INEXPENSIVE CHEMICAL INSTRUMENTATION: STUDENT VOLTAMMETERS

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ABSTRACT. — Instructions for construction and operation of inexpensive polarograhic measuring devices are presented. These simple and sturdy devices yield polarographic data in good agreement with those obtained from automatic recording commercial instruments. Three models are presented, varying with respect to cost and ultimate capability.

The objectives described in the first article of this series (Van Atta, Linnenbom, and Coleman, 1967) have been applied to the design, construction, and testing of various types of polarographic apparatus. For purposes of identification in the author's laboratory, all the instruments presented in these articles have been given the general name "Valco", with attendant model designations where necessary. Three polarographic devices are described in this article: (1) a potentiometer polarographic accessory, (2) a dual-range voltammeter (Valco V), and (3) a multi-range voltammeter (Valco VI). All employ the Valco potentiometer described in the earlier article in some phase of their operation.

MATERIALS

Lists of electrical and other components required for construction of the three devices are given in TABLES 1, 2, and 3. The prices shown are those for single-item purchase at price levels current at the time of writing; quantity purchases of some items may result in substantial reduction of total costs. Although all components listed were obtained from Allied Electronics Corporation, 100 North Western Avenue, Chicago, Illinois, equivalent components are available from a variety of other commercial electrical and electronic supply houses. Interested individuals should contact the various surplus agencies in their vicinity—many high-quality electrical components, such as helipots, meters, etc., may be obtained through such agencies at a small fraction of their commercial cost.

Commercial equipment employed in testing the polarographic devices included a modified Sargent polarographic H-cell, Cat. No. S-29401, mounted on a polarographic accessory stand of the authors' own design, a Sargent Model XV Pen-Recording Polarograph, and a Leeds and Northrup Electrochemograph, Type E. A Heathkit IN-11 decade resistance box was used in conjunction with the Valco potentiometer for determining the internal resistance of microammeters.

Construction tools required include screwdriver, appropriate pliers, a small adjustable wrench, 100-watt soldering iron and rosin-core solder, appropriate drills, and hole cutter or nibbling tool; a ½-inch chassis punch is a convenient tool if several instruments are to be constructed.

CONSTRUCTION DETAILS

Potentiometer Polarographic Accessory. — A very simple and quite inexpensive device can be employed to convert an ordinary voltage measuring potentiometer into a polarographic current measuring instrument. The schematic circuit, adapted from Lingane (1949, p. 47), is shown in FIGURE 1, a list of component parts and costs in TABLE 1, and an interior view of the device in FIGURE 2. The circuit employs the potentiometer to measure directly the output furnished to the polarographic cell by the voltage divider, as well as to determine the polarographic current by measuring the

TABLE 1.—Potentiometer Polarographic Accessory Components.

Quantity Required	Description	Allied Electronics Stock Number	Price
1	CONTROL, Mallory Type U-1 Midgetrol, 100 ohms, linear taper	46 D 3714	$1.02
1	SWITCH, slide, SPST, Continental-Wirt Type G124	56 D 5034	0.32
1	SWITCH, slide, DPDT, Continental-Wirt Type G126	56 D 4424	0.40
1	RESISTOR, precision, Dale RS-2A, 2-watt, 10K ohms ±1%	45 D 6834C	0.86
2	BATTERIES, mercury, 1.35-volt, Mallory Type RM12R	18 D 5929	2.10
1	HOLDER, battery, Keystone Type 140	18 D 5902	0.38
1	KNOB, Harry Davies Type 1600	47 D 4127	0.15
1	MINIBOX, Bud Type CU-3003A, 4 x 2¼ x 2¼, aluminum	42 D 7637	0.80
4	JACKS, banana (2 red, 2 black), H. H. Smith Type 1509	47 D 3941 47 D 3942	0.48
	MISCELLANEOUS: hook-up wire, etc.		0.05
	TOTAL		$6.56

voltage drop across a 10,000-ohm precision resistor, accomplished by connecting the potentiometer to the center terminals of a DPDT switch, one side of which connects directly with the voltage divider and the other across the measuring resistor, as shown.

In operation, one first adjusts the potential applied to the polarographic cell by means of the 100-ohm control of the voltage divider. Next, the exact output, in volts, of the divider is determined with the DPDT switch in position "E". Finally the polarographic current is measured with the switch in position "I" (the actual current, in *microamperes*, is equal to the potential measured, in volts, multiplied by 10^6 divided by 10,000, or $i = 100 \cdot E$ (Potentiometer). The observed *current* is then plotted as a function of the applied potential in the conventional manner for polarographic measurements. The *potential* actually applied to the polarographic cell is equal to the measured value diminished by the

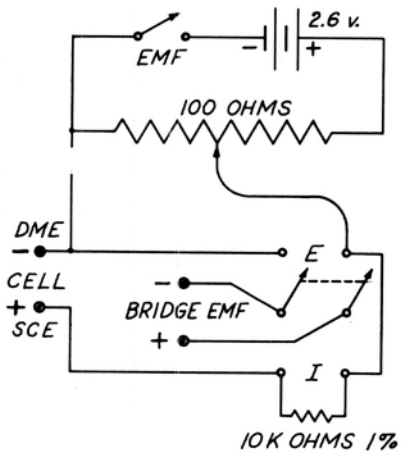


FIGURE 1.—Schematic wiring diagram for potentiometer polarographic accessory.

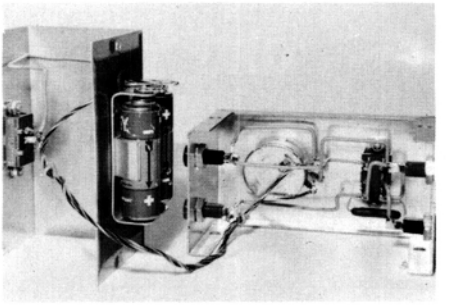


FIGURE 2. — Interior view of completed potentiometer polarographic accessory.

voltage drop throughout the circuit, or

$$E_{(Corrected)} = E_{(Applied)} - [E_{(Potentiometer)} + iR_{(Solution)}]$$

The iR drop correction term, enclosed in brackets, should be taken into consideration whenever accurate half-wave potential measurement is necessary.

This simple device has the virtues of very low cost and reasonable accuracy (current measurements are ±0.1 microampere), but the distinct disadvantage of being tedious in operation due to the two measurements required at each applied potential setting. The devices subsequently presented, although more expensive, are much more convenient and versatile in operation.

Dual-Range Voltammeter. — FIGURES 3 and 4 and TABLE 2 show schematic circuit, completed device, and component parts of the Valco V dual-range voltammeter, respectively. A 10-turn helipot with 1000-unit dial is employed in this instrument to permit convenient changing of the applied potential, while requiring the overall bridge voltage to be measured only once, at the beginning of

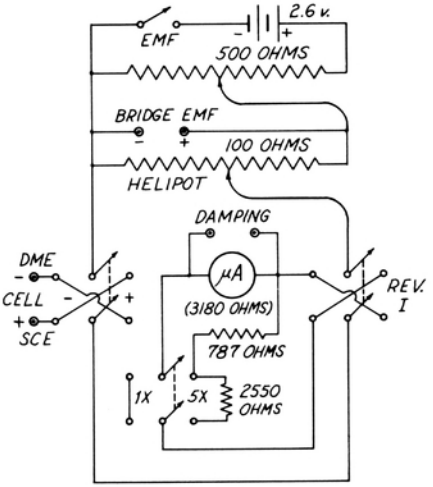


FIGURE 3. — Schematic wiring diagram for dual-range voltammeter. Multiplier shunt (787 ohm) and iR correction (2550 ohm) resistances calculated for microammeter with internal resistance 3180 ohms.

TABLE 2.—Dual-Range Voltammeter Components.

Quantity Required	Description	Allied Electronics Stock Number	Price
1	MICROPOT, 100-ohm, Amphenol-Borg Model 2151B, 10-turn, ±0.25% linearity	46 D 3510	$10.00
1	MICRODIAL, 10-turn, Amphenol-Borg Series 1320, for micropot	46 D 3696	5.82
1	MICROAMMETER, 0-25 microamperes DC, Simpson Model 29, 4½-inch	52 D 7444	25.00
1	CONTROL, Mallory Type U-2 Midgetrol, 500-ohms, linear taper	46 D 3709	1.02
3	SWITCHES, toggle, DPDT, Cutler-Hammer Type 7592 K 6	56 D 4690	2.43
1	SWITCH, toggle, SPST, Cutler-Hammer Type 7580 K 6.	56 D 4641	0.50
2	BATTERIES, mercury, 1.35-volt Mallory Type RM12R.	18 D 5929	2.10
1	HOLDER, battery, Keystone Type 140	18 D 5902	0.38
6	JACKS, banana (3 red, 3 black), H. H. Smith Type 1509.	47 D 3941 47 D 3942	0.72
1	KNOB, Harry Davies Type 1600	47 D 4127	0.15
2	RESISTORS, precision, IRC 1%, ½-watt, (specific values determined by internal resistance of microammeter)	45 D 5018C	1.08
1	CABINET, sloping-panel, 7-inch, aluminum, Universal Type AC-1613	42 D 8649	2.30
	MISCELLANEOUS: hook-up wire, etc.		0.20
	TOTAL		$51.70

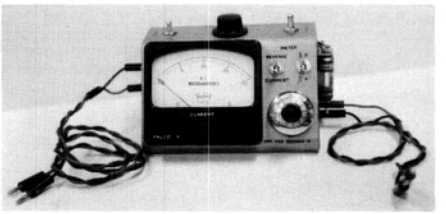


FIGURE 4. — Dual-range voltammeter.

operations, with a potentiometer. Current measurements are read directly on the microammeter with the appropriate multiplier factor. A reversing switch permits both cathodic and anodic currents to be measured, while a cell polarity switch permits the polarity at the cell electrodes to be reversed, as desired. Provision for capacitance damping (Meites, 1965, p. 10) is made by means of the terminals in parallel across the microammeter.

Multi-Range Voltammeter. — A somewhat more sophisticated voltammeter is the multi-range, direct-voltage-indicating Valco VI, shown in FIGURE 5. This instrument is essentially identical to the model V, except for the addition of an integral Bridge EMF voltmeter across the Bridge EMF output and the employment of a 4-range multiplier function switch and meter circuit (FIGURE 6). The model VI is far more convenient and versatile than either of the two previously described devices, particularly

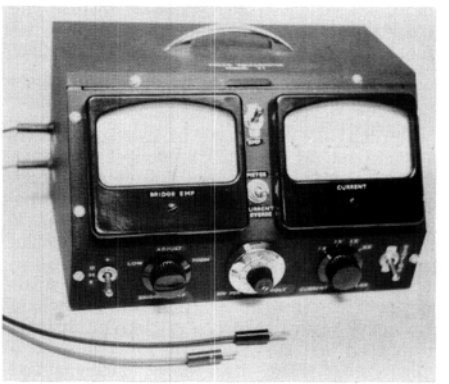


FIGURE 5. — Multi-range voltammeter.

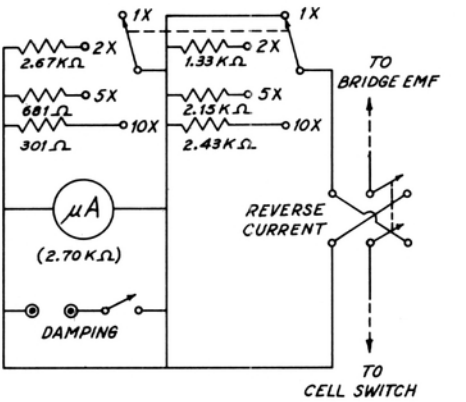


FIGURE 6. — Multiplier switch and meter circuit for multi-range voltammeter. Multiplier shunt (left side of multiplier switch) and iR correction resistances calculated for microammeter with internal resistance 2700 ohms.

with respect to its application to amperometric titrations, where Bridge EMF settings (as directly indicated by the integral voltmeter) are sufficiently accurate so that external potentiometric evaluation of Bridge EMF is not necessary. The additional current ranges also permit operation with substantially larger concentrations of electroactive species than is possible with the model V; even more ranges may be added at the discretion of the builder.

Measurement of Microammeter Resistance. — If the dual- or multi-range feature of the previously discussed circuits shown in FIGURES 3 and 6 is to be employed, it is necessary to know the internal resistance of the microammeter in order that the total resistance of the current-measuring circuit may be kept constant (for iR drop calculations) whenever the multiplier setting is changed. Inasmuch as the internal resistances of the quality of microammeters used in these devices vary from meter to meter, it is absolutely necessary that such resistances be measured with some accuracy. This cannot be done with an ordinary ohmmeter or resistance bridge because of possible damage to the meter coil or pointer. However, a simple circuit which permits safe measurement of microammeter internal resistances

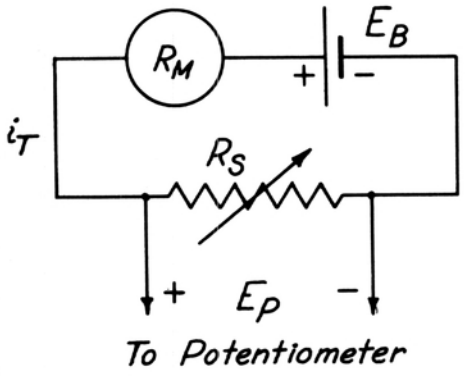
TABLE 3.—Multi-Range Voltammeter Components.

Quantity Required	Description	Allied Electronics Stock Number	Price
1	MICROPOT, 100-ohm, Amphenol-Borg Model 2151B, 10-turn, ±0.25% linearity	46 D 3510	$10.00
1	MICRODIAL, 10-turn, Amphenol-Borg Series 1320, for micropot	46 D 3696	5.82
1	MICROAMMETER, 0-25 microamperes DC, Simpson Model 29, 4½-inch	52 D 7444	25.00
1	VOLTMETER, 0-3 volts DC, Simpson Model 29, 4½-inch	52 D 7415	16.35
1	CONTROL, Mallory Type U-2 Midgetrol, 500-ohms, linear taper	46 D 3709	1.02
2	SWITCHES, toggle, DPDT, Cutler-Hammer Type 7592 K 6	56 D 4690	1.62
2	SWITCHES, toggle, SPST, Cutler-Hammer Type 7580 K 6	56 D 4641	1.00
1	SWITCH, rotary, non-shorting, 3-pole, 4-position, Mallory Type 3234 J, with knob	56 D 4355	1.05
2	BATTERIES, mercury, 1.35-volt, Mallory Type RM12R	18 D 5929	2.10
1	HOLDER, battery, Keystone Type 140	18 D 5902	0.38
6	JACKS, banana (3 red, 3 black), H. H. Smith Type 1509	47 D 3941 47 D 3942	0.72
1	KNOB, Harry Davies Type 2300	47 D 4172	0.10
6	RESISTORS, precision, IRC 1%, ½-watt, (specific values determined by internal resistance of microammeter)	45 D 5018C	3.24
1	CABINET, sloping-panel, Bud Type C-1586, 6½ x 11-1/16 x 7-5/16	42 D 7468C	4.55
	MISCELLANEOUS: hook-up wire, etc.	.....	0.25
	TOTAL	.....	$73.20

is shown in Figure 7. This circuit is a simplified version of that described by Malmstadt, Enke and Toren (1962, p. 12). The experimental procedure is: (1) measure the exact output voltage, E_B, of the battery with a potentiometer; (2) connect the meter into the circuit as shown, using a decade precision resistance box as R_s; (3) record the value of R_s required to produce a microammeter pointer deflection within 1% of full scale; (4) measure the potential (E_p) across R_s with the potentiometer. The calculations required are also shown in FIGURE 7. It should be re-emphasized that in order for constant iR drop correction factors to be employed in measuring half-wave potentials, the sum of the resistance of the network involving the meter, multiplier shunt resistance and series iR drop correction resistor must be maintained constant, regardless of the position of the multiplier function switch. Subsequent to the meter resistance evaluation previously described, conventional network resistance calculations are required to determine the proper values for the series and parallel precision resistors in the meter circuit.

PERFORMANCE AND APPLICATIONS

Typical performance of the Valco V is illustrated by FIGURE 8, compared with that of a Sargent Model XV Pen-Recording Polarograph. The agreement between the plotted points for Valco V measurements and the maxima of the automatically recorded curve demonstrates the capability of the device with respect to current measurement, while the accuracy of voltage measurements is indicated by the location of the triangular corrected half-wave potential points. Equivalent performance was obtained for the multi-range model VI;



$$i_T = E_P/R_S$$

$$\Delta E_M = E_B - E_P$$

$$R_M = i_T/\Delta E_M$$

FIGURE 7. — Measurement of internal resistance of microammeter.

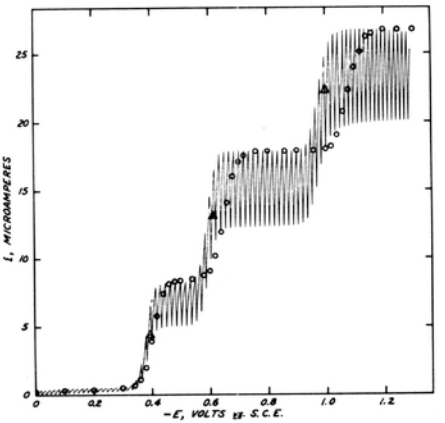


FIGURE 8. — Performance of dual-range voltammeter compared with that of Sargent Model XV Pen-Recording Polarograph. Test Solution: 1 m*M* Pb^{++}, Cd^{++}, and Zn^{++} in 0.25 *M*, KCl 0.002% Triton X-100 (maximum suppressor), after 5 minutes purging with nitrogen. Circles represent points measured with dual-range voltammeter; triangles are half-wave potentials from voltammeter data, corrected for iR drop of current-measuring circuit. Pen-recorded data secured with galvanometer-equivalent damping.

comparison with results obtained for the same test solution with a Leeds and Northrup Electrochemograph, Type E. is equivalent to that shown. The potentiometer polarographic accessory performs equally well, except for the somewhat larger iR drop due to the size of the meauring resistor and the less convenient operation previously mentioned.

The devices here described are suitable for all types of conventional DC polarographic measurements, with the model VI being particularly well-suited for use in amperometric titrations. The circuitry, in each case, is relatively simple and easily traced for instructional applications; the complementary use of a potentiometer is necessary with all three devices if potential measurements to within 1 or 2 millivolts are required. Several prototype models of these instruments have been used successfully by students in the authors' laboratory for several months.

ACKNOWLEDGMENTS

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