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MULTIPURPOSE ELECTROANALYTICAL INSTRUMENT INCORPORATING AN X-Y RECORDER

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The basic quantities measured in electroanalytical chemistry are current, potential, and time. Measurement or recording of various combinations of these quantities accounts for most electroanalytical methods:

1. Current *vs.* potential, (a) voltammetry at constant potential, (*e.g.* polarography), (b) voltammetry at continuously changing potential, (c) current-electrode potential curves with macro-electrodes.

2. Potential *vs.* time, (a) chronopotentiometry, (b) potentiometric titration curves, involving coulometric generation or constant addition of titrant.

3. Current *vs.* time, (a) chronoamperometry, (b) amperometric titration curves, coulometric generation or constant addition of titrant.

Recording of current or potential *vs.* time is generally easily performed with galvanometer or "continuous-balance" strip chart recorders. The recording of current *vs.* potential, however, involves synchronizing the chart drive of the recorder with the polarizing unit drive. Since cell voltage, rather than electrode potential, is being recorded, the polarization curve inevitably includes the *iR* drop of the circuit. Although this *iR* drop generally does not cause serious error in the measured potentials when the cell resistance and current are small (*e.g.* polarography), attempts to record large currents (up to 100 mA) *vs.* potential, for example for use in predicting current efficiencies in coulometric titrations, are doomed to failure.

The direct recording of current-potential curves, as pointed out by LINGANE[1], could be accomplished with an X-Y recorder (or "function plotter"), recording the e.m.f. between the working electrode and a reference electrode on one axis, and the current

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flowing between the working electrode and an auxiliary electrode on the other axis. A polarograph utilizing this principle for accurate measurement of half-wave potentials and polarography in high resistance media has recently been described[2].

The present paper describes the application of an X-Y recorder, with a built-in time base, for all types of electroanalytical measurements. The instrument includes a variable polarizing source, for potential (or current) sweeps of 8 sec to 80 min, and an electromechanical amperostat–potentiostat combination for application to coulometry and controlled potential separations.

APPARATUS

The amperostat–potentiostat was essentially a combined version of the Lingane amperostat[3] and the Lamphere-Rogers potentiostat[4], utilizing the same amplifier for

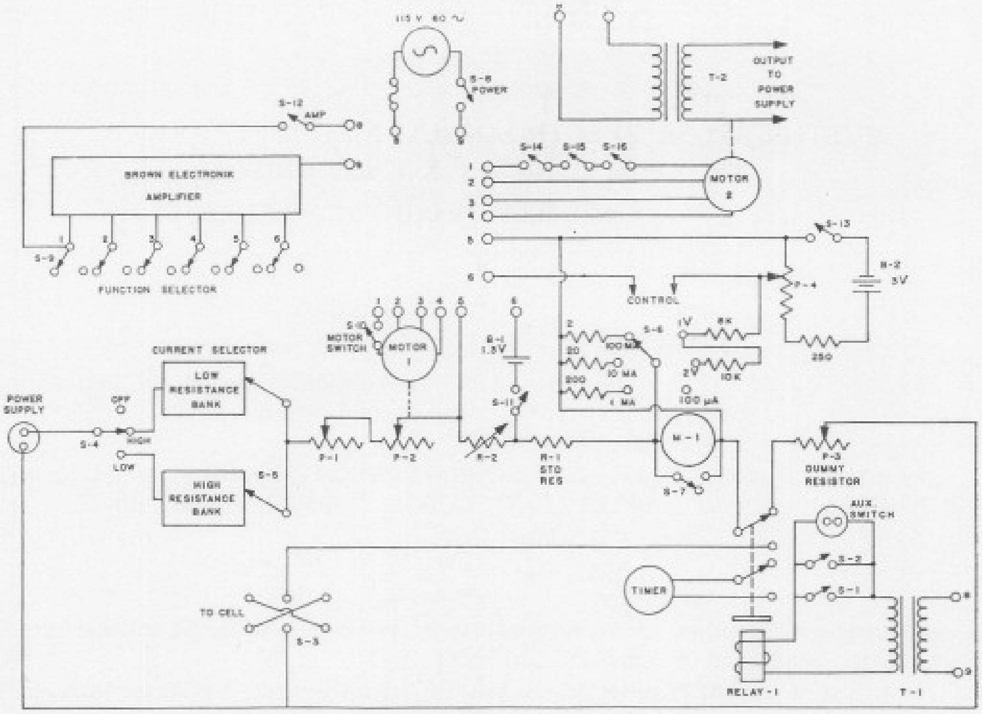

Fig. 1. Amperostat–potentiostat circuit:

M-1 = Microammeter (0–100 μA. d.c.; Simpson Panel Meter Model 29), relay-1 = Advance relay, Type AH/2C1C, T-1 = Power transformer (Merit P-2944), T-12 = General Radio Company Type V-10 Variac autotransformer (0–135 V. 10 A), P-1 = Borg micropot. Model 205, 10-turn, 0.1% linearity, P-2 = Potentiometer (General Radio Co. Type 974), P-3 = 500 Ohm potentiometer, P-4 = 500 Ohm potentiometer (General Radio Co. Type 975-J), R-1 = Precision resistor (General Radio Co. Type 500), R-2 = Decade resistor (General Radio Co. Type 1432 N), B-1 = 1.3 V mercury battery, B-2 = 3.0 V dry battery, S-1, S-7, S-10, S-11, S-12, S-13, S-14 = S.p.s.t. switches, S-2 = Microswitch, S-3 = D.p.d.t. switch, S-4 = 3-position, single pole switch (Centralab 1472), S-5 = 11-position, double pole switch (Centralab 2513), S-6 = 6-position, single pole switch (Centralab PA 2043), S-9 = 2-position, 6 pole switch (Centralab PA 2019), S-15, S-16 = Limit switches, Microswitch, leaf-action type, amplifier = Brown electronik model 356410-1, 115 V. 60 cycle. Motor 1 = Brown servo motor 364949, 115 V. 22 r.p.m., Motor 2 = Brown servo motor 364949, 115 V. 22 r.p.m., (1 : 40 reduction gear drive to T-2).

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both instruments. A schematic diagram of the circuit is shown in Fig. 1. The device is easily assembled from commercially available components, and requires little skill in electronic circuitry. The use of an electromechanical device allows currents of from 1 μA to 100 mA, by changing only the series resistances P-1 and P-2 and adjustment of R-2. The principle of operation of this instrument is discussed in detail in the literature[1,3,4]. The unit described has the advantage of versatility and reduction in cost by use of a common chopper-amplifier system for both functions.

A Moseley Model 3S X-Y recorder (F. L. Moseley Co., Pasadena, Calif.), with a built-in time base was employed throughout. This is a flat-bed recorder, utilizing standard 81/2 by 11 inch graph paper as a recording medium. Employed as an X-Y recorder, voltage input to either axis is continuously variable from 5 mV to 500 V. The time base (incorporated on the X-axis) allows full-scale sweep times of from 5 to 500 sec. Each scale may be calibrated, with an accuracy of 0.1%; changes in accuracy accruing to no more than 0.25% over a 6 month period. Both axis have identical response, and require 1/2 sec for full-scale pen travel.

Potential input

Direct input to the recorder for measurement of electrode potential is usually undesirable, as sizeable current drain through the recorder input attenuator, and consequently *iR* drop, occurs. Potential input with negligible current drain may be obtained by several devices. The X-axis of the recorder may be modified to make it a 1 V, zero current potentiometric system[2], but this has the distinct disadvantage of allowing only one potentiometric voltage range to be used. An alternate method is to employ a preamplifier in the potential input. The versatile pH meter Model 7664 (Leeds and Northrup Co., Philadelphia, Pa.) was quite suitable for this purpose. The recorder output of the meter was connected to the X-Y recorder, with the axis set for 20 mV full scale. The input to the pH meter consisted of voltage ranges of 0 to 700 mV and 0 to 1400 mV with the zero positioned anywhere on the scale. Other voltage ranges may be obtained by putting a variable resistance across the temperature compensation input of the pH meter (80–100 Ohms per 100 mV full scale deflection). Advantages of the pH meter input are the ability for use with very high input impedances (up to 2000 megOhms) for use with glass electrode measurements or high resistance voltammetry, and the ease with which orientation of the recorder scale can be accomplished. Accuracy is limited to that of the pH meter, but careful calibration provides sufficient accuracy for most electroanalytical measurements.

Current input

Current measurements are conveniently made by measuring the *iR* drop over precision resistors. Employing the 5 mV input to the recorder, current measurements of 0.1 μA to 1 mA is performed using 50,000 to 5 Ohm resistors. Higher currents may be measured using higher voltage inputs. The measuring resistors employed were either a decade box (*e.g.* Type 1432, General Radio Co., Cambridge, Mass.) or plug-in precision resistors (General Radio Co. Type 500).

Time input

The Moseley Model 3S is equipped with a built-in (charging capacitor-type) time

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base, providing 5 to 500 sec full scale sweeps. The linearity and reproducibility of this time base was good. For longer time sweeps, or for X-Y recorders not including time bases, a ten-turn precision helipot driven by a synchronous motor can be used.

Polarizing unit

The polarizing unit was a motor-driven infinitely variable, reversible speed reducer, Zeromax Model M14R (Revco, Inc., Minneapolis, Minn.) driving (through a 1 : 100 gear reduction) either an autotransformer (Variac Type W2, General Radio Co.,) or a helipot. This unit has the capability of voltage or current sweeps of 8 sec to 80 min, with any desired current (up to 2 A) or voltage range. Generally, the autotransformer was connected to 120 V.A.C. and was used as a source for a selenium rectifier power supply (*e.g.* General Radio Co. Type 1204 B). Alternately the usual bridge voltage sources were employed[2,5]. The reversibility of the motor allows scans to be made in either direction. Limit switches were included at both ends of the scanning range to protect the autotransformer and automatically turn off the apparatus. Since the recorder plots potential directly, usual considerations of slide wire linearity and motor speed constancy were unnecessary. However, the scan voltage circuit employed was sufficiently linear and constant for use in voltammetry with continuously rapid changing potential.

APPLICATIONS

Amperostat

The use as a constant current source has been described[3]. One need only select the current desired and adjust for balance and current constant to at least $\pm$ 0.1% can be obtained for use in coulometric titrations or chronopotentiometry.

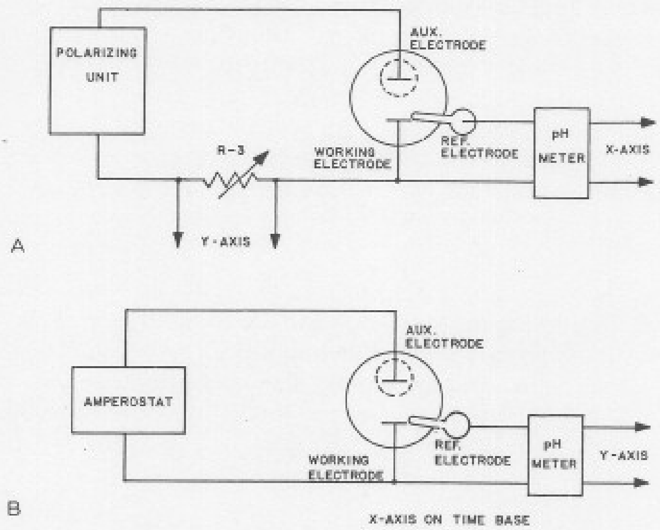

Fig. 2. A. Circuit for current-potential curves, B. Circuit for chronopotentiometry.

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Potentiostat

For use as a potentiostat, the function switch S-9 is turned to potentiostat, and the potential desired is adjusted with P-4 observing the meter (at 1 or 2 V range). Input to the autotransformer T-2 is 120 V.A.C. and the output voltage is fed to any selenium rectifier power supply. A potential of 1 V was maintained constant to within 10 mV as cell resistance varied from 500 to 1,000 Ohms in 5 min.

Current-potential curves

The set-up for any type of current-electrode potential measurement is shown in Fig. 2A. Adjustment of the variable precision resistor R-3 fixes the current range, and the total polarizing voltage and selected input to the pH meter selects the voltage range. This basic apparatus was employed for polarography (either voltage–scan or current–scan) or current–potential curves with macro-electrodes.

Chronopotentiometry

The apparatus for chronopotentiometry is shown in Fig. 2B. Current–time (chronoamperometric) curves are recorded in a similar manner, using a current input to the Y-axis. In a similar manner both potentiometric and amperometric titration curves of various types can be recorded, using separate indicator electrodes.

The unit described has proved both versatile and convenient. The total cost of the complete instrument, including the amperostat–potentiostat, pH meter and recorder was approximately $ 2,500.

SUMMARY

A multipurpose electroanalytical instrument, incorporating an X-Y recorder with a built-in time base, is described. The instrument also includes an electro-mechanical combination amperostat–potentiostat and a variable speed polarizing unit. The instrument accurately measures electrode potential (rather than cell voltage) and hence does not involve correction of recorded potentials for *iR* drop. This is especially convenient for the recording of current *vs.* potential curves with macroelectrodes. It has also been successfully used for voltammetry, chronopotentiometry, coulometry and recording of titration curves.

RÉSUMÉ

Un appareil électroanalytique à usages multiples est décrit. Il convient tout particulièrement pour l'enregistrement de courbes potentiel/courant, avec macro-électrodes. Il a également été utilisé avec succès pour la voltammétrie, la chronopotentiométrie, la coulométrie et l'enregistrement de courbes de titrage.

ZUSAMMENFASSUNG

Es wird ein elektranalytisches Mehrzweck-Gerät beschrieben, das sich besonders zur Aufnahme von Potential-Stromstärke Kurven mit Makroelektroden eignet. Ferner lässt es sich für die Voltametrie, Chronopotentiometrie, Coulometrie sowie zur Aufnahme von Titrationskurven verwenden.

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