CHAPTER II

INSTRUMENTATION FOR LINEAR SWEEP VOLTAMMRTRY

An instrument for linear sweep voltammetry, similar to one used in cyclic voltammetry (163), has been fabricated; utilizing electronic dc coupled switching which can accept either fast or slow sweep signals. Controlled electrode dc level is adjustable over –3.0 to +3.0 volt range. It can be made to sweep in either the positive or negative direction from the rest position, using single or repetitive sweeps. The block diagram is given in Fig.2.1.

The section-wise details of the instrument are as under.

Power supply

Regulated and stabilized dc power supply is obtained by stepping down the output of line voltage (220V ac) using appropriate step down transformer, rectifier and zener diode circuits. The power supplied to the instrument is in the range of +12 to –12 volts.

Fig. 2.1 BLOCK DIAGRAM OF APPARATUS

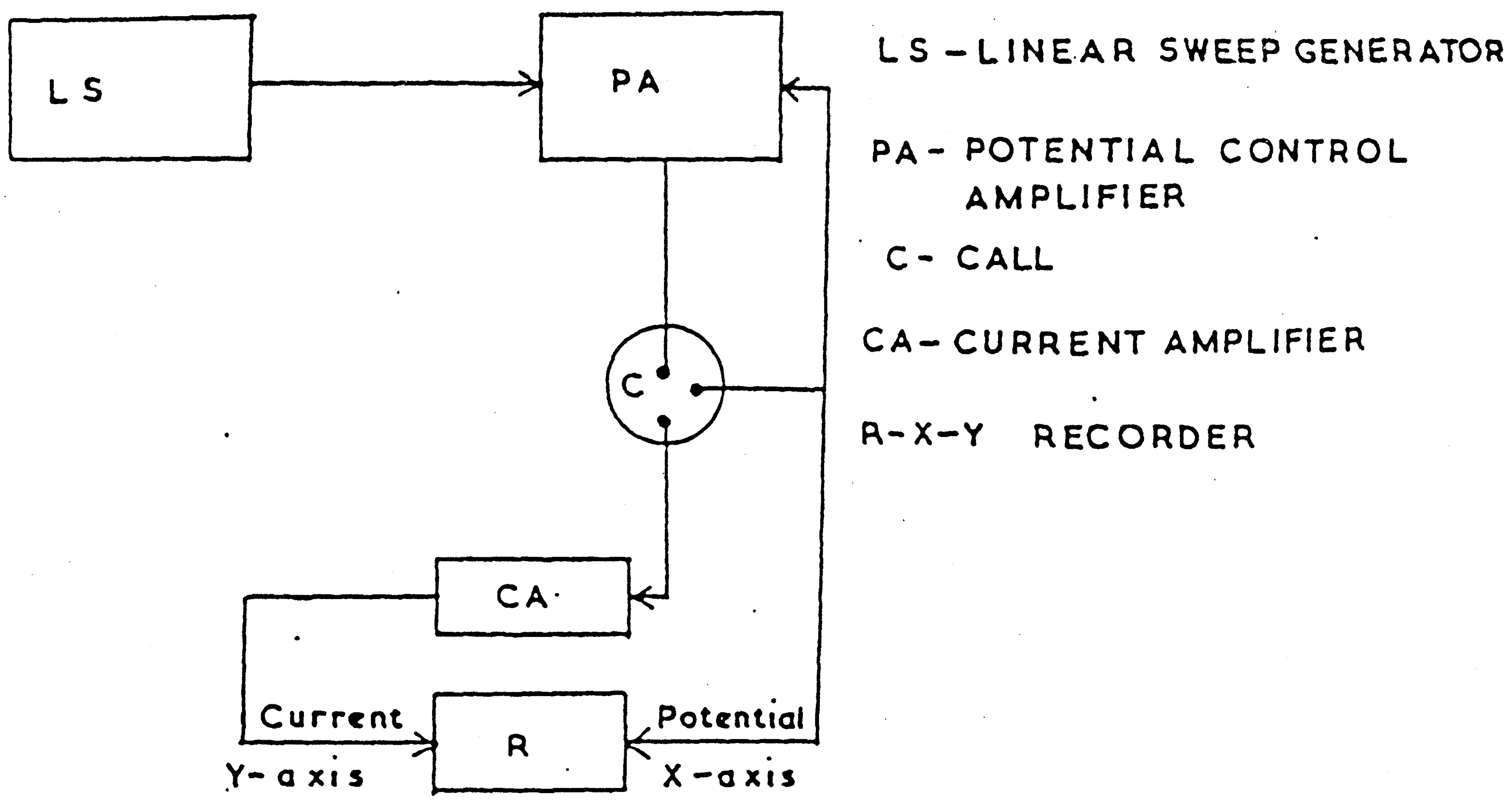
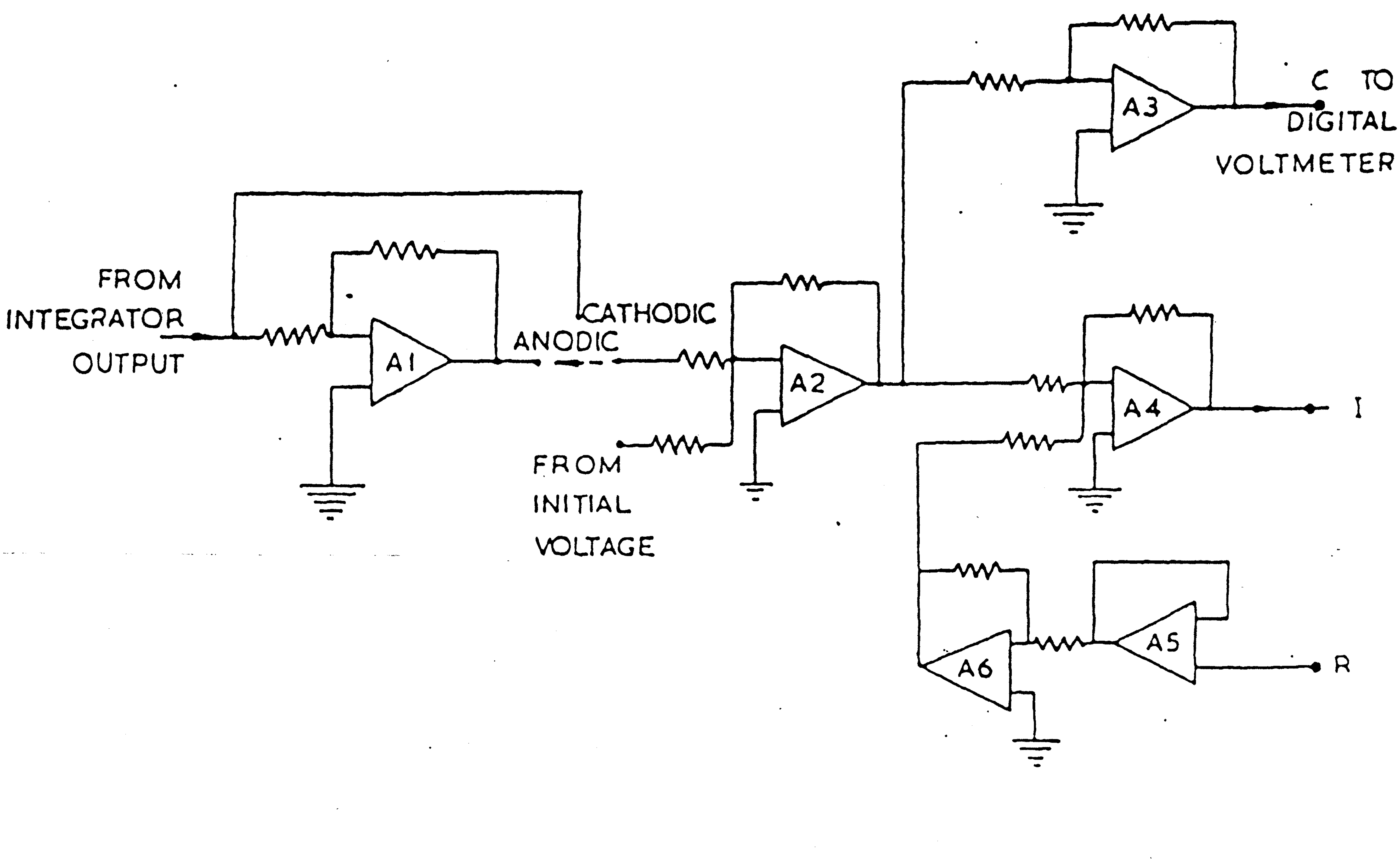


Fig. 2.2 OUTPUT CIRCUIT



Sweep generator

The linear sweep generator has been fabricated using operational amplifiers, transistors and diodes. It can be made to sweep in either positive or negative direction from the rest position, using single or repetitive sweeps.

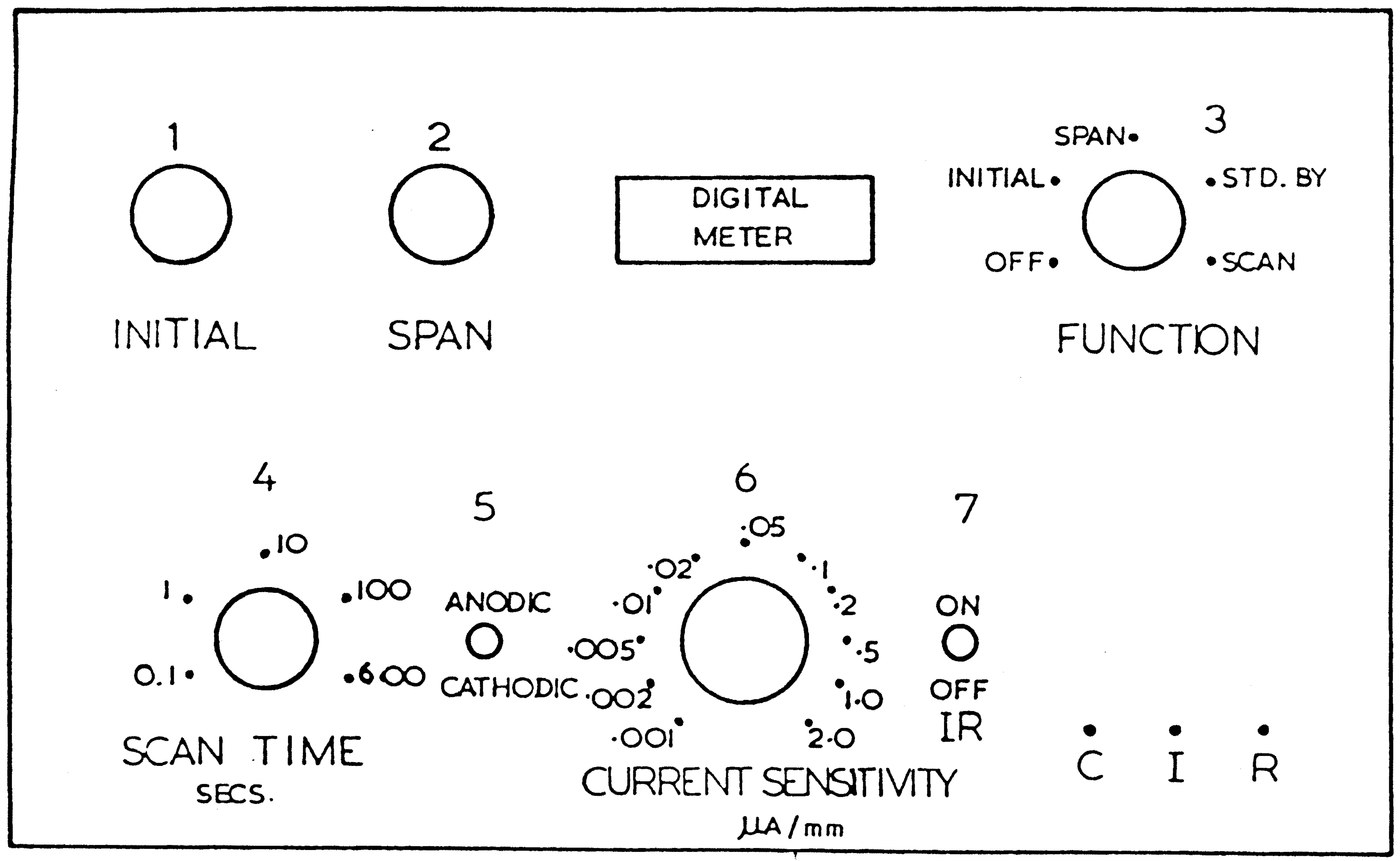
Output circuit

The block diagram of output circuit is shown in Fig.2.2. It consists of two circuits i.e., potential control amplifier circuit and current amplifier circuit.

Amplifier A_1 inverts the integrator amplifier output and making it suitable to anodic or cathodic process. The output selected through the scan switch is passed on to amplifier A_2 which adds the initial voltage in it and the output of A_2 is fed to amplifier A_3 and A_4. Amplifier A_3 inverts the voltage and feeds it to the digital voltmeter for display on the panel. Amplifier A_4 adds the IR compensation voltage to the output of A_2 so that automatic IR compensation is provided. Amplifiers A_5 and A_6 sense IR drop and feed it to amplifier A_4 in correct polarity.

The various controls used in the instrument are shown in Fig.2.3 and their operational functions are as under:

Fig. 2.3 VARIOUS CONTROLS OF LINEAR SWEEP VOLTAMETER



1. **Initial:** This control sets the starting voltage of the sweep and is adjustable from –3.0V to +3.0V. This voltage is read on the digital voltmeter when the function switch is put on the initial position.

2. **Span:** This control sets the final voltage which can be adjusted from 0 to 3V and is read on the digital panel meter when the function switch is set to read scan voltage.

3. **Function switch:** This switch has five positions 'OFF ', 'initial', 'span', 'std. by' and 'scan'. Initially it is kept at 'OFF' position.

4. **Scan time switch:** This controls the scan time, i.e. time taken for the voltage to change from initial to final state. This switch has five positions corresponding to 0.1 sec., 1.0 sec., 10.0 sec., 100 sec. and 600 sec.

5. **Polarity selector switch:** It is used for selecting the polarity of the working electrode, i. e. whether it is to be used as anode or cathode.

6. **Current sensitivity switch:** It is an eleven-position switch used to adjust the currents so that the voltammogram is within the scale of the recorder. Various current sensitivities/ mm are 0.001 μa, 0.002 μa, 0.005 μa, 0.01 μa, 0.02 μa, 0.05 μa, 0.1 μa, 0.2 μa, 0.5 μa, 1.0 μa.

7. **IR ON-OFF switch:** when two-electrode cell assembly is used, this switch is kept at OFF position. In this position reference and counter electrodes are short-circuited.

For this electrode cell assembly all the three electrodes are connected and this switch is kept at ON position. In this position IR compensation is automatic.

Working of the instrument

The sweep signal from the sweep generator is fed to auxiliary and working electrodes of the cell. As a result of this, the potential developed between working electrode and reference electrode is picked up by the voltage amplifier is made to pass through an attenuater which reduces it to 10 mV and finally it is fed to X-Y recorder.

Cells and electrodes:

Two types of cells shown in Fig.2.4 and Fig.2.5 have been used in the present work. The construction of the cells is such that the dimensions satisfy the entry criteria for Poiseuille flow and reproducible alignment of electrode elements in the cells.

A cell shown in Fig.2.4 is very simple in construction and is adaptable to rapid, routine operations. It consists of an overflow vessel of 100 ml capacity in which three electrodes are arranged in such a way that working electrode is in the middle of auxiliary and reference electrode. The

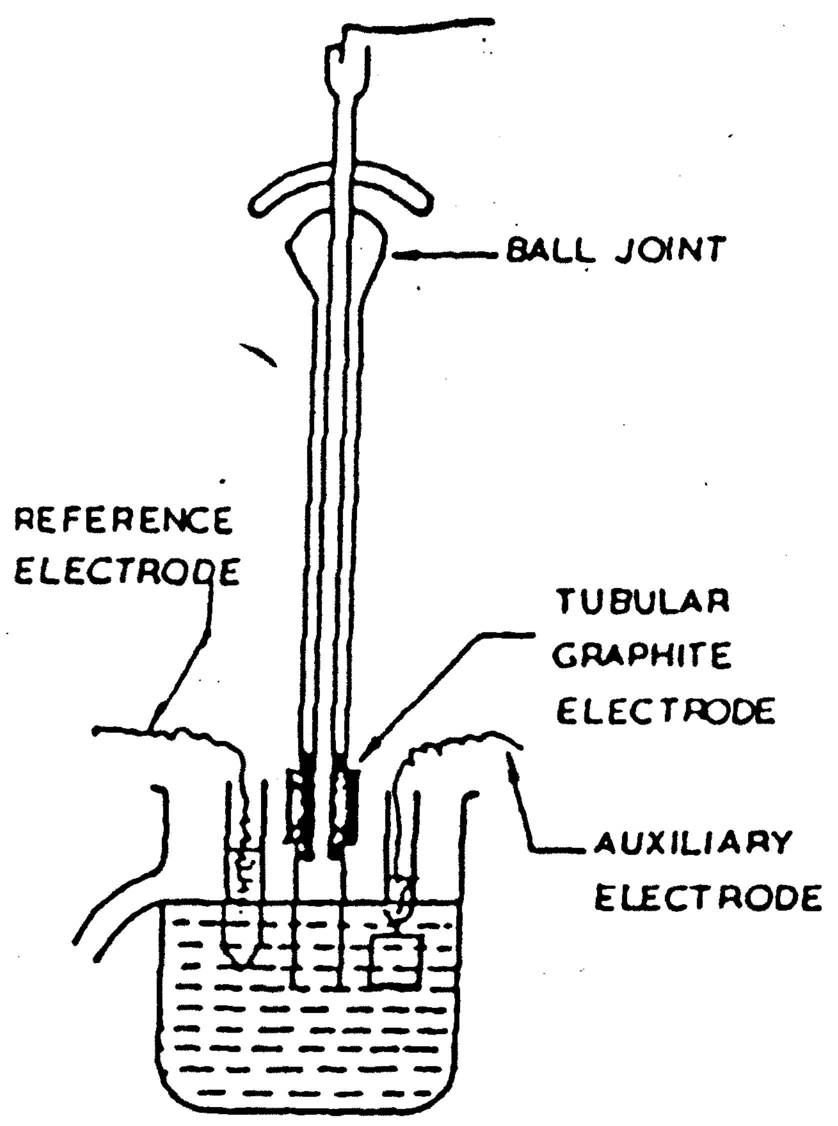


Fig. 2.4 THE TUBULAR GRAPHITE ELECTRODE ASSEMBLY

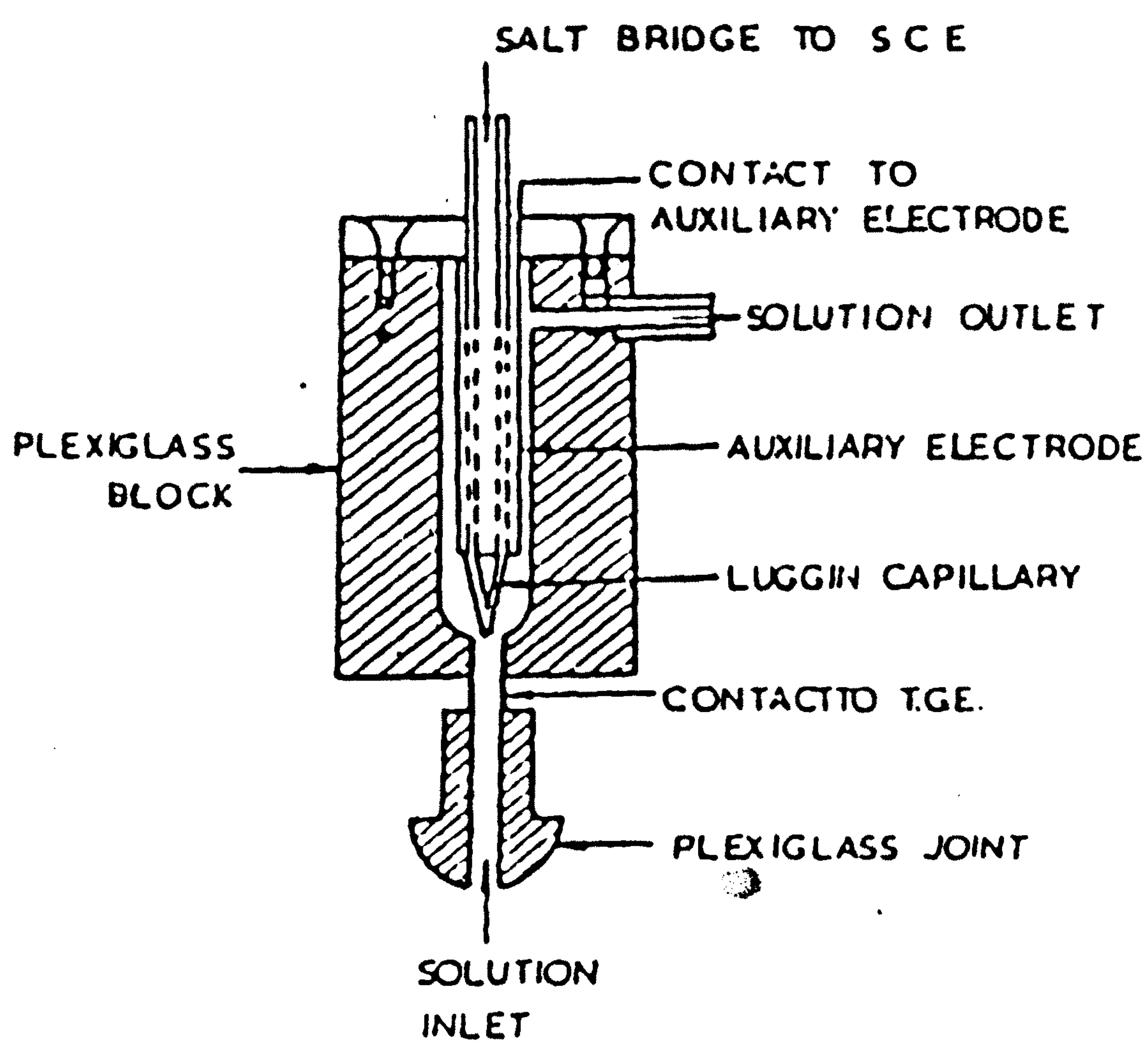


Fig. 2.5 MODIFIED TUBULAR GRAPHITE ELECTROD ASSEMBLY

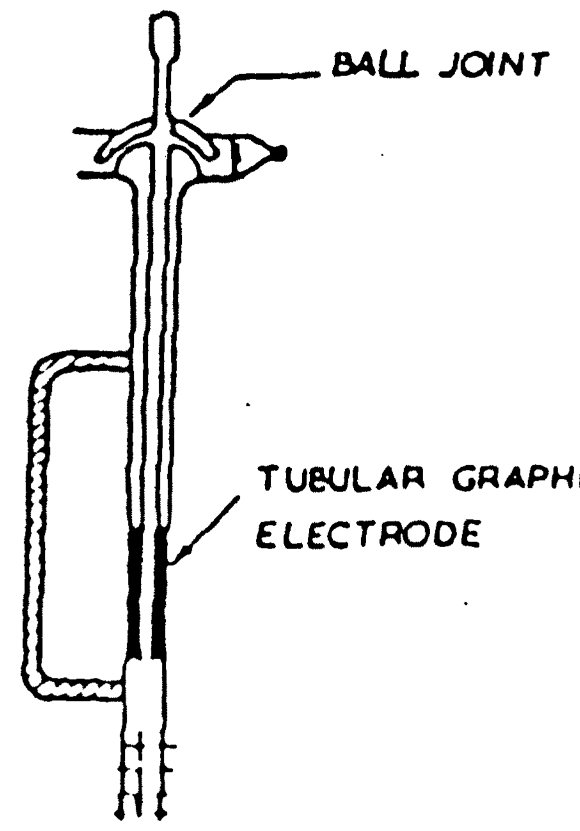


Fig. 2.6 THE TUBULAR GRAPHITE ELECTRODE ASSEMBLY

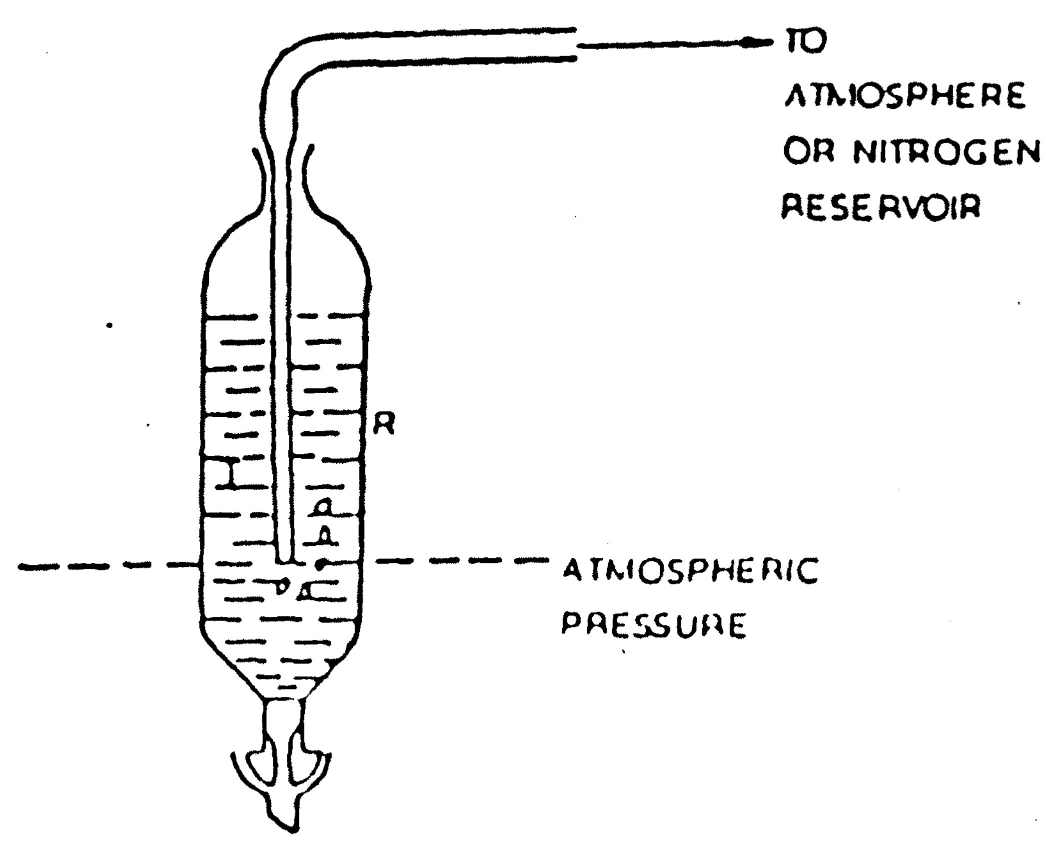


Fig. 2.7 GRAVITY FEED CONTROL

auxiliary electrode consists of a small platinum strip, which has been soldered to a platinum wire to provide electrical connection. The reference electrode is a saturated calomel electrode and is placed within few mm of the working electrode. This arrangement reduces the ohmic drop between reference electrode and the working electrode.

An alternative cell assembly, similar to the one reported by Blaedel (205) was also fabricated and used in our work. In this assembly the contact of the reference electrode to the tubular graphite electrode in the solution is maintained through luggin type capillary and the arrangement of various electrodes in the cell is shown in Fig.2.5.

Instrument performance

The precision of measurement in this instrument is comparable to that of similar instruments. The measurements of peak currents obtained with 10^{-4} M o-dianisidine at a glassy carbon electrode show the standard deviation of 2% at a scan rate of 1.0V $sec.^{-1}$. The sensitivity of the instrument is dependent upon the nature of electrode and electrode reaction being used.