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A LOW COST POLAROGRAPH*

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Details of fabrication of a low cost polarograph is described. Price of components, electronic circuitary, the procedure and performance are detailed. The total cost of the fabrication of the polarograph, if assembled from the local resources, should be around US$ 100. The polarograph, composed of a power supply and a potentiostat, is small (dimensions 2x(20x15x15 cm)), light weight (4 kilos), stable and accurate enough for routine and educational work. The polarograph was tested with Cd^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+} and MV^{2+} and found to reproduce satisfactorily the literature values of $E_{1/2}$'s.

Key words: Low-cost polarograph, Potentiostat, Power supply.

INTRODUCTION

Polarography was introduced by Heyrovsky [1] in 1920's. Soon it became a powerful analytical tool which was explored, utilised and extended by such illustrous people besides Hyrovsky himself, like Kolthoff, Lingane, Reiley, Milner, Delahey, Meites, Zuman [2] and others. Other application of polarography had been in the study of thermodynamics and kinetics of homogeneous and heterogeneous processes [3]. The instrument was developed first in laboratories and then soon commercial polarographs became available. The instrument was fabricated using simple potentiometer (or rheostats) and volt and ammeters, while more elaborate circuits were also developed for "recording" polarographs (e.g. Milner for some curcuits).

Soon it was realized that two-electrode polarographs may be inadequate particularly dealing with nonaqeous systems (of low dielectric constant). It was also found that if a stationary electrode was used instead of a dropping mercury electrode, both theory and instrumentation had to be treated differently. For a while, because of apparent limitation of classical polarography, this analytical tool started getting neglected. However, with the introduction of three electrode system, electronic circuits based on operational amplifiers (first thermoionic tubes and later semiconductors) and development of stationary electrode polarography with the (theoretical) development of other forms of polarography (e.g. linear scan, pulse A.C.), renaissance of polarography occurred. [4].

Based upon three electrode system and using operational amplifiers, from inexpensive model of Heath Kit in 1960's to expensive but versatile polarograph of Princeton Applied Research became available in the market. But the recent polarographs marketted by manufacturers like Princeton Applied Research are versatile, accurate and rapid. There are other manufacturers of polarographic instruments (e.g. IBM; BAS; Hi Tek (U.K) and others). For "home made" type polarographs, electronic circuits have been published or are available [5].

Most of these published circuits [5] are, however, not simple enough to be assembled by non-technician. It was, thus, thought necessary to fabricate a simple polarograph, which can be easily fabricated, could be used by students with confidence and, most important, be very inexpensive. In this report we present the details of such a polarograph.

Fabricated instrument. Electronic circuits of the the fabricated power supply and the potentiostat are given in Figs. 1 and 2. The block diagram of the polarograph is given in Fig. 3. The components used in the power supply and the potentiostat are given in Table 1 and 2. Their approximate prices are also included in Tables 1 and 2. The specifications of the two units are collected in Table 3.

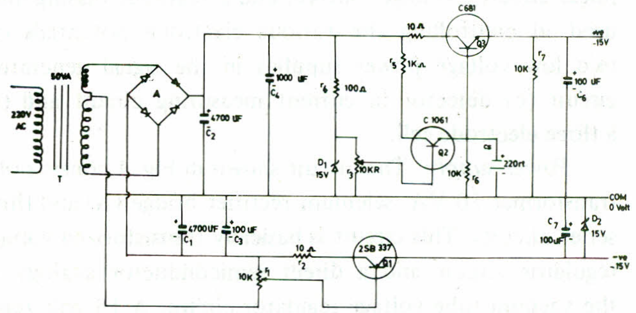

Fig. 1. C_1 . . . C_7 are capacitors, D_1, D_2 are zener diodes, R is full wage bridge rectifier, r_1· . . . r_7 are resistors, T centre tapped transformer, Q1, Q2, Q3, are transistors.

*This instrument was put on display in (a) Regional Workshop University. Industry Interaction in Chemistry (UNESCO and UGC, Islamabad) Oct. 7-5, 1985 (b) National Workshop on low cost chemical equipment, Islamabad, Dec. 15-20, 1986.

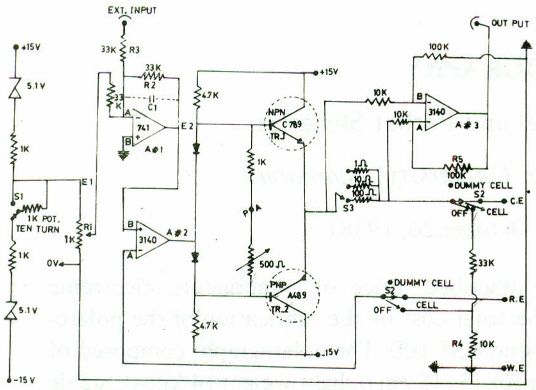

Fig. 2

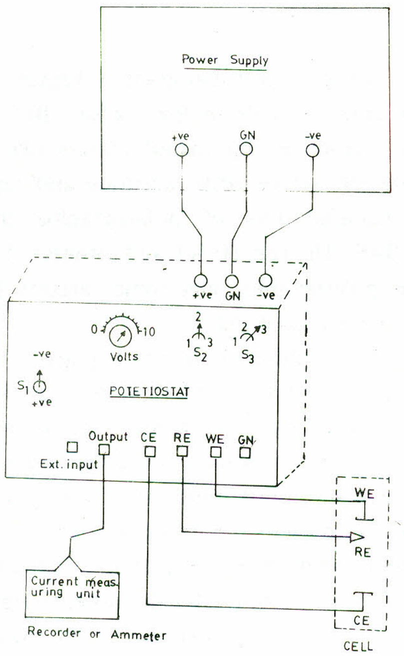

Fig. 3

The entire instrument consisted of (a) a module potentiostat based upon three operational amplifiers in the mode of linear adder, a voltage follower and a "cathode biasing unit' used in controlling the various electrode potentials (b) two low voltage power supplies in the signal generating circuit (c) detector in current measuring circuit and (d) a three electrode cell.

Power supply. The circuit shown in Fig. 1 consists of a transformer 50 VA, selenium rectifier bridge (A) and three series circuits. This circuit is basically transistorized voltage regulator circuit and a direct semiconductor analogy to the vacuum tube voltage regulator circuit. A 15 volt zener diode D1 took the place of the voltage regulator tube; Q2 is the difference amplifier and Q1, Q3 are power amplifiers, the output voltage is adjustable upto ±13 volt and upto 500 ramp can be drawn easily by the load. The capacitance C5 C6, C7 across the output prevents any high-frequency oscillation which might result from using such high gain amplifiers in the feed back circuit. The stepdown 50VA transformer serves to step down the ac line voltage (220 V) and to the desired voltage i.e. 30 volts. The rectifier bridge (A) consists of four rectifier disks and the bridge arrangement provides full wave rectification. After rectification,

Table 1. Components for power supply.

Components	Quantity	Price in £
1. Transformer 50 VA (centre taped).	1	4.05
2. Rectifier selinium (4A) of current density 0.25 amp/min.	1	1.03
3. Box (20 x 15 x 7.5 cm)	1	6.40
4. Insulating terminals 4 mm		
Yellow	1	0.852
Blue	1	
Green	1	
5. Switch (on-off) Toggle of 10 amp tolerance	1	0.75
6. Transistors (with heat sink)	1	1.05
2 SB 337 30 watt		
C 681 30 watt	1	0.75
C 1061 30 watt	1	0.75
7. Capacitors (polyester)		
4700 μF	2	2.04
1000 μF	1	0.3
220 μF	1	0.3
100 μF	3	0.6
8. Zener diode 15V	2	0.8
9. Cermet multiturn (10 K. Ohm)	2	1.5
10. Resistors (metal oxide).		
10 K. Ohm (1.0 watt)	2	0.76
10 Ohm (7.5 watt)	2	0.76
1 K. Ohm (1.5 watt)	1	0.38
100 Ohm (2.5 watt)	1	0.38
	Total.	23.90
	+ 30% of total =	7.10
	=	31.00 £
	Total = US$ 46.00	

Table 2. Components for potentiostat.

Components	Quantitty	Price in £
Box for potentiostat (20x15x7.5 cm)	1	6.40
Cerment multiturn (I KΩ) 1 watt	2	1.50
Transistor TR-1 (C 789) 30 watt	1	0.5
TR-2 (A 489) 30 watt	1	0.5
Multiturn wirewound (I KΩ)	1	4.5
Multiturn dial mechanism (10 turn) 28 mm dia	1	3.51
Resistors (wirewound 2.5 watt)		
1 Ω (Ohm)	1	0.78
10 Ω (Ohm)	1	0.66
100 Ω (Ohm)	1	0.66
Resistors (metal oxide)		
35 Ohm (1/2 watt)	4	
1 K Ohm (1/2 watt)	3	
4.7 K Ohm (1/2 watt)	2	0.532
10 K Ohm (1/2 watt)	3	
100 K Ohm (1/2 watt)	2	
Diodes (silicon singal).	2	0.62
Zener diode (5.1 V)	2	0.66
Op-amp (741)	1	1.76
Op-amp (3140)	2	0.84
BNC free plugs (50 W)	2	1.60
Switches (rated at 30 V d.c. 3A)		
Toggle S3 (1 pole, 2 way).	1	0.54
Miniature toggle S2 (4-pole D.T.)	1	2.08
Subminiature toggle S1 (4-Pole 3 way)	1	0.54
Insulating terminals 4 mm		
Yellow	2	
Blue	2	1.704
Green	3	
Plugs (banana) 4 mm		
Yellow	2	
Blue	2	
Green	2	
	Total	31.57 £
Total US$ 60.00	+ 30% of total	10.10

the pulsulating dc voltage is converted to a steady dc by its passage through the series capacitance and resistance circuit. The filter net work serves to reduce the ripple voltage to as small magnitude as desired. This power supply provides well regulated output voltage constant upto 0.5 percent of working voltage.

Table 3. General specificationof the instrument.

(i) Power supply

Characteristics	Values
Maximum output voltage	± 15 Volt.
Ripple voltage	0.005 Volt.
Maximum current limit	500 mA.
Stabilization factor	0.5 %
Weight	2.5 Kilos.
Dimensions	20 x 7.5 x 15 cm.

(ii) Potentiostat

Characteristics	Values
Voltage range	± 10 V
Current range	± 300 mA.
Reference voltage	± 5 to 10 V.
Input impedance	10 K Ohms.
Resolution	1.0 mV.
External input max.	5 Volt.
Long term drift	0.8 mV average per 4 hrs.
Current accuracy	0.04 microamperes
Weight	2 Kilos
Dimensions	20 x 15 x 7.5 cm.

The power supply circuit is assembled as a separate module having three terminals + 15,0,–15 volts which are connected with the same type three terminals present at the back of the potentiostat module.

Potentiostat. The circuit shown in Fig. 2 is basically voltage control circuit connected to the electrolytic cell. Th operational amplifier supplies current to the counter electrode (C.E) to maintain the potential of the indicator (or working) electrode (W.E) with respect to the reference electrode (R.E). In this case the current through the reference is negligible, hence polarization of the reference electrode is avoided.

Amplifier No 1 (A # 1) acts as an integrator and when E_1, R_1 and C_1 (optional, if the external input is a ramp) are constant, the output of this amplifier E_2 increases linearly with time, with a slope determined by circuit constants. The switch "S_1" towards the negative sign means E_1 is negative then E_2 is positive going, this constitutes the ramp function. An appropriate fraction of the ramp (depending on the magnitudes of R_2 and R_3) is applied to the B input of amplifier No. 2 (A # 2) which is thus kept at ramp potential above ground. The only mode or response available to amplifier No. 2 is to generate current from its output to the auxiliary electrode. This current can not go to the R.E. because the R.E. connects only to the input of an amplifier and hence can not carry current, therefore current must flow through the WE and the resistor R4.

Amplifier No. 3 is forced to put out just enough current to equal that passing through the cell, in order to ensure equality of potential of its two inputs. Because of this equality, the W.E. is essentially at ground potential at all time. The RE for a similar reason, is at ramp potential above ground. The result is that A # 2 allows precisely the required amount of current to flow to maintain the RE-WE potential difference at the desired linearly increasing voltage, with the WE negative-going. Hence the recorder will give the true polarogram. The function of resistor R5 is to lengthen the time constant to give a desired amount of damping; R4 relates to the scale of the recorder. The switch S_1 is used to start the experiment. S2 switch is used to change the mode of operation. S3 for selecting various loads. These are known as range switching; these switches are connected in such a manner that the amplifier circuit remains stable at all times.

Operational amplifier circuit is followed by a stage of power amplification, which is an emitter follower amplifier circuit designated as P.A; provides sufficient current output. This power amplifier circuit has good rapid control and in combination with operational amplifier control can be maintained even at high currents.

In manual operation, the "Ten Turn" potentiometer supplies the potential to amplifier A_1. In this mode the potentiostat acts as manual polarograph.

Operation of the instrument (potentiostat combined with power supply).

(i) Control functions. The control functions of both, the potentiostat and power supply are shown in Fig. 4.

(B) Potential current control. Ten turn wheel switch adjustable to ± 9.99 V readable to 0.01 V and accurate to ± 5 mv. This control is also used in galvanostatic mode to set the control current.

(A) Mode control. Two way switch controls current direction either cathodic or anodic.

(N) Toggle on-off. Power on-off switch.

(C) Load control swtich. It is used to isolate desired value of current and potential by selecting specific resistance variable from 1 ohm to 100 ohms.

(D) Cell operation switch. Clockwise three position rotations control the direction of constant potential and current to the external cell three electrode system.

BNC Sockets

(E) External input. BNC connector accepts externally supplied wave forms such as ramps, triangles, sinusoid from a signal generator.

(F) Output. BNC connector supplied the output to the external XY recorder or Oscilloscope.

Terminal for the external cell cable connections. GHI and S are respectively for counter electrode, reference electrode, working electrode and ground.

Power connections. K,L,M.DC-Connections. Three insulating terminals receiving external ± 15 V from DC-power supply. These are connected to the respective K,L,M terminals of the power supply by means of three respective banana leads.

(ii) *Working of the instrument.* After completing the proper checking, all the amplifiers are set to zero output by setting the functions switches to the zero position.

The potential and current monitors provide signals which can be traced on a recorder or oscilloscope to record the results of an experiment. The potential monitor on the front panel outputs a voltage which is equivalent to the potential of the working electrode, with respect to the reference electrode. The current monitor supplies a voltage which is proportional to the cell current.

The detail characteristics of the instrument are given in Table 3.

Electrochemical results. To check the performance of this polarograph, polarograms (current voltage curves) were recorded for some known system, whose $E_{1/2}$'s were known. These were the reduction of Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+} and MV^{2+} (methyl-viologen dichloride) in aqueous solution.

In recording the polarograms, first "blanks" were run for residual currents. These blank solutions were 0.1M KCl. The working electrode was a dropping mercury electrode while counter and reference electrode were a 1" (radius 1 mm) platinum wire and staurated calomel electrode respectively.

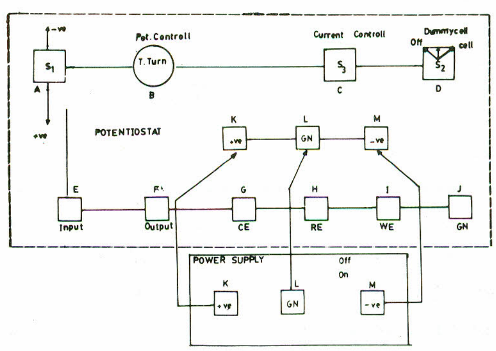

Fig. 4.

The following general procedure was adopted. The same procedure was adopted for recording a polarogram of a known sample. The schematic diagram for paloragraphic measurements is given in Fig. 4.

Procedure

Place about 10 ml 0.1M KCl solution in the cell and purge with nitrogen for 10-15 minutes (this removes dissolved oxygen).

Following figure 3, connect the power supply's three power output terminals to the power input terminals located at the back of the potentiostat by means of banana leads as blue (+ ve) with blue (+ ve), yellow (– ve) with yellow (– ve) and green (GN) with green (GN)

Connect a BNC cable from the "output" BNC socket located at the front panel of the potentiostat module to the X-axis of and X-Y recorder or to a strip chart recorded.

Connect external cell cable through banana plugs as counter electrode to blue terminal (C.E.), reference electrode to green terminal (R.E.) and test/working electrode to yellow terminal (W.E.) and ground cable to ground (GN) terminal.

To calibrate/check the potentiostat (a) Set potentiostat as follows: Potential control (ten turn) = 0.00V, up and down switch S_1 towards - ve; cathodic clockwise switch S_2 at mid (test) position; test clockwise switch S_3 and 3rd position (100 ohms) (b) Switch power on. Give a few minutes for warm up, vary the potential on ten turn control from 0.00V to higher values say 0.10V, 0.20, 0.30 . . . 1.00V, the pen of the recorder correspondingly moves along X-axis so that at 1.0 V potential it coincides with the right most vertical line of chart paper. This shows that 1.00 V is equal to ten inches (i.e. 100 mv/inch). Similarly the Potentiostat can be calibrated along Y-axis.

Record the polarogram manually by replacing the recorder by a microammeter (or a 1 K ohm resistance in series, across which a millivoltmeter is connected). Apply the potential by varying the ten turn potential control K. Record the corresponding current, at the start and the end of the drop life and average the current. This (average) current can be plotted against the applied potential (Vs. saturated calomel electrode, SCE). Same procedure is followed for a sample solution containing 1 x 10^{-3}M electroactive substance.

Current thus recorded for a solution of Cd^{2+} are given in Table 4 and Fig. 5. The results of the polarograms recorded on Cd^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+} and MV^{2+} are recorded in Table 5. Polarogram of MV^{2+} is given in Fig. 6. The polarogram clearly shows the two waves characteristic of the reduction [6] of MV^{2+}.

Table 4. For $CdCl_2$ system (air free system) (1.5 x 10^{-3}M).

$E_{e.d}$ (Volts) Vs. SCE	i_c Micro ampere (uA)
0	0
–0.20	0
–0.30	0
–0.40	0.3
–0.55	0.5
–0.56	1.2
–0.57	2.8
–0.58	4.2
–0.59	5.3
–0.60	6.3
–0.61	7.0
–0.64	8.3
–0.65	9.1
–0.75	9.6
–0.82	9.9
–0.9	10.1
–0.97	10.2
–1.15	10.3
–1.35	10.3

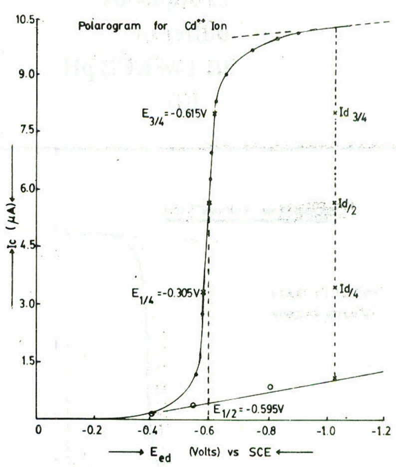

Fig. 5.

From Table 5, it is clear that the $E_{1/2}$'s calculated from the polarogram recorded using this instrument satisfactorily reproduces the literature values [7].

Performance/cost. This instrument has variety of use in various experimental configuration including controlled potential electrolysis, stationary electrode voltammetry and as a simple polarograph. This instrument has excellent sensitivity (current sensitivity 0.04 microamp.) noise rejection, stability (drift 0.8 mv) and flexibility. Its weight and dimension are quite small and it is very inexpensive.

Table 5. 5-3 comparison of results.

System	Solvent	Concentration of solution	Supporting electrolyte	Half waves potential values. $E_{1/2}$ (Volts) Observed	Reported
1. Cadmium chloride (Cd^{++})	Aqueous	1.5×10^{-3} M	Potassium chloride (kCl 0.1M)	−0.595V	−0.599V
2. Lead chloride (Pb^{++})	–do–	1×10^{-3} M	–do–	−0.400V	−0.396V
3. Zinc chloride (Zn^{++})	–do–	1.5×10^{-3} M	–do–	−1.0 V	−0.955V
4. Paraquat (methyl viologen)	a. Aqueous buffer of pH 8.6	–do–	–do–	a. I. −0.63 V II. −0.90 V	−0.65 V −0.96 V
	b. Aqueous buffer of pH 6.3	–do–	–do–	b. I. −0.55 V II. −0.82 V	−0.63 V −0.88 V
	c. Aqueous buffer of (0.1 M KCl) pH 1.0	–do–	–do–	c. I. −0.35 V II. −0.56 V	−0.32 V −0.50 V

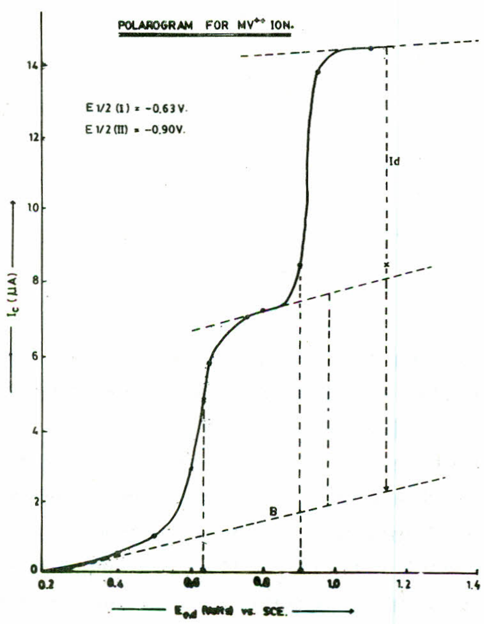

Fig. 6.

The designing/fabrication is simple and can easily be accompolished by anyone capable of reading circuit diagram and using a soldering iron. The minimal time required for construction makes this an inexpensive project. Total cost of the instrument with current range 300 mA and voltage range ± 15V is about US$ 100/-. This unit is portable (small dimension each about 20 x 15 x 7.5 cm) light weight (4 kilos) and readily useable as at-site field instruments. The most expensive part involved is a (XY) recorder (not included in the fabricated polarograph). A low cost (small) strip chart recorder, such as used in a personal computer, could be attached to the polarograph to make it a complete, inexpensive, small light weight polarograph.

CONCLUSION

This fabricated polarograph is inexpensive, easy to assemble and give reasonably reliable results. Its components are easily available in the local market except a couple of hardwares (like the box and ten turn potentiometer). It is easy to handle. It is thus suitable for routine work and for teaching purposes.

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