A versatile and inexpensive controlled potential polarographic analyzer

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A Versatile and Inexpensive Controlled Potential Polarographic Analyzer

The immediate object of a polarographic measurement is the precise determination of the current-voltage curve for the "test" or "analytical" electrode. Various features of this curve can, in turn, be related to the concentration of the electroactive species, the number of electrons in the electrode reaction, the kinetics of the electrode reaction, the stability constant of a metal ion complex, or other information. The theories and equations relating the current-voltage curve (polarogram) to the desired information are almost always based on the assumption that the polarogram is a true measure of the test electrode current versus the test electrode potential. A true measure of electrode current is obtained by simply putting the current measuring device in series with the electrolytic cell. However, the potential across the cell includes the potential of the second (counter) electrode and the *IR* drop through the electrolyte solution as well as the test electrode potential. The traditional polarographic instrument produces a plot of cell current versus cell potential and relies upon proper cell design to reduce the *IR* drop and the variation in counter electrode potential to tolerable values (*1*). Concentrated electrolyte solutions are required and a large "nonpolarizable" reference electrode with a low resistance salt bridge must be used for the counter electrode.

Recently, a "controlled potential" polarographic instrument has been described in the literature (*2*). With controlled potential polarography, a reference electrode is used only to measure the test electrode potential; the necessary current is introduced into the cell through the counter electrode. (This is the so-called "three-electrode" system.) The measurement apparatus is designed to apply automatically to the cell the exact current required to maintain the test electrode potential at the desired value. The advantages of the controlled potential instrument are: polarograms can be run in solutions with low electrolyte concentrations, e.g., nonaqueous solvents; a nonpolarizable counter electrode is not required (a piece of platinum will do very nicely); a convenient dip-type calomel reference electrode may be used in place of the large calomel and frit which require continuous maintenance and cannot be stored in a "ready" condition. The advantage of controlled potential polarography in cases of high cell resistance is shown in Figure 1. A Beckman fiber-type calomel reference electrode was used as the counter electrode in a two-electrode cell to obtain curve (a). The slope of the current-voltage curve shows the resistance of the electrode to be about 60 kilohms. The same reference electrode was used for curve (b) but with a platinum counter electrode in a three-electrode cell. This curve has the correct half-wave potential for Cd^{++} and has the theoretical slope for a two-electron reduction. Although the ability to do nonaqueous polarography is the most widely claimed advantage of the controlled potential instrument, as yet very few articles using polarography in solutions of high specific resistance have appeared. After considerable use of the instrument described in this article, we feel that the much simpler cell and electrode system required and the greater inherent precision in electrode potential measurement warrant strong consideration of a controlled potential instrument for aqueous polarography—especially for the instructional laboratory.

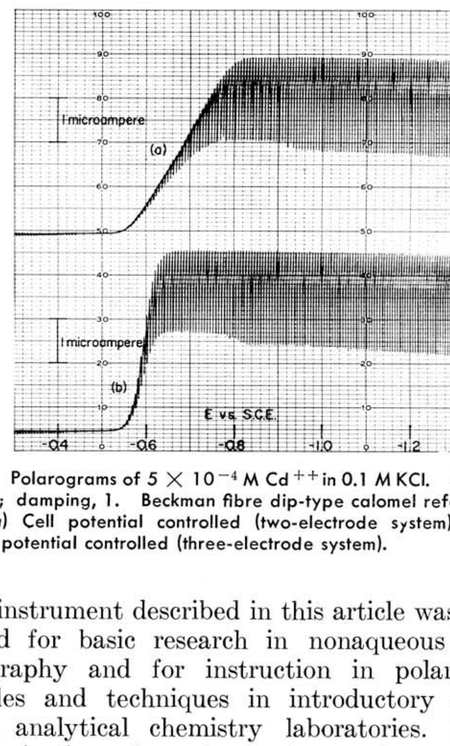


Figure 1. Polarograms of 5×10^{-4} M Cd^{++} in 0.1 M KCl. Sweep rate, 0.1 v/min; damping, 1. Beckman fibre dip-type calomel reference electrode. (*a*) Cell potential controlled (two-electrode system). (*b*) Test-electrode potential controlled (three-electrode system).

The instrument described in this article was built to be used for basic research in nonaqueous and ac polarography and for instruction in polarographic principles and techniques in introductory and advanced analytical chemistry laboratories. Modular construction is used to take maximum advantage of the economy and versatility of commercially available units. There are essentially three parts to the complete instrument: an operational amplifier system containing power supplies, control amplifiers, and connecting plugs (Heath model EUW–19A); a plug-on unit, described here in detail, which contains the connections, resistors, and switches required to use the control amplifiers for polarographic measurement; and a strip chart recorder for recording the electrode current as a function of time.

The potential of the polarized electrode is controlled within a few millivolts and is constant over a wide range of electrode current, solution resistance, or resistance in the reference electrode salt bridge. The constant or initial potential is continuously variable from −3 to +3 v. An electronic sweep generator varies the electrode potential linearly over the entire potential range in either direction at rates from 0.05 to 2.00 v/min. The electrode potential may also be controlled to follow external signal sources (ac signals, triangular waves, pulses, etc.) for special types of polarography and cyclic voltammetry (*3*). The potential between the test and reference electrodes may be read from a panel meter on the unit or by connecting a meter or recorder to a pair of jacks provided.

The sensitivity of the electrode current measurement is variable from 0.5 to 1000 μa for full scale deflection of the meter or recorder pen. Two outputs are provided for the current measurement: 100 mv full scale for a potentiometric recorder and 10 v full scale to provide a large output signal for a meter-type recorder or for special applications such as ac polarography. Six degrees of damping may be selected for the 100 mv output signal. A suppression current of 0–100 μa is available for better accuracy when measuring wave heights for the second or third wave. For easier measurement with the dropping mercury electrode at high sensitivities a linear charging current compensator is included (*4*).

Modular Construction

A block diagram of the controlled potential polarograph is shown in Figure 2. The primary function of each block is described below. The potentiostat is perhaps the key element in this instrument. The potential between the reference and test electrodes is measured by the follower amplifier, F, and compared with the control voltage sources (initial potential, sweep generator and auxiliary) at the input to amplifier 3.

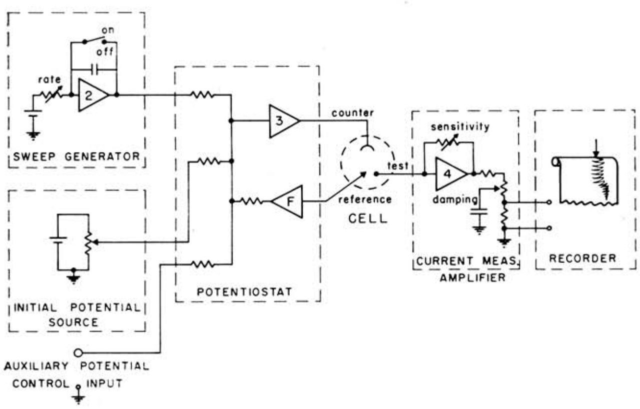


Figure 2. Block diagram of controlled potential polarographic analyzer.

The output signal from amplifier 3, which is connected to the counter electrode, is always such that the potential between reference and test electrodes is equal and opposite to the sum of the control voltages. The initial potential source is connected to the potentiostat to establish a constant electrode potential for amperometric titrations, manual polarography, or the initial potential prior to the application of the sweep voltage. The sweep generator produces a linearly increasing voltage, either positive or negative going, which is applied to the potentiostat to obtain the desired linear scan of electrode potential. The electrode current is fed directly to the current measuring amplifier. This section of the instrument converts the microampere current signals into voltage signals of suitable amplitude for measuring and recording. The output of the current measuring amplifier is connected to the panel meter for amperometric titrations or manual polarography, or to a 100 mv recorder for recorded polarograms.

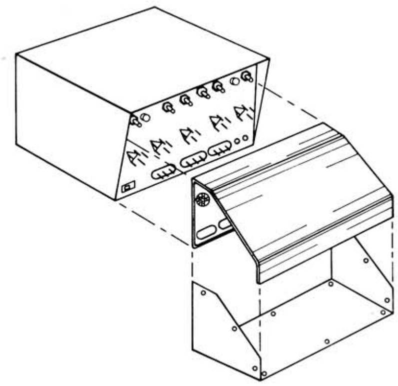


Figure 3. Heath EUW-19A operational amplifier system; controlled potential polarography module.

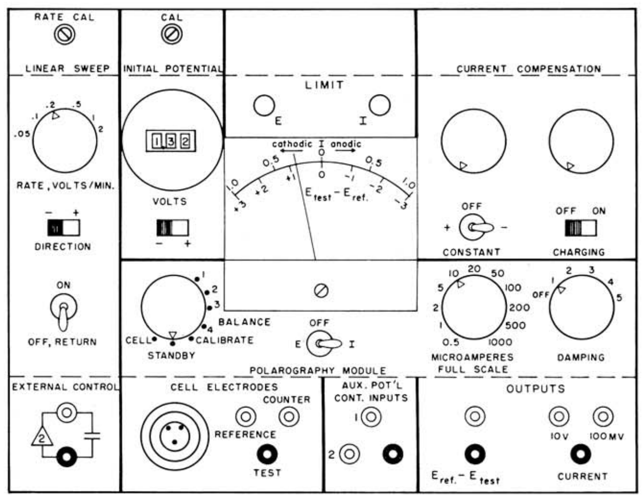


Figure 4. Front panel layout of polarography module.

Each triangle in the block diagram, Figure 2, represents an operational amplifier and its associated power and bias supplies. Descriptions of operational amplifiers and many applications of them have appeared in the recent literature (*5–9*). In the construction of this instrument, the Heath EUW–19A Operational Amplifier System was used. This unit contains four operational amplifiers, a booster amplifier, and all necessary power supplies and bias adjustments. The resistors, capacitors, switches, and connections necessary to use these amplifiers in the polarographic circuit described here were wired in a blank chassis (Heath model EUW–19A–1) which is made to plug directly onto the operational amplifier system. The operational amplifier and polarography modules, and their method of connection are shown in Figure 3. The front panel of the polarography module is shown in Figure 4. Related controls are grouped together and are clearly labeled.

Modular design of instruments offers great advantages in economy and versatility in the educational laboratory and demonstrates, by its very nature, the basic instrument components. Instead of using a specialized instrument for each different experiment, modular design allows a few versatile units to be used for many experiments. For example, the recording unit becomes a recording pH electrometer (*10*) in one set of experiments, part of a polarographic analyzer in another, part of a chromatograph in a third, and so on. The operational amplifier system can be used with various plug-on modules for polarography, controlled current and controlled potential coulometry and chronopotentiometry. Through the use of separate connecting modules for each instrument application, the instrument has the customary operating characteristics and conveniences appropriate for instruments of its type. Several other modules for teaching and research are presently being developed in this laboratory and will be reported on in future articles.

The Sweep Generator

The detailed circuit, design considerations, and operating characteristics of the polarography module will be presented in sections beginning with the sweep generator. The sweep generator circuit is shown in Figure 5; it is essentially a constant current source and an integrator. Amplifier 2 is used to integrate the constant current to produce a linearly changing potential. The charge applied to the input of amplifier 2 is accumulated on the 10-mf capacitor. The sweep output voltage is equal to the potential across the capacitor (*5*). The constant current is generated by connecting a large resistance in series with a constant potential obtained from a zener diode source.

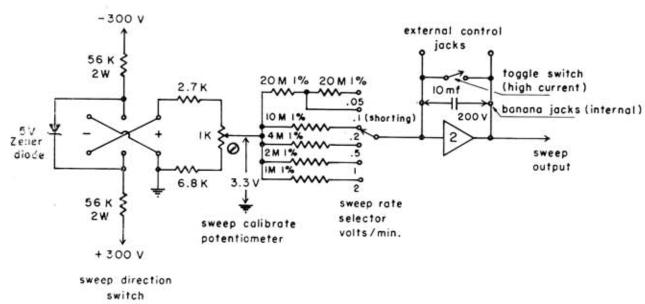


Figure 5. Circuit of sweep generator section.

The +300- and −300-v power supplies in the operational amplifier module are used to provide power for the 5-v zener diode source. It is a convenient source of power and is stable and noise free. A dpdt switch reverses the polarity of the 5-v source. A voltage divider reduces 5 v to about 3.3 v which is connected to the integrator through a large resistor. A switch selecting the value of the resistance determines the value of the current to be integrated and hence the sweep rate. When the sweep rate calibration has been properly adjusted for one sweep rate, the accuracy of the others will be within 1%. The maximum obtainable accuracy for a single, individually calibrated sweep rate is determined by the ratio of the offset drift of amplifier 2 to the constant input voltage. Since the amplifier drift can generally be kept within 3 mv, the expected error is 3.3/0.003 or about 0.1%.

The 10-mf integrating capacitor is wired internally with plug-in connections. This arrangement provides an even greater potential range of sweep speeds. For rapid-scan polarography (*11*), a 1.0 mf capacitor could be substituted providing calibrated sweep speeds from 0.5 to 20 v/min. To start the sweep, the switch across the integrating capacitor is opened allowing charge to accumulate on the capacitor. The sweep is stopped at the desired time by closing the switch. This discharges the capacitor and returns the electrode to the initial (pre-sweep) potential. A pair of jacks are provided across the capacitor for remote control of the sweep or other special external sweep control circuits. The sweep output signal, which is obtained between the external control jack at the output of amplifier 2 and ground, may be used in conjunction with other circuits or instruments. Since the sweep signal is attenuated 10 times at the input to the potentiostat, the actual sweep generator output signal is 10 times the indicated sweep rate.

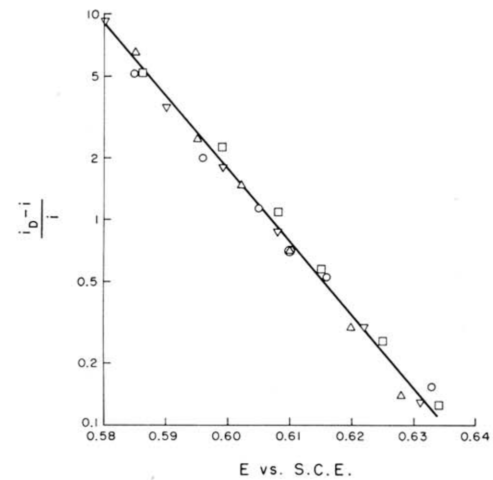


Figure 6. log(i_d − i)/i versus E for four successive scans. Run 1, ▽; Run 2, ○; Run 3, △; Run 4, □. Solution is 5×10^{-4} M Cd^{++} in 0.1 M KCl. Sensitivity, 5 μa, fullscale; damping 1.

The advantages of the electronic sweep generator over the motor driven potentiometer have been discussed by Kelley, Fisher, and Jones (*2*). The primary advantage is in having a wide range of switch-selected sweep speeds. Other advantages are the elimination of the potentially noisy wiping contact of the potentiometer and the precisely reproducible initial potential. This latter advantage can be of great value when precise voltage measurements are to be taken from a series of polarograms. Figure 6 is a plot of $(i_d - i)/i$ versus the electrode potential in the half-wave potential region. The points on the line were obtained from four successive runs beginning at 0.50 v with a sweep rate of 0.05 v/min and a span of 0.3 v. The voltage measurements on successive runs are shown to agree within 3 mv. Clearly, precise repetitive scanning improves the accuracy of the measurement.

The Initial Potential Source

With an electronic sweep, it is impossible to stop the sweep at a particular potential and hold that potential indefinitely. For this reason, the initial potential source is calibrated and continuously variable for use in constant potential measurements.

The circuit of the initial potential source is part of the potentiostat circuit diagram, Figure 7. A 5-v zener diode is used to provide a constant potential from the 300-v supplies as in the sweep generator circuit. A 1000-ohm, 3-turn potentiometer in a potential divider circuit is used for the initial potential adjustment. The calibration control is adjusted for exactly one volt per turn of the 3-turn potentiometer. When the initial potential knob is set at zero (3-turn potentiometer at the counterclockwise stop) the output of the initial potential source would be from 2 to 5 mv due to end resistance in the potentiometer. The effect of this end resistance is eliminated by the bridge circuit composed of the 4.7-K resistor and the 10-ohm potentiometer. The 10-ohm potentiometer is not panel-mounted because a single, initial adjustment is all that is necessary. When this potentiometer is properly adjusted, no movement of the panel meter will be detected when the initial potential polarity switch is reversed with the initial potential control set at 0.00 v, the function selector switch at CALIBRATE the current sensitivity at 10 μa, and the meter switched to measure current.

The Potentiostat

The circuit of the potentiostat section is shown in Figure 7. This circuit is actually identical to the simple circuit of Figure 2 except for the addition of an output meter and a function selector switch SF. When SF is in the CELL position, position 7, the potentiostat and current amplifier are connected to the cell electrodes as in Figure 2.

The follower amplifier has a gain of exactly one and an input resistance of about 10^8 ohms. Therefore, the follower amplifier output voltage is equal to the potential between the reference and test electrodes, but the current through the reference electrode will not exceed a few hundredths of a microampere. The follower amplifier output, the initial potential source, the sweep generator, and the auxiliary potential control inputs are all connected to the input of amplifier 3 through precision resistors. Due to the very high gain of amplifier 3 and the negative feed back employed in the potentiostat circuit, the algebraic sum of all the input potentials must be zero (*5*). In other words the potential between the reference and test electrodes is equal in magnitude but opposite in sign to the sum of all the signals connected to the input of amplifier 3. Since the resistance to the sweep generator is 1 megohm compared to 100 kilohms for the other inputs, the sweep signal is attenuated 10 times with respect to the other input signals.

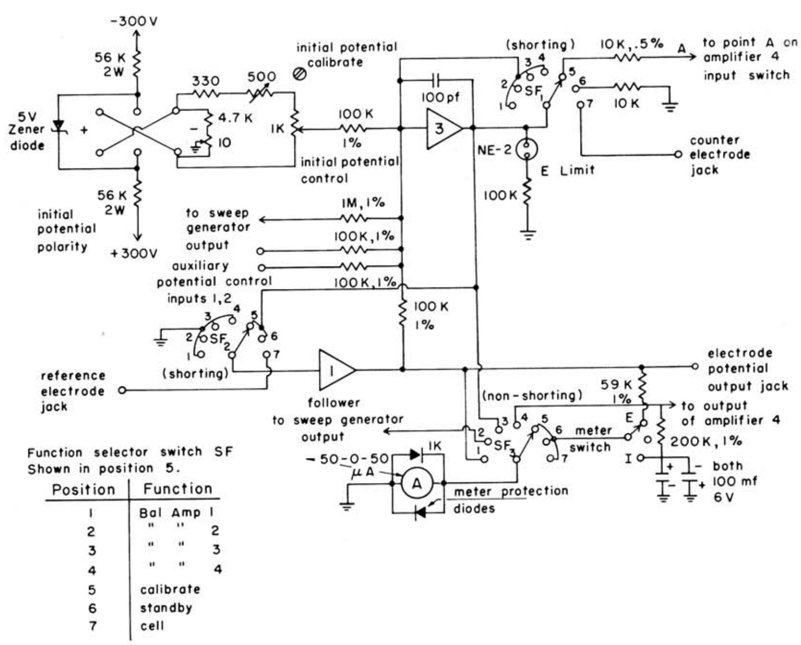
The 100-pf capacitor across amplifier 3 is required to prevent a high frequency oscillation in the potential control circuit. A neon light at the output of amplifier 3 goes on when the amplifier output voltage exceeds 60 v. This limit light indicates that the desired cell potential has not been obtained even though 60 v has been applied to the counter electrode. Normally this is an indication of an open circuit in one of the electrode connections or possibly an excessively high resistance in the cell.

The 50–0–50 microampere meter may be switched to the follower amplifier output to measure the test electrode potential or to the current amplifier output to measure the cell current. In the current measuring mode, two 100-mf capacitors are connected in parallel with the meter movement to damp it for proper response with a dropping mercury electrode. Meter protection diodes protect the meter from damage under all measurement conditions.

In the STANDBY position of Switch SF, a 10-K resistor is connected from amplifier 3 to ground in place of the cell. The follower input is connected to the potentiostat output to maintain the negative feedback path. The current measuring amplifier is out of the circuit. The CALIBRATE position is identical to the STANDBY position except that a 10-K precision resistor is connected in place of the cell, and the current through that resistor is applied to the current measuring amplifier. This position may be used to calibrate the sweep rate, the initial potential, or the recorder as described in the instrument calibration section.

The four BALANCE positions are used for checking and adjusting the bias control on each of the four operational amplifiers. In all BALANCE positions, amplifiers 1, 2, and 3 are connected for unity gain, while amplifier 4 approaches unity gain at full scale current settings less than 10 μa. The output voltage of each amplifier should be zero if the bias is correctly adjusted. In positions one through four of SF, the panel meter is connected to the outputs of amplifiers one through four respectively and the balance can be checked and easily adjusted to within 1 mv.

The potential of the test electrode is controlled to within a few millivolts of the desired value. The greatest source of error is the drift of the amplifiers away from the proper bias adjustment. After sufficient warm-up, the potential will remain within 5 mv of the desired



Position	Function
1	Bal Amp 1
2	" " 2
3	" " 3
4	" " 4
5	calibrate
6	standby
7	cell

Figure 7. Circuit of potential control section.

value for many hours. Over the period required to run a polarogram, the drift rarely exceeds 2 or 3 mv. For critical work, the balance could be checked before each run by briefly turning the selector switch through the four balance positions. In regions where large line-voltage changes are encountered, it may be desirable to use a constant voltage transformer such as the Sola Type 23–22–112 to stabilize the line voltage supply to the operational amplifier system.

The polarography module has been used successfully with chopper stabilized amplifiers in place of the Heath EUW–19A Operational Amplifier System. With stabilized amplifiers, the control potential is stable to ± 0.5 mv. The balancing of the unstabilized unit is such a simple procedure and the drift is so small that it is felt that only rarely would stabilized amplifiers be used to advantage.

The noise level at the follower output, and consequently at the reference electrode, has been measured with this module and is typically less than 1 mv peak-to-peak and is largely 60 cycles. For minimum noise, unused auxiliary potential control inputs must be shorted to ground.

Current Measurement Circuit

The cell current is fed directly to the input of amplifier 4 (Fig. 8). The current in the feedback path is equal to the input current and therefore the output voltage is equal to the product of the input current and the value of the resistance in the feedback circuit (*5*). The current sensitivity selects the value of the feedback resistor. In each case, a current of the full scale value marked on the panel will result in a 10-v signal at the output of amplifier 4. Note that a current boosting amplifier is used in series with amplifier 4. This provides a current of up to 20 ma at the 10 v, current measuring output. The 10-v full-scale output signal is connected to a voltage divider where it is reduced to 100 mv for use with a potentiometric recorder. Several taps in the voltage divider are used in conjunction with a 10-mf capacitor to provide a wide range of RC damping for the 100-mv output. For damping positions one through five, the damping time constants are: 0.1, 0.35, 0.69, 1.28, and 2.5 sec, respectively. There is no detectable difference between polarograms run with the damping off or in position 1. However, the damping at position 1 reduces the noise which appears at the output of amplifier 4 when the very high sensitivity ranges are used. For this reason, damping position 1 should be considered the "normal" position for obtaining polarographic curves. The "off" damping position is useful for ac polarography where capacitance in the output circuit must be removed.

A neon light is connected to the output of amplifier 4 which goes on when the output voltage exceeds 60 v. This is generally an indication that the current sensitivity is turned up too high.

Current Compensation

Currents from the charging current compensator and constant current compensator circuits are connected directly to the current measuring amplifier input where they are added algebraically to the cell current. The constant current compensator may be used to suppress large residual currents or previous polarographic waves so that the wave of interest may be run at optimum sensitivity. The polarograms in Figure 9 illustrate this point. Figure 9*a* is a polarogram of $2 \times 10^{-4}M$ Cd^{++} with a full scale current sensitivity of 5 μa. When $10^{-3}M$ Pb^{++} is present in the solution, it is necessary to reduce the sensitivity to 20 μa in order to observe the Cd^{++} reduction wave (Fig. 9*b*). When current compensation is added which is opposite to the limiting current of the Pb^{++} wave, the Cd^{++} wave can be observed at the optimum sensitivity of 5 μa (Fig. 9*c*). It was necessary to use damping position 3 in order to reduce the current fluctuations to a reasonable value. The effective compensating current magnitude is independent of the current sensitivity setting.

When polarograms are run at high sensitivities, the current required to charge the doub'e layer capacitance of a dropping mercury electrode introduces a considerable slope to the current voltage curve. As seen in the residual current curve run at 1.0 μa sensitivity (Fig. 10*a*) the charging current can take up a large part of the chart width. Under such circumstances it is necessary to construct a geometric figure on the polarogram in order to determine the true values of the limiting current and the half-wave potential. The charging current compensator circuit applies a compensating current to the current measuring amplifier which increases in magnitude as the sweep progresses. This is done by using the sweep generator output as the source of compensating current. Since the slope of the potential-capacitance curve is not linear for a mercury electrode in 0.1 *M* KCl, it is only possible to compensate for the charging current within a particular potential range. Thus, the polarogram in Figure 10*b* is exactly compensated in the region from 0.0 to −0.6 v, but is slightly over compensated at more negative potentials.

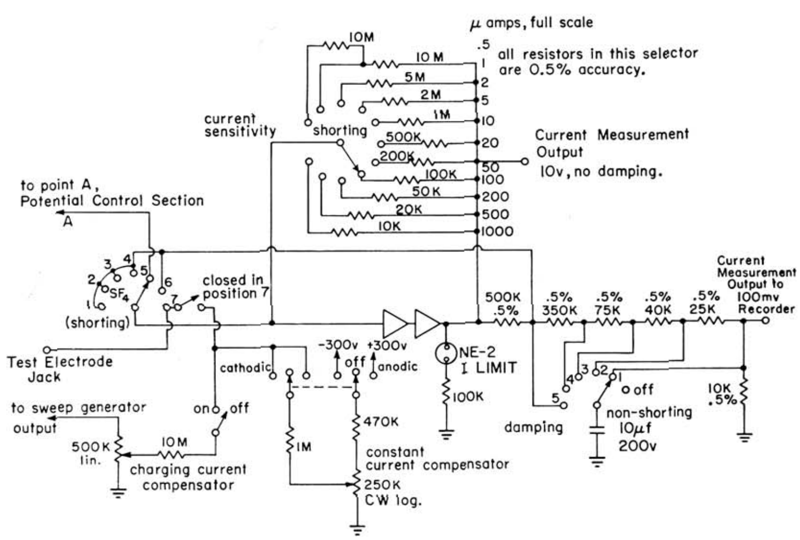


Figure 8. Circuit of current measurement section.

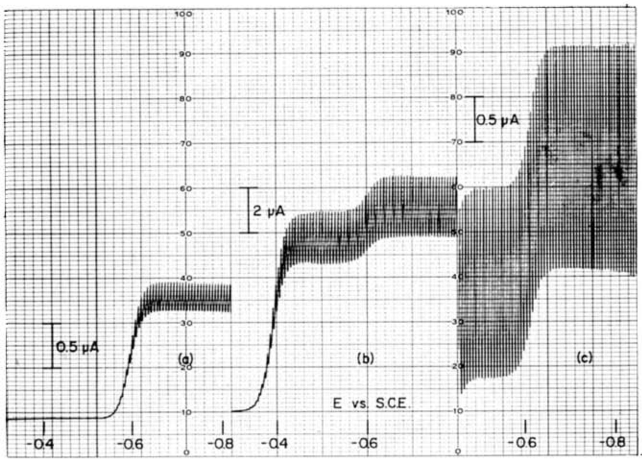


Figure 9. Polarograms illustrating an application of the constant current compensator. Solutions 0.1 M KCl, 0.1% Triton X-100 plus reducible species; damping 3; sweep rate 0.1 v/min. (a) 2×10^{-4} M Cd^{++}, (b) 2×10^{-4} M Cd^{++} plus 1×10^{-3} M Pb^{++}, (c) same as (b) with current compensation.

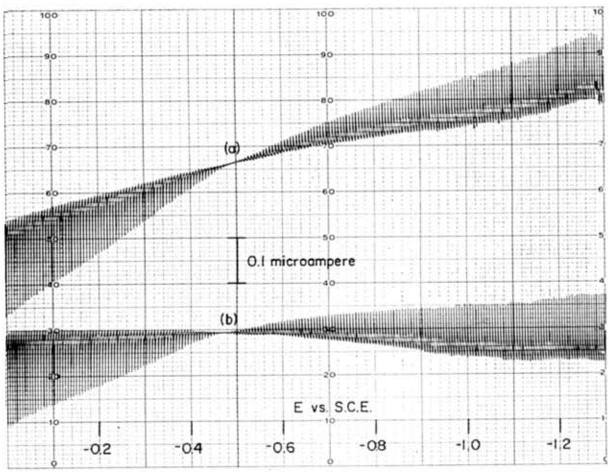


Figure 10. Residual current curves. 0.1 M KCl; damping 1; sweep rate 0.1 v/min. (a) uncompensted, (b) with linear charging current compensation.

Recording Polarographic Curves

Normally, polarographic curves are recorded by connecting a 100-mv potentiometric recorder to the 100-mv current output jacks. A 10-mv recorder may be used by connecting a 1.1-K precision resistor across the recorder output terminals. A cathodic current at the test electrode produces a negative potential at the current measurement output. When a recorder is used which deflects to the left for positive input voltages, as most do, an upside-down polarogram will result. Though this orientation hardly interferes with the evaluation of the curve, it can be inverted with the Heath EUW-20A recorder by simply reversing two pairs of leads in the recorder as shown in the recorder operation manual.

An X-Y recorder may be used with the Y axis connected to the current output and the X axis connected to the electrode potential output jack. This mode of operation is particularly desirable for cyclic voltammetry or recording polarograms which are independent of the sweep rate. A recorder with a large input capacitor should not be connected to the voltage output terminals without a 10- to 50-K isolation resistance connected in series with the recorder.

Instrument Calibration

Only two parts of the polarography module require calibration; one is the sweep rate and the other is the initial potential amplitude. Each of these calibrations involve adjusting the current in a voltage divider which is connected across a zener diode. Because of the high stability of the zener diode potential, it is only necessary to check the calibration every few months after the initial calibration. These calibrations are essentially independent of the adjustment or stability of the ±300-v power supplies in the operational amplifier system. Three calibration procedures are described below. One includes a calibration check on the recorder; one assumes the recorder is properly calibrated; and the third, which uses the panel meter and is accurate to a few per cent, is good for quick checks and sufficient for many applications.

Procedure 1. (a_1) *Zero Adjustments.* Turn on the Operational Amplifier System and allow one hour warm-up time before beginning the calibration. Turn the function selector to STANDBY, the meter swith to OFF, and adjust the meter zero screw to zero. Critically balance amplifier 1 by switching the function selector to position 1 and adjusting the bias control of amplifier 1 until the panel meter reads zero. Amplifiers 2, 3, and 4 are balanced in the same way. For the best balance of amplifier 4, the current sensitivity switch should be set at a full scale current of 10 µa or less. Amplifier balance should be checked every few hours of continued operation and more often during initial warm up.

(b_1) *Initial Potential Calibration by Null Procedure.* Set the initial potential adjustment to read the known potential of a mercury cell or other standard potential source. Turn the function selector to STANDBY. Adjust the recorder (or other sensitive voltmeter) zero control and connect the recorder and the standard potential source in series across the potential output jacks. Adjust the initial potential calibrate control until the recorder again reads zero. If no null can be obtained, the standard potential source connections are probably reversed. Check this calibration every few months.

(c_1) *Recorder Calibration.* Connect the recorder to the appropriate current measuring output terminals (see the section on recording polarographic curves). Set the initial potential to −1.00 v and the current sensitivity to 100 µa. When the function selector is turned to CALIBRATE, a current of 1.00 v/10,000 ohms = 100 µa is applied to the current amplifier input. Adjust the recorder for full-scale deflection.

(d_1) *Sweep Rate Adjustment.* Set the sweep rate at 0.1 v/min, the current sensitivity at 20 µa, and the function selector at CALIBRATE. Connect the recorder to the current output terminals. Full-scale recorder deflection will occur when the potential across the calibrate resistor is 20×10^{-6} a $\times 1 \times 10^4$ ohms = 0.2 v, i.e., 2 min after the sweep is turned on. Adjust the sweep rate calibrate control until full scale recorder deflection requires exactly two minutes. This calibration should be checked several times each year.

Procedure 2. This procedure differs from the first procedure above in that a calibrated recorder is used to calibrate the initial potential source. Follow steps (a_1) and (d_1) from procedure one and step (b_2) below.

(b_2) *Initial Potential Calibration Using a Calibrated Recorder.* Connect a 100 mv recorder to the current output terminals. Set the initial potential to −1.00 v and the current sensitivity to 100 µa. With the function switch on CALIBRATE, adjust the initial potential calibrate to give full scale recorder deflection.

Procedure 3. This procedure uses the panel meter for calibration and consequently is accurate to only a few per cent. Follow step (a_1) of procedure one and steps (b_3) and (d_3) below.

(b_3) *Initial Potential Calibration Using Panel Meter.* Switch the meter switch to the voltage position, set the initial potential adjustment at 3.00 v, and adjust the initial potential calibrate control until the meter reads 3.00 v.

(d_3) *Sweep Rate Adjustment Using Panel Meter.* Set the sweep rate selector at 1 v/min, the meter switch to the voltage position and the function selector to STANDBY or CALIBRATE. Adjust the rate calibrate control until exactly 3 min are required for a full scale (3.0 v) deflection of the panel meter.

Polarographic Measurements

Two-electrode Cells. This unit is readily applicable to the plotting of current-voltage curves for two-electrode cells or other two-terminal devices. The reference and counter electrode input jacks should be shorted together and the cell connected between the test electrode and reference electrode jacks. Connections from the electrodes may be made to either the banana jacks or the three-pin amphenol connector on the front panel. In this mode, the unit plots cell current versus cell potential. All controls are operative and function as described in previous sections. Before running the first polarogram of a series, it is convenient to use the panel meter to determine the voltage span of interest and the proper current sensitivity. Switch the meter to the current position and the function selector to CELL. A quick voltage scan may be made with a fast sweep rate or by turning the initial potential control. When the region of interest is reached, adjust the current sensitivity for optimum meter reading. Turn off the sweep, set the sweep rate, adjust the initial potential for the desired value, and turn on the recorder chart motor. When the recorder pen reaches a convenient reference line, turn on the sweep. The electronic sweep begins immediately with no lag or back lash. When the current-voltage curve is complete through the region of interest, turn off the sweep. Use the constant current compensator to suppress any large residual or prewave currents and the charging current compensator to level current-voltage curves taken at high sensitivity with a dropping mercury electrode. The compensations provided by these controls are completely independent of the setting of the current sensitivity and recorder zero adjust controls. Either the panel meter or an external recorder may be used for measuring the current during an amperometric titration. Quick-scan polarograms of the reactant and titrant solutions are helpful in selecting the operating potential to be set on the initial potential control.

A coulometer for integrating the cell current may be placed in the cell circuit without affecting the cell potential. Remove the shorting jumper between the reference and counter electrode jacks and connect the coulometer to these two terminals. The potential across the cell will be accurately controlled even though the voltage drop across the coulometer may be many volts.

Three-electrode Cells. All the operating modes and conveniences mentioned above may be applied to three-electrode cells. In addition, high resistance reference electrodes and low conductivity solutions may be used while maintaining or improving on the accuracy of the potential measurement. Shielded leads for connection to the electrodes are recommended. If a coulometer is used with a three-electrode cell, it should be connected in series with the counter electrode. It should be remembered that in three-electrode applications especially, the cell is part of the potential control loop and, as such, unavoidably affects its dynamic characteristics (*12*). Under most ordinary conditions, the system will be stable. However, instability or oscillations may be encountered under some circumstances. Instability can be detected by the lighting of the current limit light even though the panel meter and the recorder do not indicate full scale current. The best check is to connect an oscilloscope across the voltage output terminals. In most cases, the instability can be overcome by an improvement in cell design, by connecting a small capacitor across the feedback resistor in the current measuring amplifier (between the 10-v output and test electrode jacks on the front panel), or by connecting a resistance in series with the counter electrode.

Applications

The polarographic analyzer is suitable for performing experiments ranging from those encountered in a freshman course with emphasis on quantitative techniques to those found in a course in advanced analytical chemistry. Experiments such as those suggested by Delahay (*13*), Reilley and Sawyer (*14*), Willard, Merritt, and Dean (*15*) and Skoog and West (*16*) designed to verify the Ilkovic relationship can readily be performed down to concentrations of 0.01 millimolar Cd^{++}. The high current sensitivity and the charging current compensator are ideal for experiments demonstrating double-layer capacitance, the electrocapillary maximum, the need for complete deaeration and the presence of small amounts of reducible impurities (*13–15*). The constant current compensator is applicable to the polarographic determination of mixtures of ions such as alloys containing three or four reducible species (*14, 15*). Thus, it is possible to suppress the limiting current due to copper when determining lead and to surpress the limiting current due to both of these when determining zinc. In these cases, it is usually necessary to apply sufficient damping to suppress the oscillations due to the prewave. The excellent reproducibility of the initial potential and the variety of scan rates available aid in the recording of current-potential curves for reversibility studies (*13*). It is possible to obtain the necessary data by running at a slow scan rate and thus expanding the polarogram. The running of a number of consecutive polarograms also increases the available data. Consecutive polarograms may be obtained for any span by merely turning the sweep switch off and then on. The reproducibility of the initial potential is also critical when determining the formula and stability constant of a complex ion by measuring the shift in the half-wave potential as a function of concentration of complexing agent (*14*). Amperometric titrations (*13–16*) are conveniently performed by applying known potentials with the calibrated initial potential control and reading the current directly off the panel meter. The instrument is not, of course, restricted to use with the dropping mercury electrode, but is equally suitable for use with solid electrodes, rotating electrodes, hanging mercury drops, etc.

The instrument thus described has proved to be a very versatile and flexible research tool and has been used in this laboratory for research in new electrode materials and in recently developed voltammetric techniques and applications. At the same time, its convenience for the more traditional polarographic and amperometric measurements and its simple, functional control layout make it suitable for use by students at all levels.

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