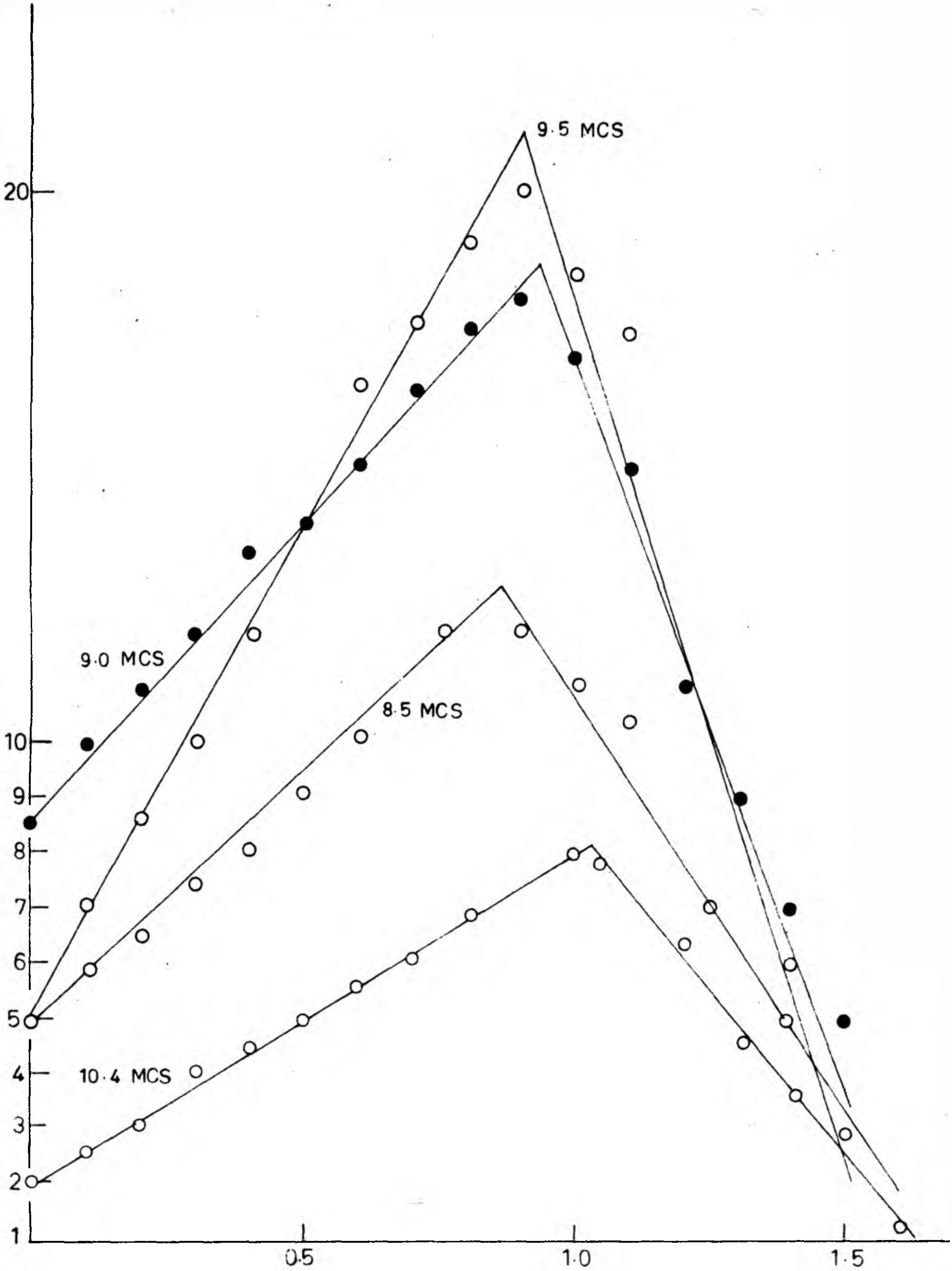


FIG. 19. H.F. TITRATION PLOTS USING TITRI METER

The system used was HCl - NaOH both being of analytical reagent grade (The HCl was double distilled before use). Concentration of HCl was 0.1 N while NaOH was approximately 0.009N. 10 ccs of NaOH solution were introduced into the cell and titrated with HCl from a microburette. Meter readings from the difference amplifier output were plotted against ccs of HCl added. The end points were very sharp and well defined.

SECTION - D:

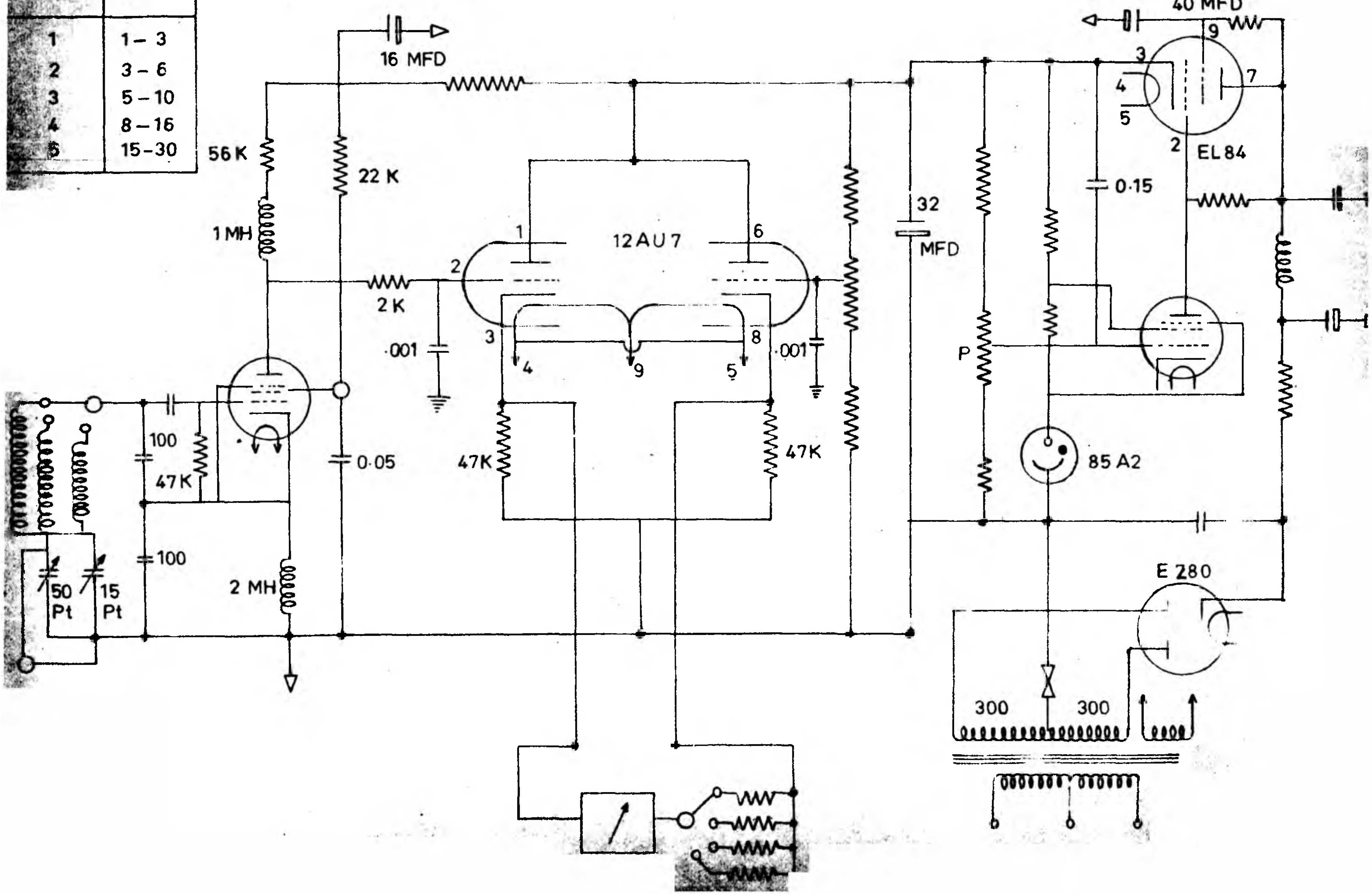
Improved Titrimeter (Integrated direct-reading Titrimeter)

The design of the titrimeter was guided by the concept of an instrument that would be able to provide reliable, easy, operation with high precision and sensitivity. It would also be able to deal with concentrations as high as 0.1 m without sacrificing any useful sensitivity. It would operate at frequencies that did not cause difficulties of shielding or instability or require special components. The instrument design would also enable its use as a tool for investigation of the physicochemical principles and details of high frequency titration analysis. The drawbacks observed in the cell design of apparatus used till now, i.e. the comparatively small volume available for reaction, as well as the volume effect observed, have been eliminated in the new instrument.

The instrument (fig.20) may be best analysed by considering its component systems:

(i) Power supply: It consists of a power transformer with an output voltage of 300-0-300 and 6V AC filament supply, and a power rating of 50 watts. An indirectly heated rectifier valve EZ80 which has a current rating of 80 ma was used as a full wave rectifier. The filter section has a choke input followed by an RC filter consisting of a 10 watt wire wound 1000 ohm resistor and

BAND	MCS
1	1 – 3
2	3 – 6
3	5 – 10
4	8 – 16
5	15 – 30



two 16 mfd electrolytic capacitors. The use of a choke input smoothing circuit provides a power supply source with better regulation of output voltage with load. It also prolongs the valve life by limiting current surges.

The electronic regulator has been incorporated to prevent fluctuations in the ac mains input from affecting the stability of the oscillator as well as the detecting amplifier. The stability of the voltage output is maintained at 0.1 % for a 10 % variation in mains voltage.

The use of an electronic regulator follows good instrument design practice since the measured parameters are read out on a direct deflection instrument and drift has to be minimized. The design of the regulator is conventional. The sampling voltage from a potential divider across the output is compared with a fixed reference voltage provided by a glow discharge tube VR- 85A2.

The error signal is amplified by a high gain pentode EF86 and applied to the grid at the series conductance valve, a power pentode EL84.

By providing a loop gain of 100 the voltage could be maintained constant within the required limits of 0.1 % for 10 % variation in mains voltage.

The large AC feedback applied to the grid of the amplifier effectively reduces the output ripple (100 CPS) to less than 1 mv (rms).

The output voltage could be adjusted to a value between 200 and 300 volts DC by the potentiometer P.

Choice of Oscillator

Various basic oscillator circuits were evaluated against the requirements of versatility of frequency range and high sensitivity.

The tuned grid tuned plate oscillator suffers from lack of stability at high sensitivity.

The reasons for this behaviour are proposed as follows:

(i) The oscillator depends for its operation on the inphase excitation voltage from the plate tuned circuit.

(ii) The ratio of exciting to output voltage is equal to the ratio L'g/L'p of the equivalent inductances, i.e. the inductance from K to g, K to p.

These inductances are in turn determined by the amount the corresponding grid and plate resonant circuits are detuned from resonance.

If the inductance from K to a is dampled by the presence of a conducting fluid in a test tube in it, the excitation ratio decreases.

(iii) The frequency stability of the tuned grid circuit is poor.

It is affected by changes in inductance and capacitance both in the external circuit and the inter-electrode capacitances within the valve.

The Franklin oscillator, though possessing a fairly good frequency stability, does not readily lend itself to the measurement of damping or capacitance changes in an cell element.

It has been used as an r.f. source which can be applied to a cell and the potential across it measured.

This is a complicated arrangement which does not commend itself, as it would require amplification of a small signal (with components in quadrature) developed across a variable impedance.

The crystal oscillators based on designs by Pierce and Miller are unsuitable for application in this instrument, because of the difficulty in procuring crystals of adequate frequency range. However, an instrument using a crystal oscillator is described elsewhere in this work.

The crystal oscillator has the drawback that its response to damping in the plate circuit is much more abrupt, because the high Q of the crystal tends to compensate for changes in impedance of the anode load without affecting the frequency materially. The anode current therefore remains substantially constant until the critical capacitance is exceeded, or the resonant frequency of the tuned circuit is pushed beyond the crystal resonant frequency. This results in a sudden change from oscillation to a non oscillating condition. This is useful as an indicator for measurements of capacitance changes.

The Hartley oscillator, together with its modified circuit, the Colpitts oscillator, has the advantage of requiring only a single coil. Oscillation can be maintained more readily than in the tuned anode or tuned grid types.

The condition for maintenance of oscillations is given by:

$$\frac{\frac{C_2}{C_1} - 1}{C^2} = \omega^2 RRa$$

The frequency of oscillation is given by

$$\omega^2 = \frac{1}{LC}$$

where

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$

The Hartley oscillator is capable of responding to changes in the circuit constants of the tuned LC circuit. Thus a capacitative type of cell could be used in parallel with the tuning capacitance C and capacitance and conductance changes could be monitored as a function of plate or grid current.

The circuit that has actually been used is the modified Hartley circuit known as the Clapp oscillator. This oscillator has a series tuned LC circuit compared with the parallel tuned circuit of the Hartley oscillator. Thus the arrangement becomes intrinsically more sensitive to the incremental or decremental changes in capacitance and conductance associated with a titration processe

The use of series capacitors for dielectric measurements may be cited here as an example of increased sensitivity obtainable by this means.

The past work done on HF titrations led to the following guiding principles for the design:

i) The capacitance change measurement described by Hall
was unsuitable for effective concentrations greater than 10^{-3}m (while using sleeve electrodes).

ii) The beat frequency method gives a stepped response and involves complicated electronic circuits and measuring devices.

iii) The relationship between the frequency and concentration at which optimum sensitivity is obtained:

$$f\ peak = \frac{1.8 \times 10^{12} K}{D}$$

implies that a fairly wide frequency range is desirable which together with suitable cells could cover the concentration region without a decrease in sensitivity of detection.

The oscillator:

The sensitive oscillator is based on the Colpitts circuit discussed previously. A 6AG7 valve is used as the oscillator. It has the specifications of high transconductance and good internal shielding which make it suitable for oscillator operation at high frequencies upto 10 mcs. (fig.20)

The oscillator is operated as a class B oscillator with a bias of -3 volts. This bias is obtained by a series resistance of 100 ohms. This in turn, is in series with an R.F. choke of 10 mH.

The tuned circuit:

Considerable attention has been paid to the layout of the components in the tuned circuit. Coils were wound on bakelite formers with superenamelled wire. A five-way two pole switch was used in the tuned LC circuit to select the appropriate inductance for the range of frequency. The frequencies were arranged to overlap by a small amount so that a continuous range could be obtained.

The variable air capacitor was a ceramic mounted linear unit which was fitted with a 180° dial and spindle reduction drive.

The nominal value of the capacitor was 100 pf.

Stiff leads were used in all the wiring and lead length was kept to a minimum. The tuned circuit was coupled to the grid across a capacitative divider and the grid leak to ground. The grid leak was a 56,000 Ω $\frac{1}{2}$ watt carbon resistor, with leads cut short.

The valve was mounted on a low loss bakelite socket in order to minimise losses.

The detector circuit

The detector circuit was a d-c amplifier using a dual triode valve 12 AU7.

The difference amplifier design used here has the great advantage of being insensitive to fluctuations in supply voltages, as they affect both the valves, and hence cancel out. Stability is increased by the use of a regulated d-c supply.

The very large negative feedback introduced by the cathode follower action gives the detector two important advantages:

(i) A high input impedance.

The use of negative feedback reduces the input admittance of the system to the applied signal if the feedback factor A is large, as given by the formula

$$\frac{\text{Input admittance with negative feedback}}{\text{Input admittance without negative feedback}} = \frac{1}{1 - \beta}$$

Where β is the feedback factor.

The use of a high input impedance is dictated by the need to prevent the detector from loading the oscillator, which acts as a signal source.

(ii) Improved linearity of output with respect to input signal.

The amplitude distortion of a cathode follower stage is small.

Let a distortion voltage Vd appear at the output stage of a feedback amplifier. Then, if β is the feedback factor the distortion voltage fed back is $V\beta$. The resulting amplified voltage is therefore $\beta V_D A$ where A is the amplification, i.e. the distorted output voltage is $V_D + V_D A$ hence $V_D = V_d + \beta V_D A$

$$\text{Distortion with feedback} = \frac{\text{Distortion in absence of feedback}}{1 - A\beta}$$

if $A\beta$ is made large, a great increase in linearity is possible.

The valve used in the d-c amplifier has a high g_m which enables it to give a large output signal. The output impedance is $1/g_m$ which is low enough to provide a maximum power transfer match to the indicating instrument.

The indicating system used in this instrument is a microammeter and shunt arrangement, which enables different values of response to be accommodated.

The signal from the push pull d-c amplifier output is taken from across the cathodes of the 12 AU7. It then goes to a selector switch S_1 which is a 5 way two pole rotary switch. The switch is connected across 3 wire wound resistors (values given in figures) which enables the instrument to have 4 sensitivity ranges (including meter directly connected). An off position for disconnecting the internal microammeter is one of the 5 positions provided. This was done so that an external instrument of larger diameter and closer divisions could be used. A jack for an external meter is also provided at the rear of the instrument.

Operation:

The instrument, when connected to 200 V AC mains, can be switched on by depressing the toggle switch at the left. A red pilot lamp indicates that power is on. The instrument takes three minutes to warm up which is indicated by a neon glow lamp lighting up on the left of the meter. The frequency band can be set on the switch marked BAND - 1-2-3-4-5. The frequency range for each band is given in table alongside the fig. The oscillator frequency can be tuned by the use of a knob directly below the capacitor dial at the right. The cell is then connected and the meter needle adjusted to any arbitrary point on the right side of the scale.

During the course of the titration, the readings will progressively decrease to a minimum and then increase.

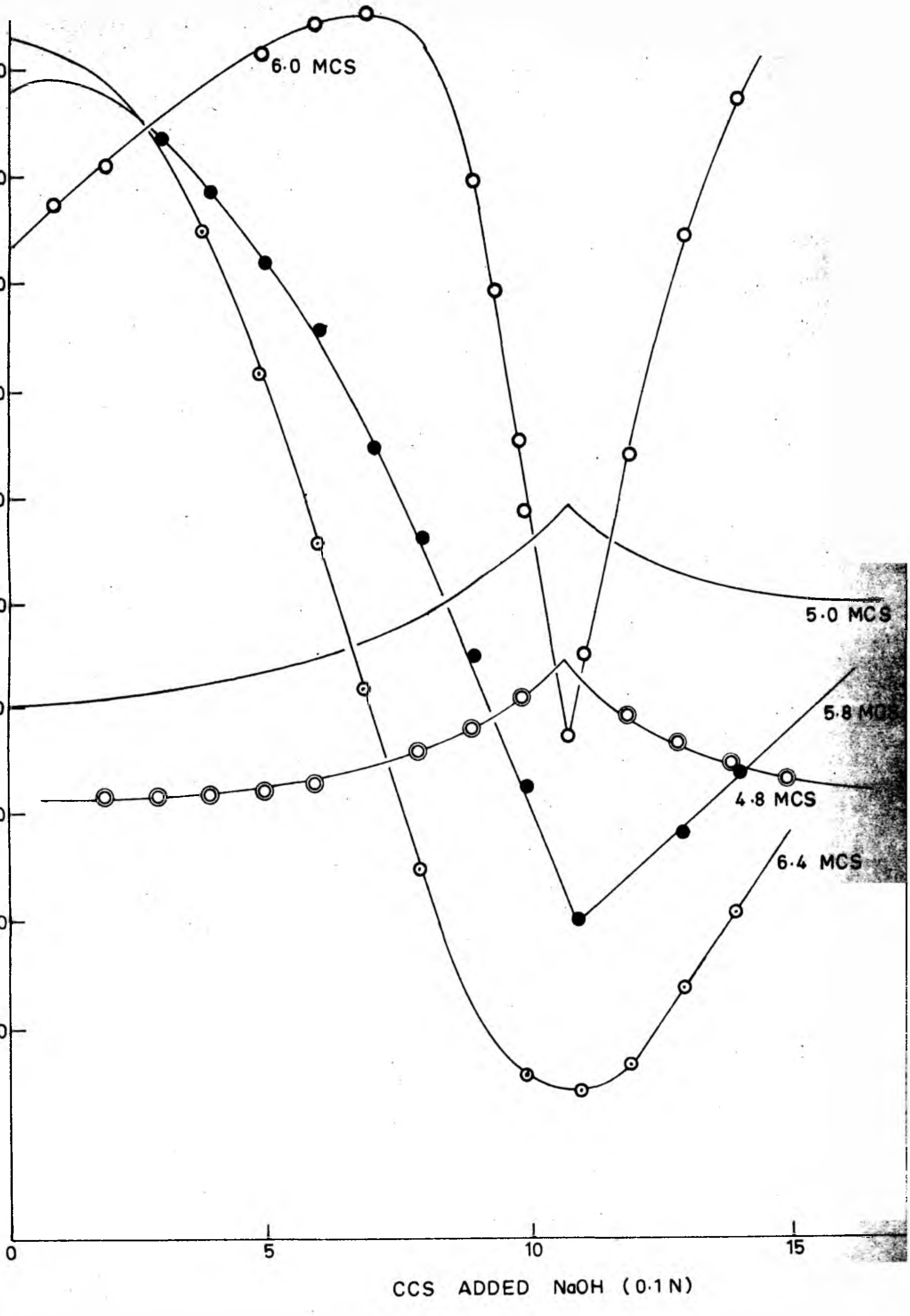
A pilot titration is generally advisable to determine the most suitable meter sensitivity range, and the initial setting of the indicator needle.

Figs. 21 and 22 show the titration of 0.1 N HCl with NaOH using the thin bulb electrodes described earlier. It is interesting to point out that between 2 and 5 megacycle the slopes at end point decreased from 13 μa/cc at 2 mcs to 4 μa/cc at 4.8 to 5 mc/sec as per the following

Frequency mcs	slope μa/cc
2 mcs	+ 13
4.8	- 4
5	- 4
6	- 20
6.8	flat
6.5 Transistor circuit	+ 375

These highly anomalous results bring out the importance of finding accurately the optimum frequency with a given set of electrode and a given apparatus (in all the above measurements frequencies were determined by a standard wavemeter and continuously monitored by a US signal corps trans-receiver).

The phenomena observed are, perhaps, related to anomalous dispersion of conductivity with concentration



90
80
70
60
50
40
30
20
10
0
6·0 MCS
5·0 MCS
5·8 MCS
4·8 MCS
6·4 MCS
0
5
10
15
CCS ADDED NaOH (0·1 N)

IMPROVED TITRIMETER: H.F. TITRATION PLOT

FREQUENCY 2 MCS

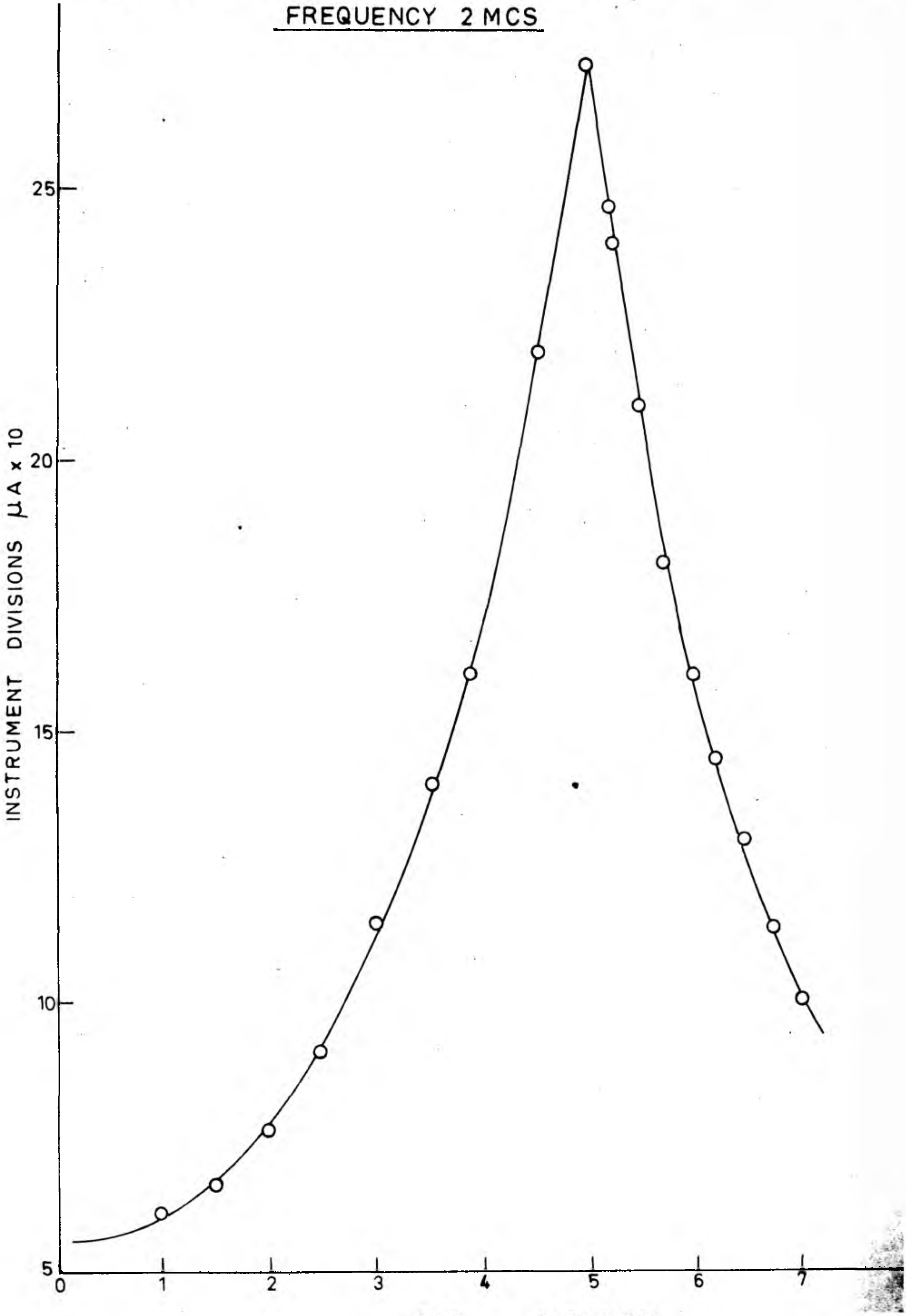


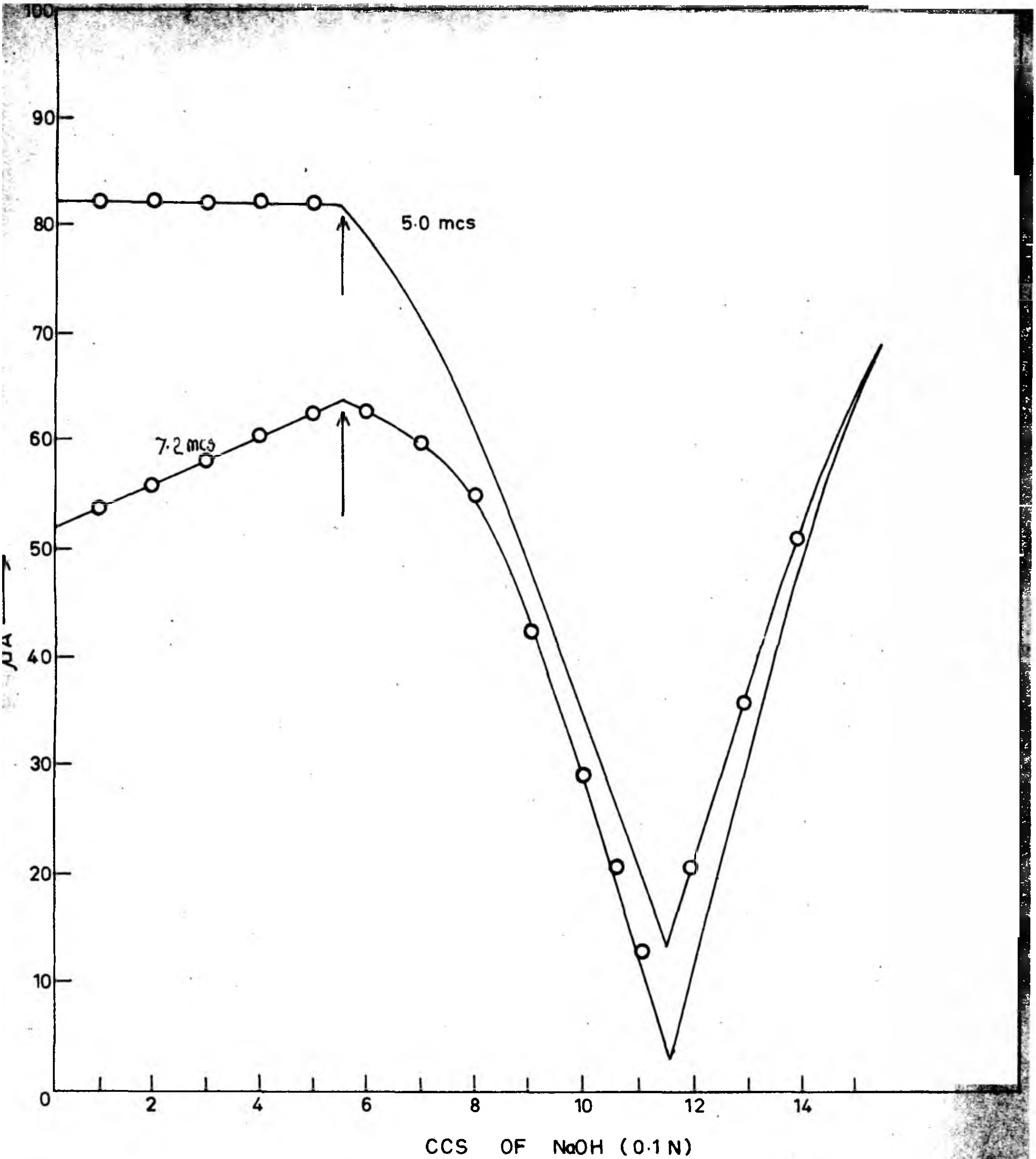
FIG. 22.

and still more so with the difference in the mechanism of conduction of H^+ and OH^- ions and Na^+, Cl^+ ions.

Fig.23 shows the titration of 0.1 N H_2SO_4 with 0.1 N NaOH at 5 mcs and 7.5 mcs using new bulb electrodes in the titrimeter just described. The graph distinctly shows the double end point; the first, being stepped and highly assymetric with a slope of 2.5 ua/cc and the second with a slope of 17 ua/cc. It may be pointed out that these results are exactly the opposite of what is observed in normal conductometric titrations.

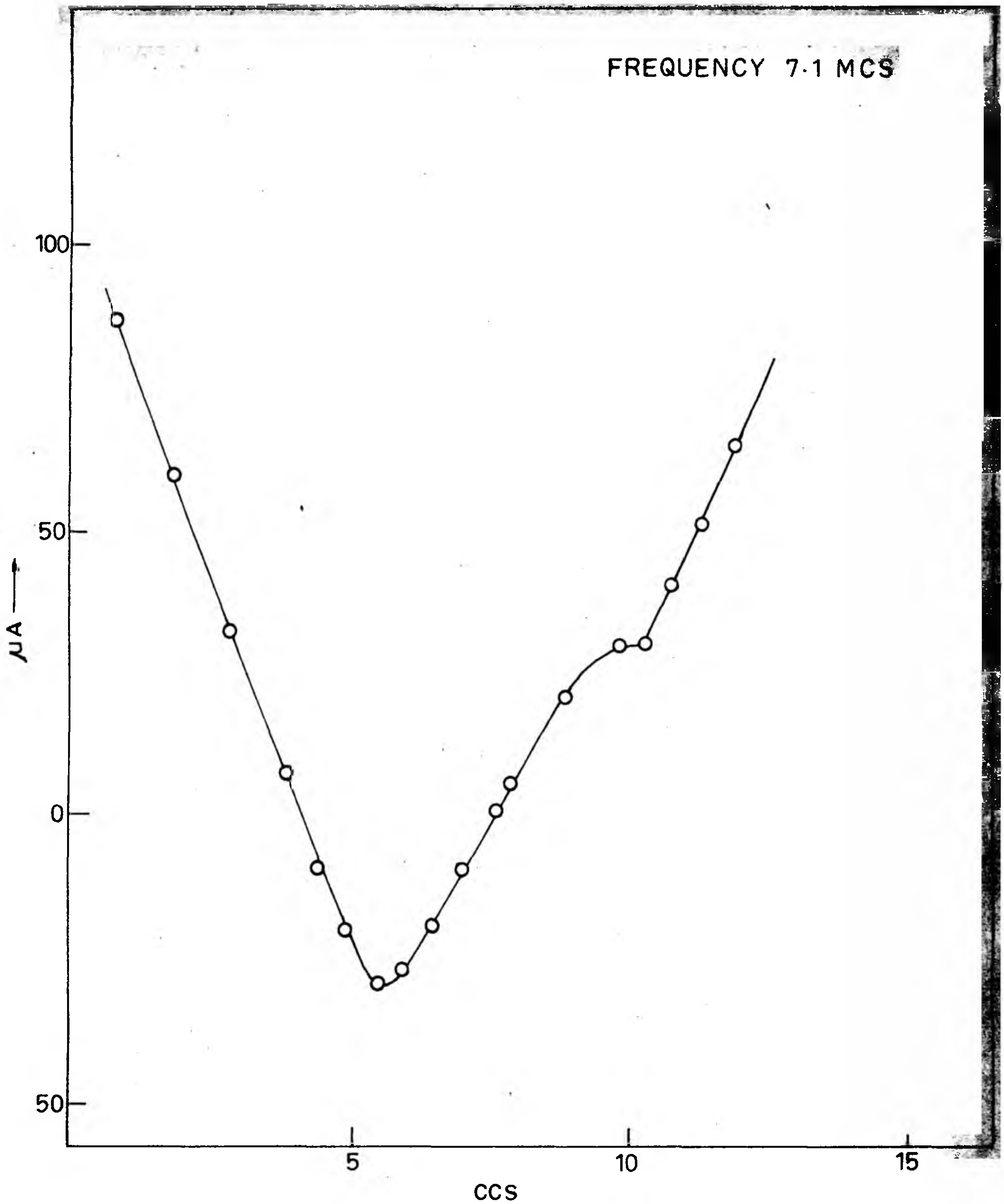
The previous workers have reported only one end point.

Fig.24 shows the titration of 0.1 N oxalic acid with 0.1 N NaOH. This shows the prominent half neutralization point and a very weak end point as in normal conductometric titration curves.



TITRATION CURVES FOR H_2SO_4 – NaOH SYSTEM AT 7·2 & 5·0 MCS

H_2SO_4 – 0·12 N (APPROX)



TITRATION GRAPH OF OXALIC ACID VS NaOH

FIG. 24.

SECTION - E

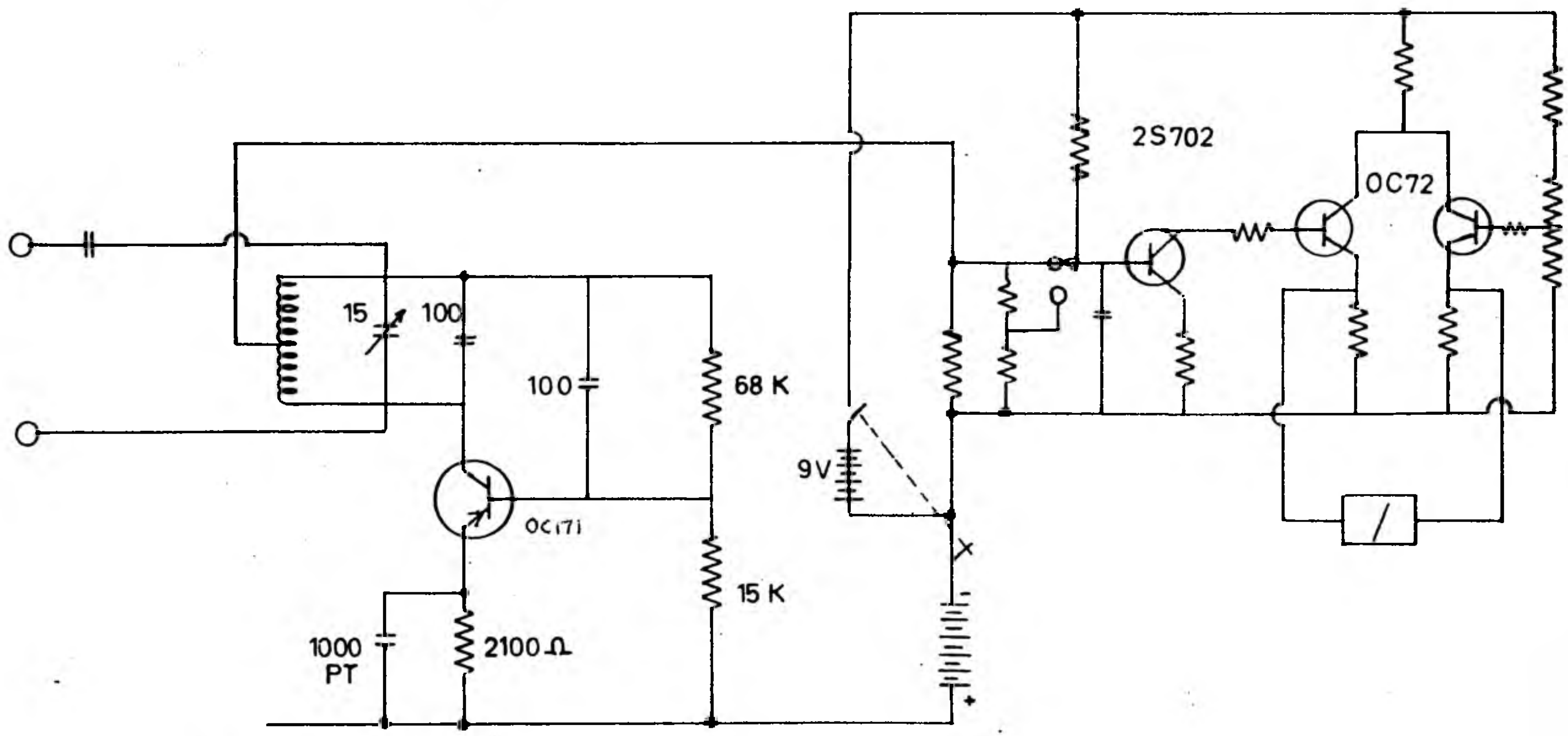
A new Transistor titrimeter

Previous circuits used for conducting high frequency titrations have been based on the use of electron tubes. The use of transistors in such circuits is limited by some of the following factors:-

(1) High impedance of the conductance cell because of the small capacitance offered by the external sleeve electrodes.

(2) Low input impedance of the transistor when used in the conventional common emitter or common base connection where a voltage gain is obtained.

In view of these difficulties no circuit has appeared using a transistorized circuit for H.F. titrimetry; the first difficulty encountered when using conventional cells has been effectively overcome by the use of the new thin walled cell described in this work. The low impedance offered by this makes it possible to effect a power match between the r.f. generator and the cell which forms a part of the regenerative circuit; thus making the oscillator sensitive to changes in the conductive and capacitance (susceptance) components of the cell current. The transistor titrimeter described here consists of a transistor Hartley oscillator using a high α cut-off frequency transistor the 06171. This can be used upto about 15 mcs and has a high gain ($\beta' \simeq 100$).



TRANSISTOR TITRIMETER

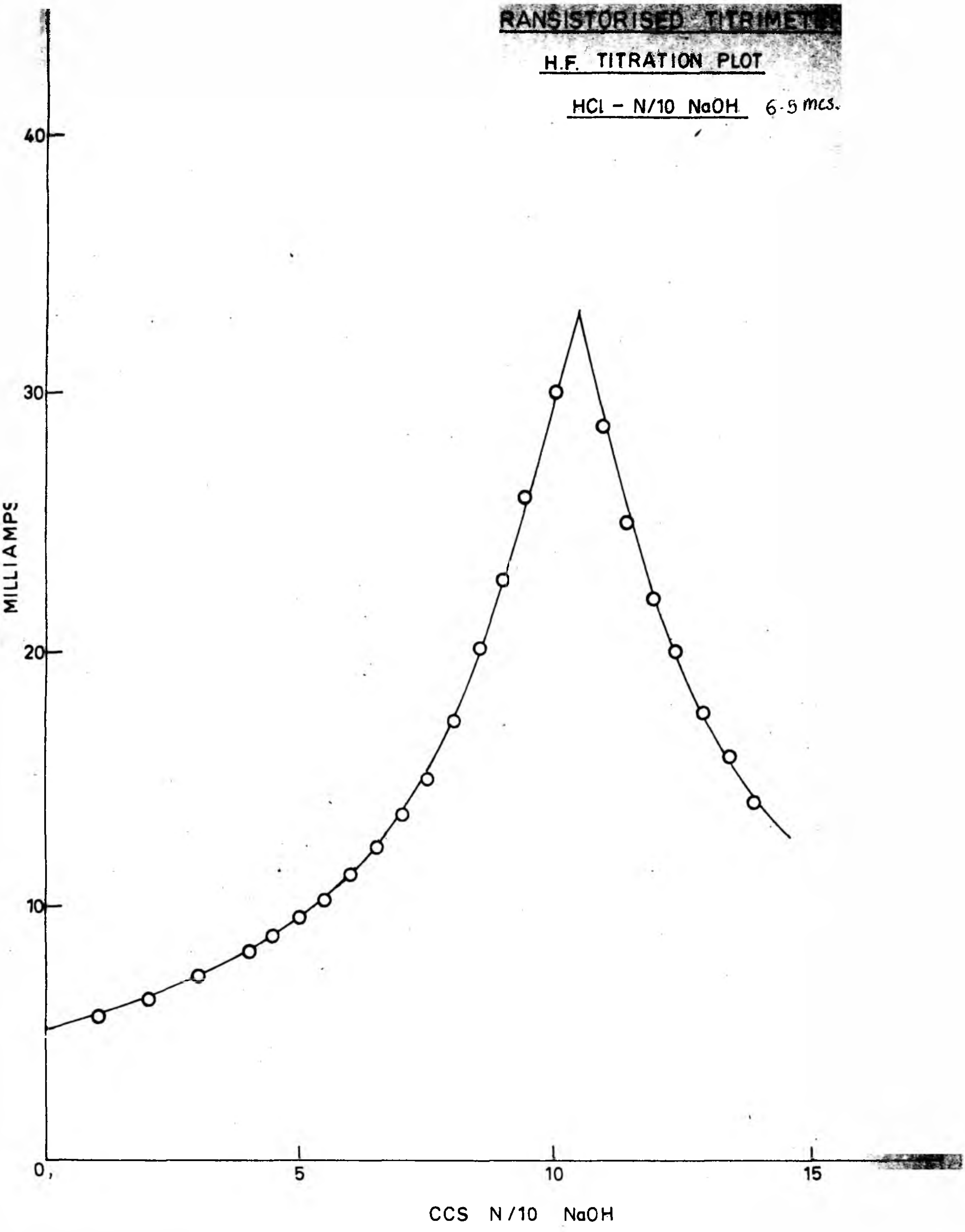
FIG. 25

The coil for the titrimeter operating at 16 mcs used 10 turns of 24 SW6 copper enamelled wire wound on a polystyrene former one inch indiameter. The tuning capacitor had a nominal value of 100 pf, while the trimmer used, had a range of 3 to 15 pf. The coupling to the conductance cell was made by connecting it across the tank coil, with a coupling condenser in series. The temperature current stabilization network of 68K and 15 K ohms in series provided the base bias for the OC171, with a current stabilization factor $S_i = 7$.

The loading of the oscillator by the conductance cell changes the collector current and this is monitored by the two stage complementary transistor d-c amplifier which forms the sensing stage of the titrimeter. The d-c amplifier input stage has a range selector switch which has two positions, with a sensitivity range of 10:1. The oscillator current flows through the load resistance which is bypassed by a capacitor to prevent feeding of r.f signals to the d-c amplifier. The first stage of the amplifier uses the silicon n.p.n. transistor 2S702 directly coupled to an OC 71 difference amplifier stage, with a milliammeter and zero suppression circuit forming the read-out system. The milliammeter was a Gaumont-Kalee 0-5 ma moving coil instrument with a needle pointer. Drift of the amplifier was found to be negligible particularly as the changes in current at the meter during the course of a titration were very large compared to any small drift signal.

The drift did not exceed 1/100 of the full scale deflection over a period of one hour.

Typical titration graph$ are given in fig.26
The results show the extraordinarily high sensitivity of the 6 mc. transistor titrimeter circuit developed by the author, which, coupled with thin walled (High capacitance) electrodes gives a sensitivity of 675 μA/cc. as contrasted with 13-20 μA/cc for valve circuits.
This is due to the matching of the impedance of the electrodes to that of the transistor oscillator and of the amplifier to the milliammeter.



RANSISTORISED TITRIMETE
H.F. TITRATION PLOT
HCl - N/10 NaOH 6·5 mcs.
MILLIAMPS
40
30
20
10
0
5
10
15
CCS N/10 NaOH

FIG. - 26.

D I S C U S S I O N

Very little experimental work has been reported on the high frequency conductivity of strong electrolytes. Falkanhagen (1928) had predicted, and Sack and others (1928) experimentally verified, that the conductivity increases by about 5 % at frequencies of 10^7 to 10^8 cps for 0.01 and 0.001 N HCl. For 0.01 M $MgSO_4$ solution an increase in conductivity occurs at a frequency of 10^8 cycles. This small change in conductivity with frequency cannot explain the nature of high frequency titration curves which show relatively high sensitivity to frequency. The explanation of these curves has therefore to be based only on the parameters of the circuit used and the conductivity cell adopted for titrations. It is important to point out the need of studying high frequency conductivity using modern techniques.

PART - 2

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PART - 3

PART - 3

INTRODUCTION

The application of thermistors for measurement and control of temperature has received considerable attention. Thermistors have the useful characteristics of a high temperature sensitivity, absolute temperature indication, low cost and a wide range of resistance values.

The temperature sensitivity is due to the large negative temperature coefficient of resistance which is of the order of 4 % per degree centigrade. This compares with the value of $4.2 \times 10^{-3}\,\Omega$ / °C for copper and $3.5 \times 10^{-3}\,\Omega$/ °C for platinum.

Bridge circuits

The most widely used circuit for using the thermistor as a temperature sensing element is the null or unbalanced Wheatstone bridge, described by Zeffers and Hormats,[1] Cole,[2] Andrews[3] and others.[14-22]

The conversion of resistance values into corresponding temperatures is complicated by the nonlinear relation between the resistance and temperature of a thermistor.

The equation is given by:

$$R_T = A\ e^{B/T}$$

where A, B are constants for a thermistor

T is the absolute temperature

R_T is the resistance of the thermistor at temperature T.

This requires a plot of log R against $1/T$ to obtain a straight line relating resistance with temperature.

Linearization of the R/T characteristic

The problem of linearizing the resistance temperature characteristics of a thermistor bridge circuit has been of interest, especially for measurement of small temperature changes.

Farhi and Groves[4] have been able to linearize the characteristic of a thermistor by the expedient of shunting it with a resistor (non temperature sensitive) of value equal to that of the thermistor at the mid point of the temperature range over which linearization is required.

A thermistor thermometer bridge with a digital display (sensitive to 0.1°C) using a shunted thermistor has been described by Priestley.[5] The bridge uses a servo mechanism actuated by the unbalance from the bridge to balance it and indicate the resistance on a digital dial. The value of shunt resistor to be used in parallel with the thermistor has been shown to be

$$s = R_o \frac{(b - 2T_o)}{(b + 2T_o)}$$

where R_o is the resistance of the thermistor at temperature T_o.

Direct reading D.C bridges in which the unbalance current (through the galvanometer) is a linearized function of temperature have been devised by Godin.[6]

A two thermistor bridge for direct measurement of temperature differences has been described by Godin.[7] It is shown that by choosing the fixed resistors (two arms) in a certain ratio to each other, equal temperature differences give equal currents.

Beakley[8] describes a thermistor thermometer which is linearized by the use of a large resistance in series with the bridge voltage source. The deviation from linearity is reported to be 0.024°C. The equation relating the galvanometric current with the thermistor resistance R is given by

$$i_g = \frac{E S_1}{R + r}$$

The methods used for linearization of the resistance temperature characteristics may be summarized thus:

1) The use of a resistance in series with the thermistor
2) The use of unequal ratio arms
3) The use of a resistance in parallel with the thermistor.

Almost all the methods so far described depend on the linearization of the unbalance current through a galvanometer, and thus suffer from the drawbacks characteristic of direct reading devices e.g. the instability of higher voltage sources or higher galvanometer sensitivity.

There is, therefore, a need for a device which would give a linear scale and use a null balanced bridge. The design of such a bridge for thermistor thermometry is described in the next section (Experimental).

Power dissipation

One of the factors limiting the available precision and sensitivity of thermistor thermometers is the effect of pwer dissipation on the measured values of temperature.

Cole[9] discusses the effect of power dissipation on the temperature indicated by a thermistor. The variations in current with changes in resistance of the thermistor may vary the dissipation by a factor of five between 0°C and 40°C.

Beakley[8] suggests the use of a very low current through the thermistor to reduce the error due to heating of the thermistor. Unfortunately, in (conventional) D.C. bridges higher sensitivity can be obtained only by increasing the bridge current.

The attainable sensitivity of D.C. Wheatstone bridges is thus limited by the power dissipation ratings and the need to reduce the current to eliminate errors in measurement of temperature.

It may be pointed out that the use of an alternating current source with amplification of the bridge unbalance signal could minimize the problem of power dissipation as a much lower current could be passed through the thermistor for the same sensitivity obtainable with D.C. bridge circuits.

Applications to cryoscopy

The applications of thermistors to cryscopy have been described by Jeffert and Hormats[1]. Among the advantages to be obtained by the use of thermistors in cryscopic measurements are the large temperature coefficient of resistance and the small heat capacity of the thermistor element. Both the absolute and relative sensitivities increase as the temperature is decreased. At -60°C the temperature coefficient reaches 10^4 Ω /°C compared to 80 Ω/°C at 25°C. The thermistor described is a Western Electric Type 14B with a normal resistance of 2000Ω at 25°C.

The use of thermistors for the determination of freezing points of solutions and soils has been described by Richards and Cambell[9]. A calibration curve was constructed for a five degree range using a standard thermometer. Becker, Green and Pearson[10] have described the application of thermistors to freezing point determinations.

McMullan and Corbett[11] have described the application of a thermistor bridge of the D.C. Wheatstone type to cryoscopic measurements and the measurement of small temperature differences. The thermistor was one arm of an equal arm Wheatstone bridge, the other three arms being made up of the fixed resistors and a variable standard resistor. Sensitivity of the bridge enabled a balance to be obtained within 0.023 Ω, so a temperature difference of 10^{-4} degrees could be detected. Calibration of the thermistor response as a function of temperature was done by measurement of the resistance of the thermistor at the freezing point of solutions of known concentration (assuming ideal behaviour).

McGee and Iyengar[12] have described an A.C. thermistor bridge for the determination of osmotic coefficients. The bridge uses two matched thermistors and the temperature difference due to vapour pressures of solvent and solute is obtained as a resistance differential δr ; this is measured by a resistance in series with one of the thermistors. Calibration is effected by using a standard solution of KCl.

Kulkarni[13] has described the use of the above bridge for determination of molecular weights.

EXPERIMENTAL

A.C. Thermistor Bridge:

Since most of the thermistor bridges described so far in the literature were D.C. Wheatstone bridges, and the temperature was measured in terms of resistance or deflection of the galvanometer, it was felt that the use of an audio frequency bridge would have several advantages over the bridges described so far.

1) The A.C. Bridge can be used with a smaller applied voltage; this drastically reduces the dissipation of power in the thermistor. Power dissipation has been a limiting factor in D.C. thermistor bridges.

2) The A.C. bridge can be used with a power source that provides effective matching between the bridge and source impedances.

3) A high sensitivity null detector can be incorporated as a null indicator (The limit of sensitivity being the signal to noise ratio).

Using an A.C. bridge, very high resistance thermistors can be used provided a suitable measuring bridge could be designed.

An A.C. Thermistor bridge could be made into a compact instrument independent of storage or primary cells with self contained power supply, oscillator and detector.

The design and performance of two such bridges is now discussed.

The thermistor bridges are based on the Kolhraush type of slide wire ratio bridge. This bridge is characterized by continuously variable ratio arms; the ratio for any given setting is given by $x/1-x$ where 1 represents the unit resistance of the slidewire and x is the resistance of that part of the slide wire constituting a conjugate arm of the bridge. $(1-x)$ is then the other arm of the bridge. $P/x = Q/1-x$.

1. TRANSISTORIZED THERMISTOR BRIDGE

A transistorized thermistor temperature sensing bridge is now described. This bridge incorporates a Kolhraush type of bridge arrangement in which the thermistor forms one arm of the bridge. The apparatus is compact, portable and independent of mains power supply, being battery operated.

In order to ensure a low dissipation A.C.techniques have been used for supplying the bridge, as well as for amplification of the unbalance signal from the bridge.

The circuit used is given in fig. 27 alongside; a brief description follows:

(a) The Bridge Power Supply: The bridge voltage is supplied by a two stage transistor oscillator. The oscillator is an RC tuned audio frequency unit operating at a frequency of one kilo cycle. The output is taken from the secondary of the output transformer and applied to the bridge.

The tuned R.C. oscillator provides an audio frequency signal of high stability and good wave shape; the emitter follower output stage ensures that the bridge does not load the oscillator, and provides a suitable matching of bridge and source impedances.

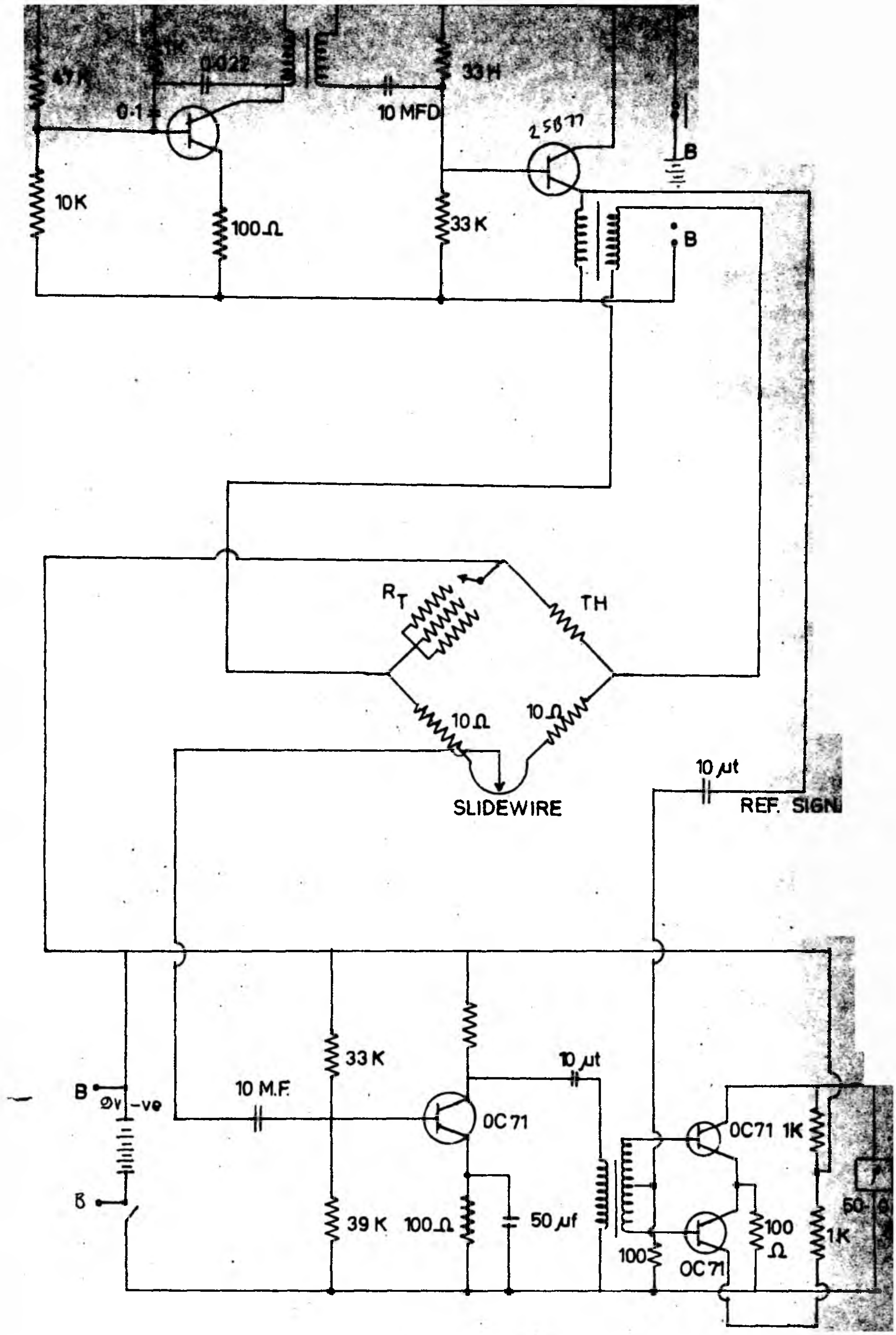


FIG. 27. TRANSISTORISED THIRMISTOR THERMOMETER BRIDGE

A reference signal is taken from the output stage via the coupling capacitor C to the phase sensitive detector.

The primary of the output transformer forms the load for the emitter follower (25B77). No gain control is provided since a steady output signal of 1 v is adequate to operate the bridge at full sensitivity.

Both T_1 and T_2 are output transistors capable of dissipating 500 mw of power at an ambient temperature of 30°C. The oscillator has proved to be a rugged unit and can be built on a small tag board 10 cms x 3 cms. The oscillator operates on three torch cells (1.5 v) and draws a current of 50 ma at 4.5 volts.

(b) Phase Sensitive Detector

The transistorized phase sensitive detector was designed to act as a bridge null indicator giving a phase sensitive deflection on a center zero instrument.

The signal from the bridge is applied through capacitor C to the base of the transistor T_1 (25B74) where it is amplified by a factor of 15 and fed to the phase splitting transformer T. This driving transformer provides the signal to the push pull output stage consisting of two 25B75 transistors with matched characteristics. The meter is connected across the 1 kΩ load resistors of the transistors. The transistors are operated in the common emitter configuration.

The reference phase from the oscillator is compared with the amplified signal from the bridge. The transistors therefore are effectively detectors of the inphase and out of phase signals between the oscillator reference and the bfidge output.

Using a 100 μa center zero instrument the sensitivity of the detector was better than a millivolt for changes in bridge balance.

(c) Bridge Circuit

The bridge consists of a slide wire R_x in series with two extensions A, B each equal to 100 Ω. The slide wire, also of 100 Ω, has a dial divided into 100 divisions with digits from 0 to 10. The other two arms of this ratio bridge are:

(1) The resistance bank R_T, which enables the thermistor resistance to be approximately matched at the mean value of the thermistor resistance for the temperature range under investigation. The bank consists of a decade of 2 % high stability resistors with values from 1 K Ω to 10 K Ω. They are selected by a rotary wafer type switch of good quality.

(2) The thermistor: The thermistor used is the Western Electric 14B bead thermistor encased in a glass tube. It has a nominal resistance of 2000 Ω at 25°C and a temperature coefficient of nearly 4 % per degree of this temperature. The change in resistance of the thermistor

is indicated by an unbalance in the phase sensitive detector which can be rebalanced by adjustment of the slide wire R_x. The sensitivity to temperature changes is determined by

i) the value of estension resistances in the arm. Increasing the value of the extension resistors increases the sensitivity and precision at the cost of temperature measuring range. It was found that for a temperature range of 10°C to be covered by the slide wire, the best compromise was the use of extension arms equal to 100

ii) Sensitivity of the detector. The simple two stage phase sensitive detector used has adequate sensitivity to detect unbalance signals of the order of 3 millivolts using a 50 UA center zero instrument.

The bridge circuit does not use equal resistors in the four arms; the loss of sensitivity for current detection on this account is offset by the use of voltage sensitive electronic detection in place of the conventional galvanometer.

The use of phase-sensitive detection renders the balancing operation more precise as well as extremely facile.

The response of the instrument to temperature was determined by following the change in temperature of a

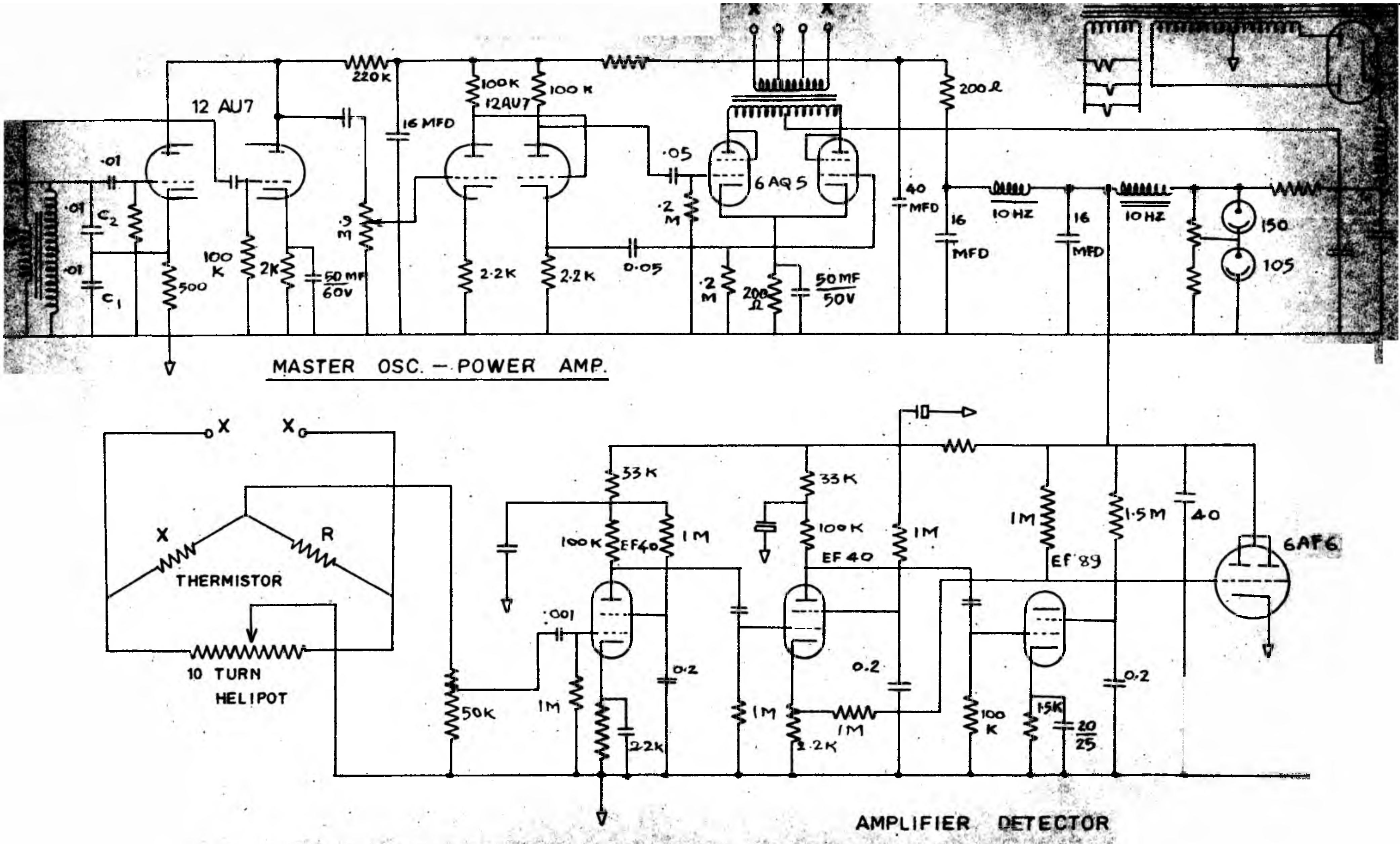


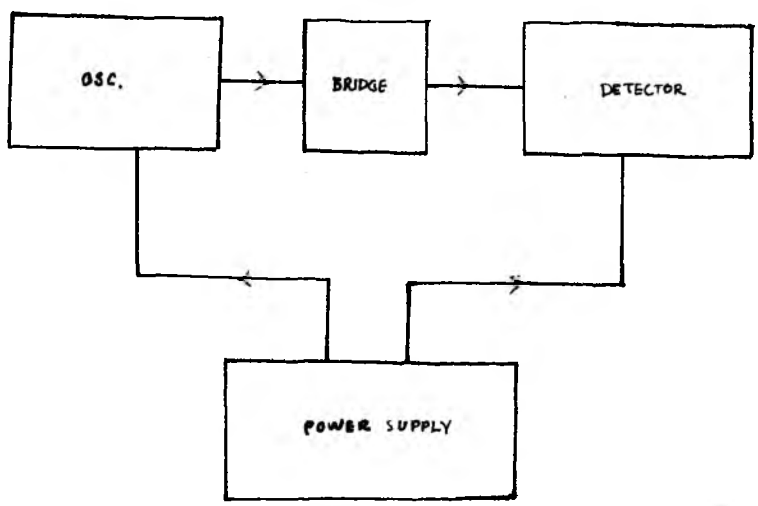
FIG. 28. CIRCUIT DIAGRAM : ELECTRONIC THERMISTOR BRIDGE

laboratory thermometer reading to 0.05 °C. In this way the response of the instrument was calibrated over a range of ten degrees over which a linear response was obtained as shown in the graph No.

The graph shows the temperature observed on the monitoring thermometer against dial readings of the thermistor thermometer bridge.

2. ELECTRONIC THERMISTOR BRIDGE

The thermistor bridge is shown below in a schematic block diagram, the components of which are best treated individually. The complete circuit is given in fig.28.



This instrument also uses the principle of a continuously variable ratio bridge based on the Kohlraush bridge. The bridge A.C. voltage used is nearly ten times less than the voltage applied in conventional D.C. thermistor bridges. This is a decided advantage as it eliminates the problem of heating in thermistors caused by bridge current.

Power Supply

The power supply is a 250 volt glow tube stabilized unit operating from A.C. 50 cps mains.

The transformer primary has tappings which enable supply voltage variation to be compensated for.

The output is 250 volts D.C. at 100 ma and 6.3 volts A.C. at 3 A.

Oscillator

The design of the oscillator is governed by some of the requirements of a resistance bridge of the Kohlraush type.

The oscillator is of the Master-Oscillator-Power Amplifier type (MOPA)

The first stage of the four stage circuit consists of a 1000 cps colpits oscillator, the frequency of oscillation can be varied by varying the value of C across the inductance L. The second stage acts as a buffer stage. The third stage incorporates a gain control over the input to the push pull amplifier stage which drives the two 6AQ5 triodes connected in the output stage (IV). The oscillator and buffer are the two sections of the 12AX7 double triode.

The gain control stage and phase inverter are provided by the two sections of the low μ twin triode 12AU7. The 6AQ5 pushpull output valves are triode connected to give low third harmonic distortion.

The pushpull design practically eliminates second harmonic distortion.

The output (matched into a suitable impedance) showed a harmonic distortion of less than 2 % when applied to an oscilloscope. This design therefore provides a power source which fulfills all the requirements of a bridge circuit which would ensure high sensitivity:

1) Balanced output voltage to ground
2) Low harmonic content.
3) Output impedance variable through a tapped transformer.
4) Variable output voltage through a non reactive volume control.
5) Complete independence of load impedance and oscillator loading.
6) Correct matching of source and bridge impedances.

<u>Bridge</u>

The bridge circuit consisted of a L & N precision 10 turn slide wire mounted on a drum, together with a Leeds and Northrup precision decade resistance box with values of resistance upto ten thousand ohms.

The fourth arm of this bridge was the S.T.C. thermistor (Stantel Type F2311/300) with a nominal resistance of two thousand ohms.

The thermistor thermometer assembly was made up of concentric glass tubes with the bead thermistor mounted in the innermost glass tube. The whole assembly was placed within a Dewar flask to maintain isothermal conditions.

Detector

The amplifying stages were designed in accordance with design practice outlined by Terman. It was felt necessary to provide an effective voltage gain of 100,000 (80DB) to utilize the inherent sensitivity of the thermistor to small changes in temperature.

Design considerations

The requirement for a null detector of a sensitivity of the order of a few micro volts for use with a bridge capable of marking precision measurements led to the development of an electronic amplifier that satisfied some of the following conditions:

1) A voltage sensitivity not less than 10 microvolts (10×10^{-5} V)
2) A high input impedance.
3) Low noise figure and freedom from hum.
4) A variable sensitivity control.

5) A visual indication of balance on the bridge.

6) The signal voltage would be a 1000 cps sine wave.

Since the signal to be amplified was of 1000 cps and this is well within the audio frequency range, it was decided to apply conventional audio frequency amplification techniques.

Since the total amplification required exceeded a value of 10^5 overall, it was decided to incorporate three amplifying stages each of which would provide a gain of at least 100, and allow the use of negative feedback for stabilization.

The next design step was the selection of appropriate amplifying valves to enable the required amplification to be obtained without any danger of instability.

Since the amplification required per stage exceeded 100, it was decided to use A.F. pentodes which provide the highest possible amplification together with a high input resistance which thus satisfied one of the design conditions.

Suitable valves for such an application include among others the 6SJ7, 6J7, 6SH7, and among miniatures the new valves EF40, EF42, UF40, 6AU6, EF91.

The EF40 was selected for the first and second stages at the amlifier as it had the following characteristics and had a low noise level a plate resistance

EF 40 - Low noise a.f. pentode

V_f	I_f	V_a	V_{g2}	$-V_{g1}$	I_a (mA)	I_{g2} (mA)	g_m (mA/V)	r_a (M Ω)
6.3	200	250	140	2.0	3.0	0.55	1.85	2.5

of 2.5 megohm, 6.3 v filament and a sharp cut off characteristic with a high slope.

The low noise characteristic makes it especially useful in detecting low level signals and contributes to the stability of the amplifier.

Detector Amplifier

The detector incorporates a four stage resistance--capacitance coupled amplifier. The first two stages are low noise voltage amplifying pentodes (EF40) followed by a variable U pentode EF89 which is directly coupled to the 6AF6 electron ray tube. Negative current feedback is provided in the amplifier through the cathode resistors of the three stages following the input stage. The overall gain of the amplifier was 80d (with negative feedback).

The amplifier could be made selective for a given audio frequency (e.g. 1000 cps by the use of a twin-T filter in the negative feedback loop. This entails a minor modification of the circuit and was not found necessary in the present set up. The 6AF6 electron ray tube is directly coupled to the output stage of the amplifier. This arrangement has been found to be more satisfactory than an R.C. coupling, as the direct coupling gives a bright steady electron beam pattern on the luminescent target, and no flicker is noticeable. The voltage sensitivity required to change the target shadow angle by 10° was approximately 50 microvolts applied through a low impedance source of 600 ohms. This sensitivity was found to be more than adequate for all the bridge measurements made.

The response of the amplifier was tested at audio frequencies from 200 cps to 20 kc by using a variable frequency audio oscillator and measuring the gain in db using an A.C. VTVM. The response was found to be quite uniform over the region above mentioned when used without selective filters of the twin-T-type. This ensured that the detector would be useful for studies of the response of the thermistors at different frequencies.

Sensitivity and Reproducibility:

The sensitivity of the bridge to small changes in one arm was measured directly by introducing increments in the measuring arm and rebalancing the bridge to a null point. Reproducibility was tested by measuring the resistance of a manganin resistance at intervals of one hour between observations.

The reproducibility of observations of resistance was found, by a number of readings, to be better than one part in 10^5 and overall sensitivity was $\pm$ 2 in 10^5.

This sensitivity in measurement of resistance if translated into temperature sensitivity would give a value of sensitivity of 10^{-4} °C or equal to the best d-c bridge using considerably higher bridge voltage and sensitive galvanometer.

Cooling curves for the system H_2O - NaCl and H_2O - KCl were obtained by using bridge described.

The calibration of the temperature scale for such a thermistor bridge involves the problem of a primary standard of precision. A Beckmann thermometer was used for preliminary tests. The Beckmann thermometer read~~s~~ to 0.01°C. It was felt that the bridge could be made sensitive to changes in temperature of the order of 0.005°C. Thus, in order to establish the temperature scale, recourse has been made to known data of depression of the freezing point of standard concentrations of 1:1 electrolytes like KCl available from the literature.

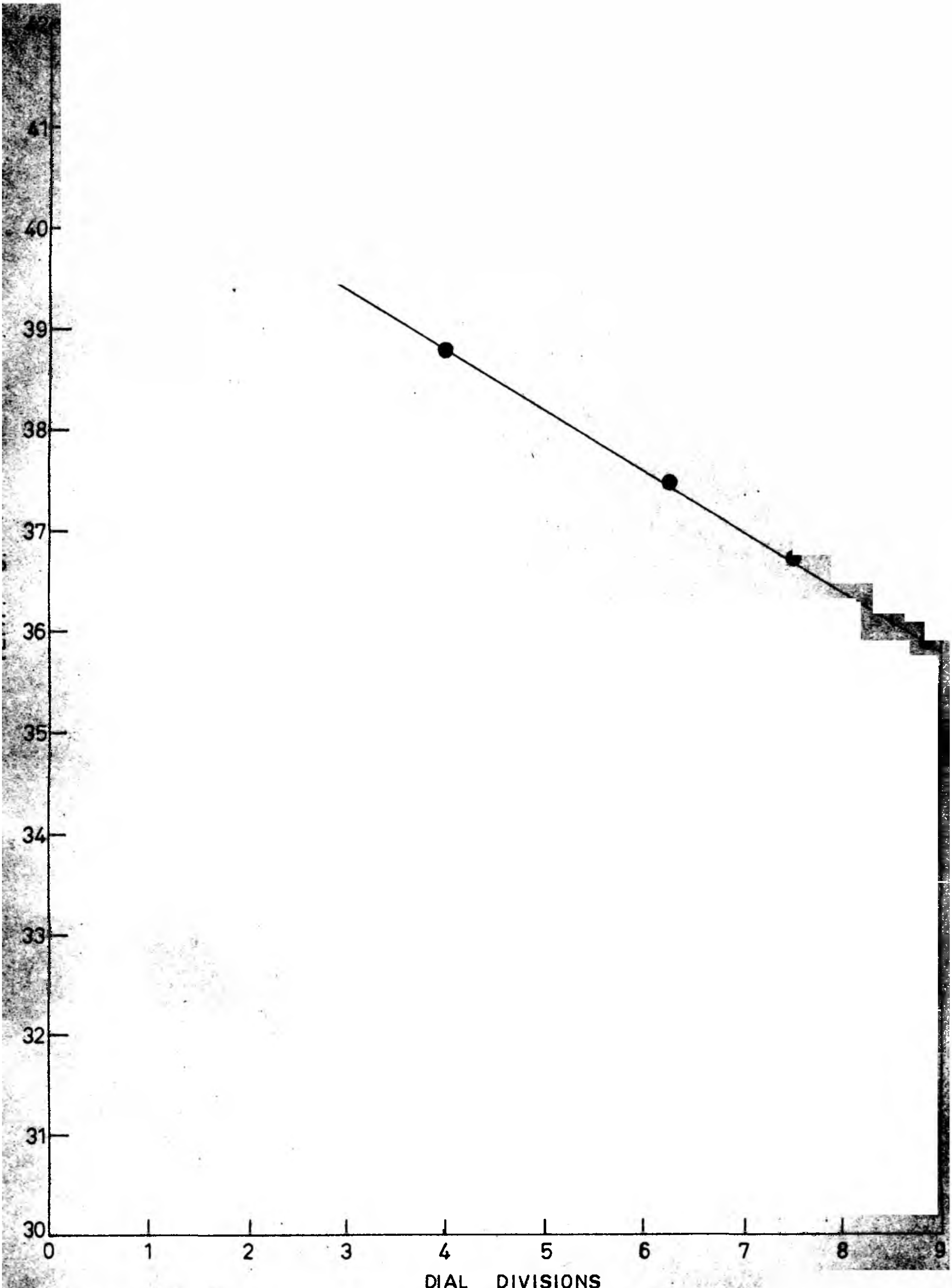


FIG. 29. GRAPH OF DIAL DIVISIONS VS. TEMP °C FOR TRANSISTORISED THERMISTOR BRIDGE

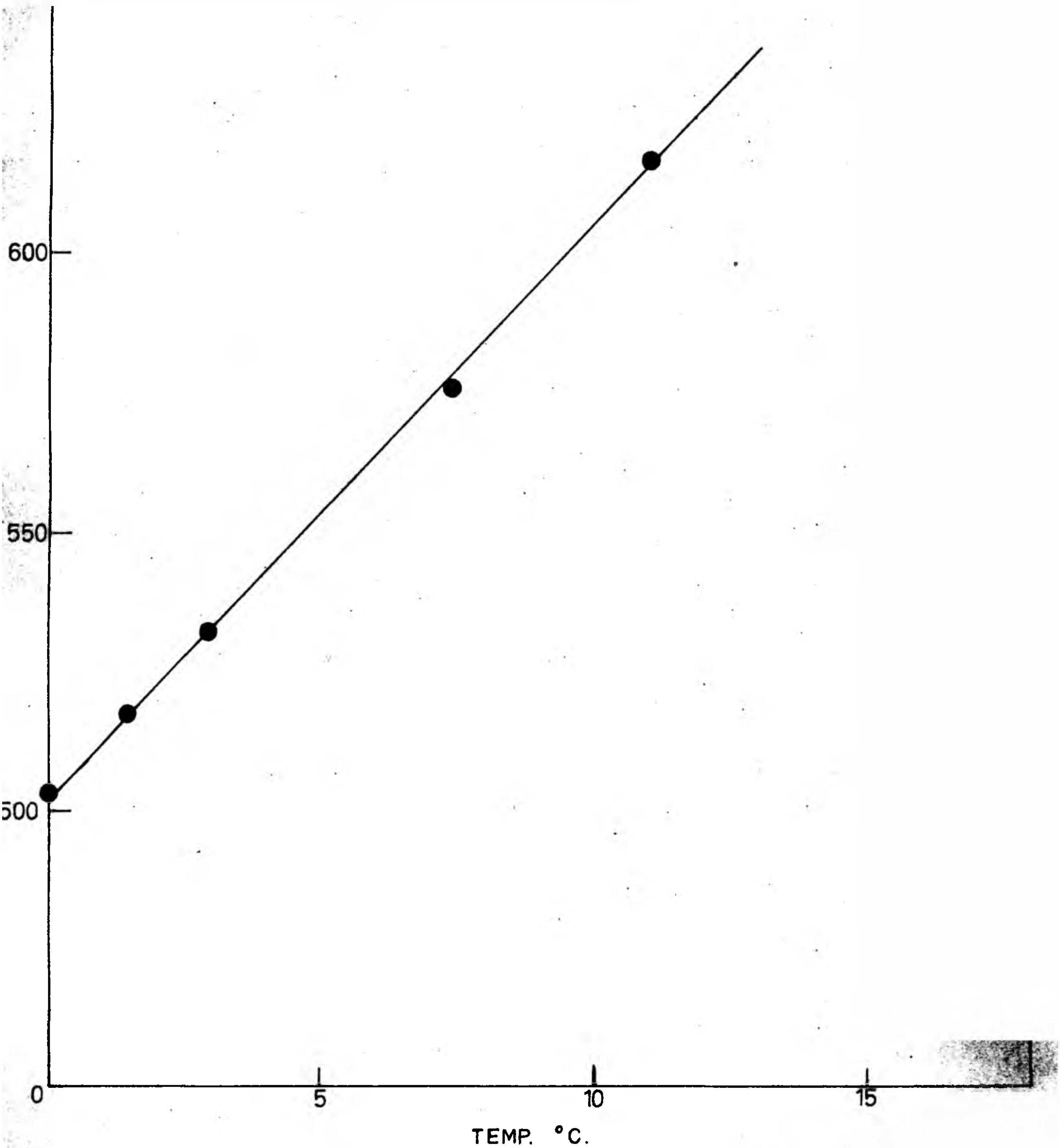


FIG. 30. GRAPH OF DIAL DIVISIONS VS. TEMP. °C. FOR ELECTRONIC THERMISTOR THERMOMETER

The accompanying graphs (figs.29,30) show how a nearly linear calibration can be obtained from the known freezing point depression at different electrolyte concentrations and the dial readings at bridge balance.

Apparatus for cryoscopy

The set up for cryoscopic measurements consisted of a system which provided adequate thermal insulation. The thermistor (Stantel, Type F/300) was contained in a Pyrex tube which also held the electrolyte under study. This was further encased in a concentric pyrex test tube which was in contact with the freezing mixture (ice and salt). The freezing mixture was placed in a large dewar flask with a bakelite cover through which ports were drilled for the thermometer and thermistor assembly. Provision was made for stirring both the freezing mixture and the electrolyte.

SUMMARY OF RESULTS

Author	Method	Temp. range	Sensitivity	Linearity
Cole	E.C.Wheatstone equal arm bridge 3 volts input	0°C to 40°C	0.1°C	
Farhi and Groves	Digital display d.c bridge		0.1°C	
Beakley				± 0.024°C
Richards and Cambell		5°C		
McMullan and Corbett	D.C. bridge caliorated by standard solution F.P.		10^{-4}°C detectable	
Present author				
A.	Transistorized thermistor thermometer	10°C (linear)	0.05°C	± 0.025°C
B.	Electronic thermistor bridge	15°C (linear)	(a) 0.05°C from dial (b) 10^{-4}°C from resistance change.	

SUMMARY

The apparatus described enables small temperature differences (upto 10°C difference) to be measured on a linear resistance scale with a deviation from linearity of 0.01°C and sensitivity of 0.01°C.

The use of a ratio arm bridge (Kolhraush type) with a 10 turn helipot as the measuring resistance for the measurement of temperature has enabled a linear calibration over a span of 10°C to be obtained.

The balance equation for the bridge is given by

$$\frac{R_t}{R} = \frac{x}{10 - x}$$

Changes in the resistance of the thermistor are measured in terms of changes in x. A linear relation between x and T the temperature of thermistor is obtained for

$T = 10°C$ at $T_m = 0°C$ and also at $T_m = 30°C$.

PART - 3

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SUMMARY

In part 1 a critical study of the design of commercial pH meters revealed several drawbacks, particularly due to difficulty of securing special components. The author has designed and connected five different types of pH meters and described their performance, using readily available components.

In part 2, the author has studied the several factors involved in the design, construction of high frequency titrations apparatus. An analysis of the circuits revealed the shortcomings of the design of the cells and the involved theories of conductivity of electrolytes as well as the circuits employed. By using thin walled glass electrodes and new types of transistor circuitry very high sensitivities are obtained even in concentrated solutions.

Part 3 describes a new type thermistor thermometer circuit designed and constructed by the author to measure temperatures from -5 to 45°C ± 0.5°C and from 21° to 39°C with linear scale.

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