A SIMPLE POLAROGRAPH

By C T Abichandani and S K K Jatkar

The polarographic method of chemical analysis invented by Heyrovsky (J Chem. Listy, 1922, **16**, 256, 304, Phil Mag, 1923, **45**, 303) depends on the interpretation of current-voltage curves obtained by the electrolysis of solutions containing electro-reducible or electro-oxidizable substances, carried out in a cell in which the anode is a pool of mercury resting at the bottom of a vessel, containing the solution to be analysed, and the cathode is dropping mercury electrode

The arrangement of the apparatus

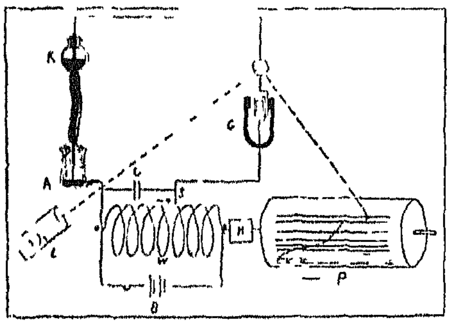

Fig 1 Recording the course of an electrolysis with the mercury dropping cathode

A = *mercury anode overlaid by*
E = the solution under test
K = the dropping mercury cathode
B = Source of current (storage battery)
W = potentiometer wire coil
S = sliding contact
M = motor
P = polarogram
G = moving coil reflecting galvanometer
L = *Illuminating lamp*
C = condenser

FIG. 1

The principle of the method is shown in Fig 1 The current voltage curves are obtained by applying a steadily increasing potential on the electrode system of the cell and measuring the current in a galvanometer connected in series. Every electrolytic reduction or oxidation takes place at a definite voltage, which is the characteristic of the electro-reducible or electro-oxidizable substance and is known as its decomposition potential As the voltage applied to the cell is increased, a very small current (residual current) flows through the galvanometer, until the decomposition potential of the ion under examination is reached, at which a current proportional to the concentration of the substance flows through the galvanometer This current does not increase indefinitely with the increasing potential after the decomposition potential is exceeded, but attains a limiting value and remains constant, being unaffected by any further rise in the applied potential.

It is possible to determine the nature and concentration of a number of substances simultaneously, as the current at each point on the current-voltage curve, is a function of the potential applied to the dropping electrode and is independent of the previous course of electrolysis. For simultaneous analysis of a number of salts, however, it is necessary that the decomposition potentials of different ions must differ from each other at least by 0.2 volts in order to get well defined waves for each substance, since the waves of two substances, having decomposition potentials very near each other, will coalesce and a single wave will be recorded. The method of chemical analysis by polarographic method, is specially suited for small concentrations of the order of 10^{-6} to 10^{-2} molar, and under proper conditions it is possible to conduct qualitative and quantitative analysis in a solution, in which as many as six ions are present. The method of electrolysis being generally applicable to all oxidation and reduction reactions, is capable of wide application in the analysis of many inorganic, organic and biological substances. An exhaustive account of such work has been given by Kolthoff and Lingane (Chem. Reviews, 1934, **24**, 1) and Muller (Chem. Reviews 1939, **24**, 95).

Polarographic methods have been mainly developed by Heyrovskey and his school at Paraque, Hohn in Germany, Somerano in Italy and Shikanta in Japan. Many models of Heyrovsky's automatic recording Polarograph and Fisher's Electrode (non recording) are on the market, but the instruments are very expensive. Kolthoff, and Lingane (loc. cit.) have described a circuit by means of which the current-voltage curves can be recorded manually, but the method involves a complicated working.

The authors have constructed a simple and cheap polarograph which automatically draws the curves with a high degree of accuracy. The instrument can be further modified and be made both hand recording and hand operative.

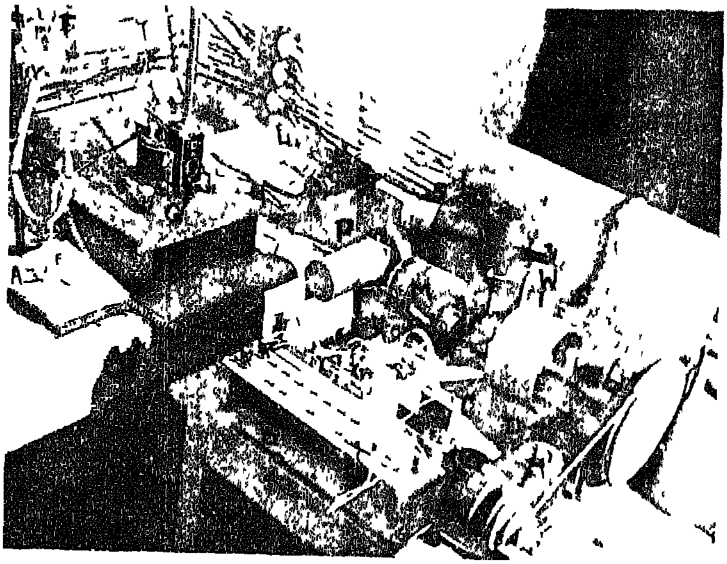

FIG. 2

Electrolytic System.—The solution E, to be analysed is contained in a vessel above a layer of mercury A, which serves as an anode. The cathode K is formed by the drops of mercury which fall in the solution at an interval of 2 to 4 seconds from a narrow capillary tube, connected to the mercury reservoir F by means of a long pressure tubing. By levelling the mercury reservoir, the time interval between the succeeding drops can be controlled as desired. The connection to the cathode is made by fusing platinum wires to the capillary (Fig. 2).

Electrical equipment.—The electrolytic system is operated by applying a uniform increasing voltage on the two electrodes by the movement of the sliding contact S along the resistance wire W (Potentiometer wire) wound round a paxolin drum and the increasing voltage is steadied by means of condenser C. The sliding contact is operated slowly by means of a system of pulleys driven by the motor 'M' with a reduction gear. The wire used for the potentiometer is nichrom No. 20, having a total resistance of 16 ohms. The voltage on the potentiometer wire W is regulated by means of an external resistance X and is measured on a voltmeter V. By applying a fixed potential of two volts on the potentiometer wire, the voltage increase per turn was 0.085 of a volt instead of 0.1 volt owing to the faulty voltmeter used in the experiments. The current flowing in the circuit during the course of the electrolysis is read on a mirror galvanometer G, provided with a shunt R, so that a sensitivity ranging from 1/1 to 1/5000 is obtained.

Recording device.—A cylinder round which the photographic paper is attached, is mounted on a spindle which is geared perpendicularly to that of the sliding contact. The gear ratio is 1 : 20, so that for 20 turns of the sliding contact, the cylinder completes one rotation. This cylinder is encased in a cassette P, having a narrow horizontal slit. The galvanometer lamp L_2 casts a fine pencil of light on the photographic paper. A special device marks the abscissa lines on the photographic paper. The sliding contact S, while rotating round the drum, presses the contact D momentarily, which flashes the abscissa lamp L_1 on to the slit of the cassette and a line is printed on the photographic paper after every turn of the potentiometer wire i.e., after every 0.1 volt (actually 0.085 of a volt in this research).

It has already been pointed out, that for a simultaneous estimation of a number of ions, it is necessary that the decomposition potential of the ions should differ by at least 0.2 of a volt. This difficulty can, however, be overcome, by incorporating an arrangement by means of which the voltage scale is enlarged three times, so that a single turn of the potentiometer wire corresponds to 0.1/3 of a volt. Two resistances of exactly the same value as that of the potentiometer wire are joined in series with the wire, and by means of suitable switches, the voltage on the wire is divided in three ranges, 0 to 0.66, 0.66 to 1.32 and 1.32 to 2.0 volts, so that the analysis between any range can be carried out with great accuracy and ions having decomposition potentials very near each other can be detected easily.

The capillaries used for the dropping electrode are usually made by drawing out the end of 20 cm long capillary tubing of 0.5 mm. internal diameter, until the tip is about 0.03 to 0.04 mm internal diameter. This method was however found very troublesome,

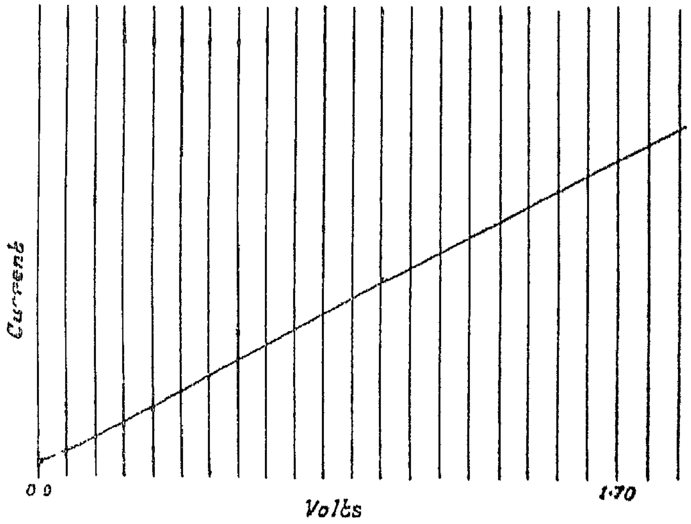

FIG. 3

as it was very difficult to draw out a capillary to specific internal diameter A commercial thermometer capillary was found very satisfactory

Fig 3 shows the polarogram of the current-voltage curve taken with a fixed resistance (4000 ohms) connected in place of the electrolytic system The curve is a straight line showing that the mechanical system of gears and the uniformity of the potentiometer wire were satisfactory The instrument has been used both for qualitative and quantitative analysis, the former depending on the decomposition potential and the latter on the magnitude of the limiting current The limiting current in certain cases, however, does not remain constant after the decomposition potential is exceeded, but shows a maxima Fig 4 shows such a maxima obtained in the case of analysis at commercial lead salt

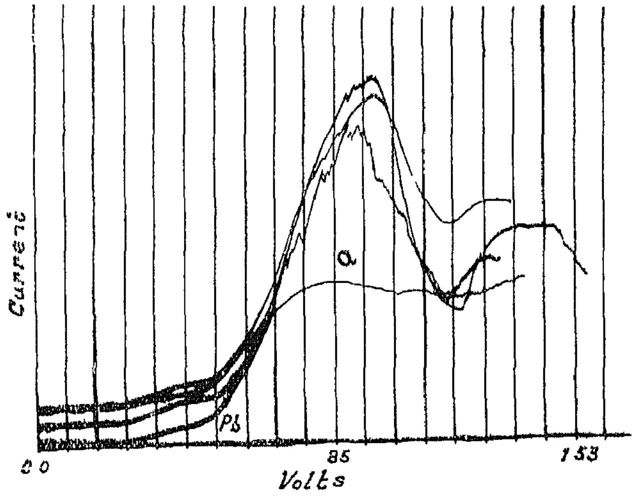

Fig 4

This maxima has been attributed by Heyrovaky to an adsorption of the electro-reducible substance on the growing mercury drops, whereby the concentration of the reducible ion is increased and the normal concentration polarisation is prevented This maxima can be suppressed and in certain cases entirely eliminated, by adding to the solution, traces of certain capillary active electrolytes and non-electrolytes and various charged colloids Kolthoff and Lingane (loc cit) have used methyl red in acid and neutral solutions with satisfactory results It has also been established that the presence of gelatine in concentrations greater than 0.013 suppresses the maxima In Fig 4 curve 'a' shows the suppression of maxima due to addition of the solution of gelatine

The limiting current, which is the basis of quantitative polarographic analysis consists of two components (1) the diffusion current, proportional to the concentration of the gradient between the surface of the mercury drop and the body of the solution and (2) the migration current (Ilkovic, Collection Czechoslov Chem Commun, 1934, **6**, 498) proportional to the electrical potential gradient around the mercury drop To avoid the second component a large excess of indifferent salt is added so that the current is practically carried by the ions of this salt and the electrical migration of the electro reducible substance is avoided, so that the limiting current is entirely the diffusion current, which is proportional to the concentration of the reducible ion The diffusion current is influenced by various factors, such as the nature of the capillary, the weight and the drop time of the mercury drop, the diffusion coefficient of the electro reducible substance and the temperature

In order to obtain the best possible results proper attention should be paid to purification of mercury, the purity of the salt used for standardization, the fabrication of capillaries used for the dropping electrode, the conductance and temperature of the solution, the proper selection of the supporting electrolyte (indifferent salt) and the maxima suppressor

The theory of the dropping electrode requires that there be present in the solution under examination, an ion other than that for which the analysis is being conducted in concentration about 1/10 N This ion (indifferent salt) should be such which should have a decomposition potential very much higher than the ion under examination, so that no increase in current occurs before the decomposition potential is reached A common indifferent salt is 1/10 N potassium chloride, which does not affect the current, until the voltage is well above two volts The selection of the indifferent salt, however, depends on its effect on the ion under analysis and the possibility of the complex ion formation

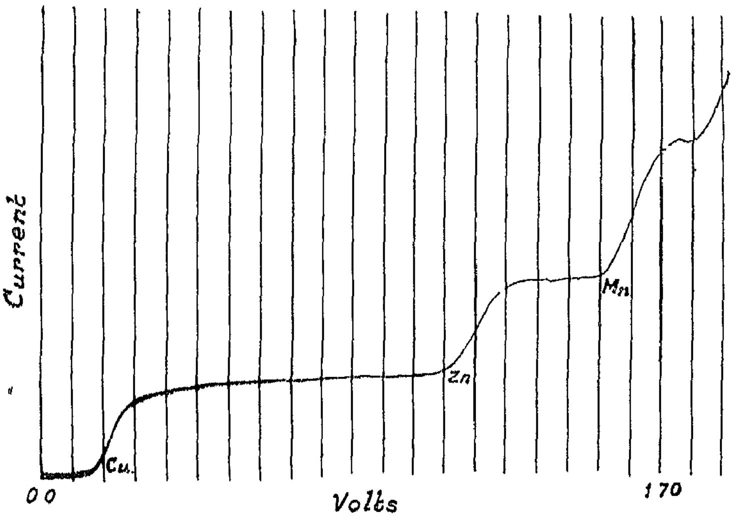

FIG 5

Fig 5 shows a quantitative analysis of a solution containing copper, zinc and manganese The analysis was carried out in a solution of indifferent salt containing 10% sodium nitrate and 0 1% gelatine For every quantitative analysis, it is necessary to calibrate the instrument and mark the magnitude of the current due to a particular quantity of the substance The current-voltage curve obtained in the figure corresponds to 3 4 mg of Cu, 1 8 mg of Zn and 3.5 mg of Mn at 1/100 sensitivity of the galvanometer

SUMMARY

A simple and inexpensive Polarograph has been constructed to record current-voltage curves which permit a detailed study of the course of electrolysis by means of a dropping mercury electrode The Polarograph has been used for qualitative and quantitative analysis of solutions

Department of Pure and Applied Chemistry,
24-9-1940 *Indian Institute of Science,*
Bangalore