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MODULAR SOLID-STATE UNIT FOR ELECTROCHEMICAL STUDIES

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A number of electrochemical instruments based on operational amplifiers have been recently described (*e.g.*, ref. 1–3). These units are generally of limited versatility, although GOOLSBY AND SAWYER[4] have more recently described a versatile solid-state potentiostat–amperostat which could be used for a variety of electrochemical techniques. The latter paper and SMITH's[5] excellent discussion of the technique of alternating current polarography prompted us to design an even more versatile unit than that of GOOLSBY AND SAWYER[4], which could be used as an alternating current polarograph as well as being suitable or adaptable for many other types of electrochemical studies.

The apparatus developed and subsequently described in detail is suitable for conventional constant potential direct current polarography, alternating current polarography, linear scan voltammetry, cyclic triangular scan voltammetry, and coulometry and macroscale electrolysis at controlled potential. The instrument can be adapted to many other uses; particularly useful circuits are described, for example, in references 2–6. The performance of the unit in conjunction with a three-electrode configuration electrochemical cell allows it to be used for electrochemical studies on solutions of high resistance.

Excluding the X-Y recorder, the total cost of the instrument is less than $1000.

INSTRUMENTATION

Instrument arrangement

Each of ten operational amplifiers is so mounted that their functional terminals are connected to identical sets of banana jacks mounted onto the front panel of a suitable cabinet, *e.g.*, a recessed panel mounting chassis; outlets for the +15 and −15 V power supply are also provided within each set of jacks, giving a total of nine jacks per set. The panel layout is shown in Fig. 1; numbers refer to amplifier terminals, which are the same for all the amplifiers used except the P66A current booster amplifier (Unit H) and P6154 voltage booster amplifier, where normally keying terminal 4 replaces terminal 3. A strict color code was employed: red, +15 V; yellow, −15 V; black, ground; green, amplifier inputs; blue, amplifier output; white, all other terminals. Jacks are 0.75-in. center-to-center relative to one another on a diamond spacing in a given set of nine.

The electrical components necessary to program each amplifier to perform

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the required operation are mounted within a $2 \times 5.25 \times 3$ in. aluminum mini-box, which has a set of external banana plugs arranged to fit into the set of 9 banana jacks mentioned. All controls, *i.e.*, switches, potentiometer knobs, etc., are mounted on the front of the mini-boxes (Fig. 2).

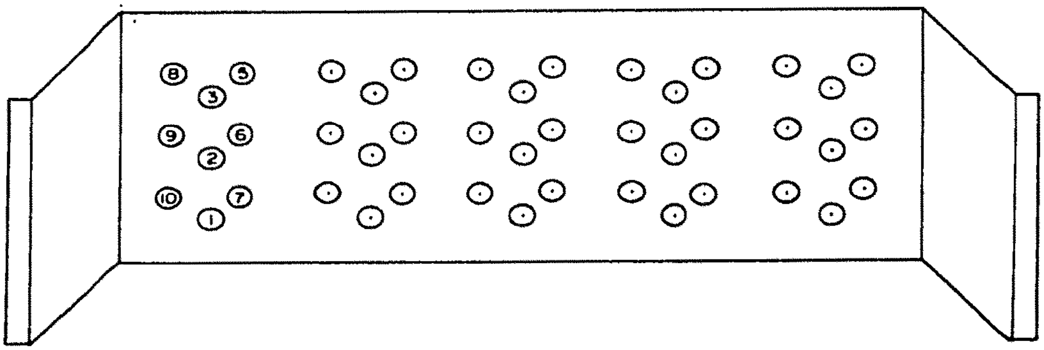

Fig. 1. Arrangement of amplifier terminal jacks on a 7×19 in. recessed panel mounting chassis.

Basic circuit design

The basic circuit is essentially that of a simple potentiostat (Fig. 3), with provision for boosting the output of the control amplifier with regard to both current and voltage, and with means for converting the signals into forms that can be readily recorded on an X-Y recorder.

For convenience, the circuit is divided into a series of individual mechanically discrete units, each enclosed within broken lines on the circuit diagram and designated as Unit A through J. Each unit is mounted in a separate mini-box and will be individually described in respect to construction and function.

Power supply

A Philbrick Model Pr300-R solid-state power supply (± 15 V d.c. ($\pm 0.01\%$); 0 to 300 mA) was used. When it is necessary to use the P6154 voltage booster amplifier, two such power supplies are used in order to provide the ± 30 V power requirements for the amplifier[7].

Sine-wave generator (unit A)

A very stable sine-wave generator was constructed, which utilizes a Philbrick P65AU amplifier (Fig. 4). REILLEY[8] has shown that the frequency of the signal from this circuit is given by:

$$\omega = 2p^{\frac{1}{2}}/(RC)^{\frac{1}{2}} \qquad (1)$$

where p is the proportion of the output fed back into the input of the amplifier, R is the resistance in ohms of R_1 ($R_1 = R_2$), C is the capacitance in microfarads of C_2 ($C_2 = C_3$), and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency in Hz). When $\pm 10\%$ capacitors were used, the useful frequency range of the oscillator was between 50 and 250 Hz. The unit is set to oscillate by means of R_4; the frequency and amplitude are then adjusted by means of R_6 and R_7, respectively.

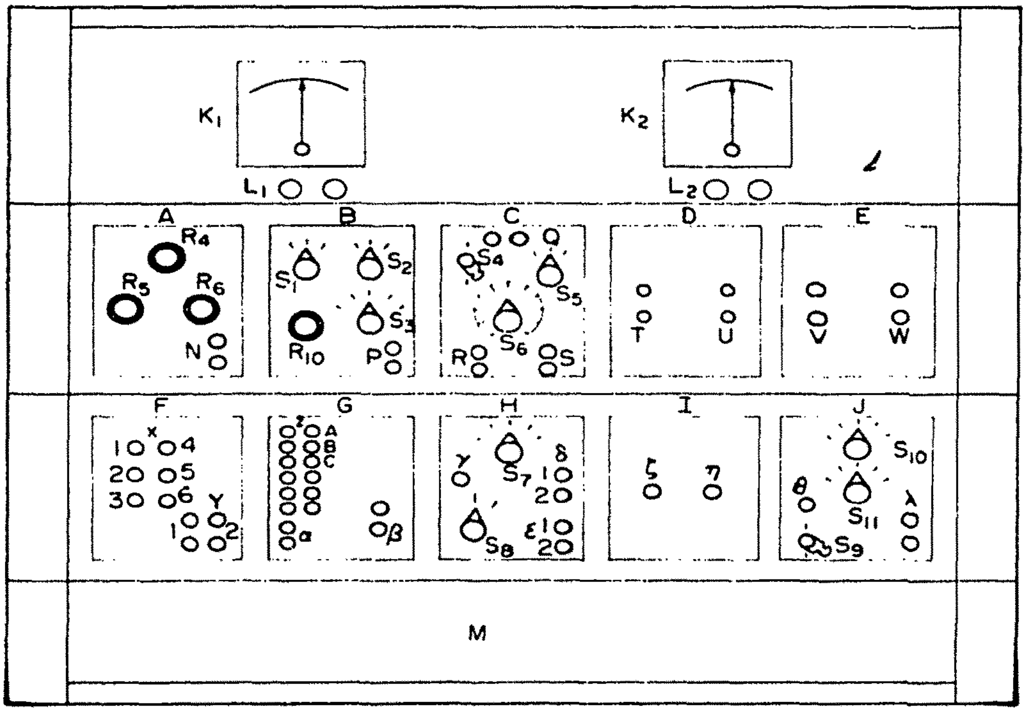

Fig. 2. Arrangement of front of instrument (housed in a 26-in high conventional 19-in cabinet). The units are mounted on three 7-in recessed panel mounting chassis above the power supply M.

(A) Sine-wave generator. R_4, amplifier oscillation adjustment; R_5, frequency adjust; R_6, amplitude adjust; N, signal output.

(B) D.C. voltage level. S_1, polarity set (Off–Negative–Positive); S_2, voltage range set (Off–o to $\pm$1.0 volt–o to $\pm$10.0 volt); S_3, damping adjust; R_{10}, voltage adjust; P, output voltage.

(C) Ramp generator. S_4, sweep polarity (Positive–Negative); Q, jacks for 1.0-μF capacitor; S_5, integrator function switch (Sweep–Hold–Reset); S_6, sweep rate set (2 mV/sec to 1.0 V/sec); R_{26}, current trim; R and S, output jacks.

(D and E) Full-wave rectifier. T, input from current amplifier; U, output to unit E; V, input from unit D; W, rectified output signal (to recorder).

(F) Reference electrode follower. X_1, to reference electrode; X_2, to counter electrode; X_3, to working electrode; X_4, from unit H; X_5, output from control amplifier (unit H); X_6, input to current amplifier (unit J); Y_1, output to voltage axis of recorder; Y_2, output to control amplifier (unit G).

(G) Control amplifier. Z, set of 6 identical input jacks; α, output jacks to d.c. voltmeter K_1; β, output jacks to current booster amplifier (unit H).

(H) Current booster amplifier. S_7, booster select (Current Booster–No Booster–Voltage Booster); S_8, Cell In–Cell Out switch; γ, output from control amplifier (unit G); S_1, output to voltage booster (unit I); S_2, input from voltage booster; ε_1, output to reference electrode follower (X_4 jack); ε_2, to counter electrode (X_5 jack, unit F).

(I) Voltage booster amplifier. ζ, input from current booster (jack S_1); η, output to current booster (jack S_2).

(J) Current amplifier. S_{10}, damping adjust; S_{11}, amplification adjust (1 μA = 1 mV–10 mV–100 mV–1 V); θ, input from working electrode (X_6 jack, unit F); S_9, cell In–Out switch; λ, output signal (to recorder or rectifier).

D.C. voltage level (unit B)

The initial potential of a voltammetric scan or the potential for an exhaustive electrolysis can be set anywhere between +10 and −10 V by means of a unit based on a Philbrick P65AU amplifier (Fig. 5). The polarity of the voltage is set with S_1 (note that the output voltage is of opposite sign to the input voltage); the range is

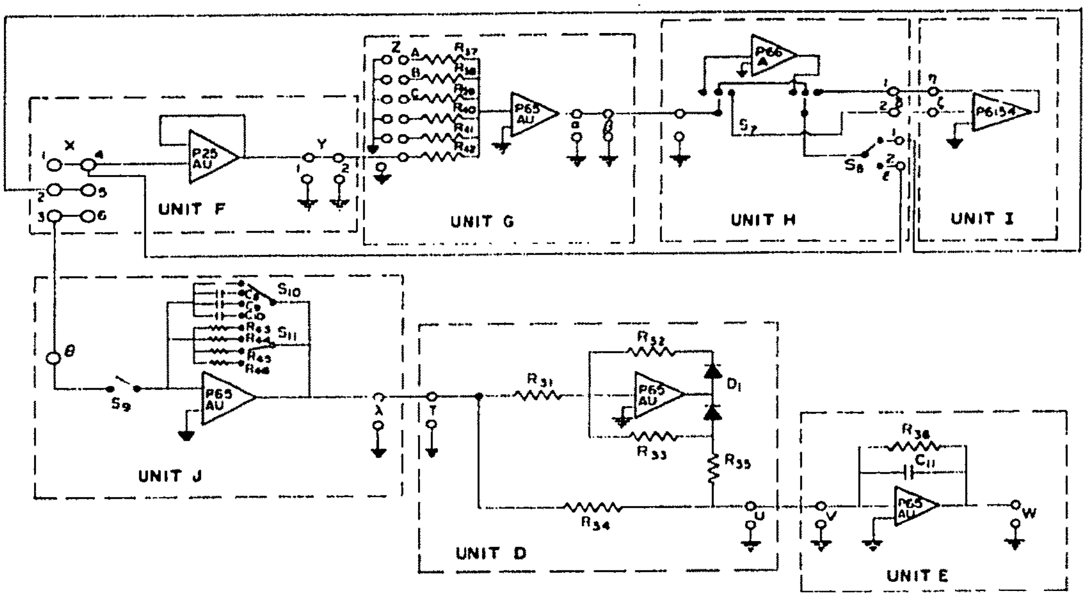

Fig. 3. Basic potential control and measuring circuit of instrument. The components are also identified in Fig. 2, where applicable, to which reference can be made for items not identified in the present figure caption. Dashed lines indicate circuit within each marked unit. Open circles correspond to banana jacks which appear on the front panel of each unit. Solid circles indicate switching points.

S_7, double-pole 3-position shorting; S_8, SPDT shorting; S_9, toggle; S_{10}, S_{11}, single-pole 4-position shorting; R_{31}, R_{32}, R_{33}, R_{34}, R_{36}, 20K; R_{35}, 10K; R_{37-42}, 100K; R_{43}, 1K; R_{44}, 10K; R_{45}, 100K; R_{46}, 1M; C_8, 0.001 μF; C_9, 0.01 μF; C_{10}, 0.1 μF; C_{11}, 100 μF; D_1, Motorola silicon diode, 50 V/V. Except where otherwise stated, resistors are $\pm 1\%$ tolerance and capacitors $\pm 10\%$; the latter are rated at 600 V d.c.

A, B and C: Inputs from units A (Fig. 4), B (Fig. 5), and C (Fig. 6), respectively.

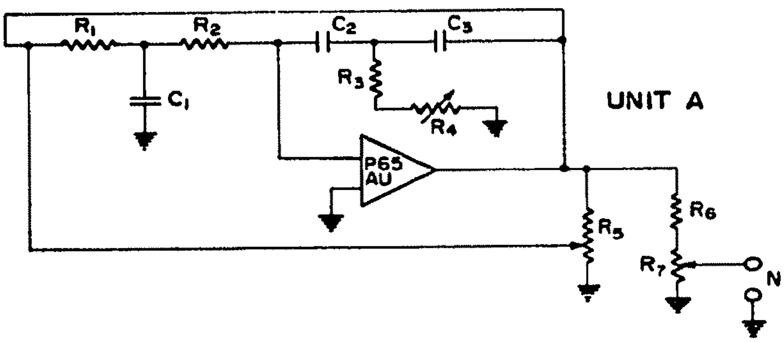

Fig. 4. Sine-wave generator (unit A). R_1, R_2, 20K; R_3, 9K; R_4, 10-turn, 2K potentiometer; R_5, 10-turn, 5K potentiometer; R_6, 100K; R_7, 10-turn, 1K potentiometer.

changed by altering the magnitude of the input resistors R_8 and R_9 to the amplifier by means of switch S_2. Optional dampening of stray noise is provided for by switch S_3 and the associated capacitances.

Ramp generator (unit C)

A suitable ramp generator was built, based on a Philbrick P25AU amplifier

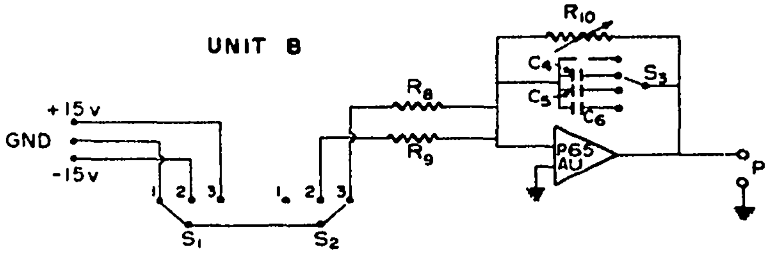

Fig. 5. D.C. voltage level (unit B). S_1, S_2, rotary single-pole 3-position non-shorting; S_3, rotary single-pole 4-position shorting; R_8, 15K; R_9, 150K; R_{10}, 10-turn, 10K potentiometer.

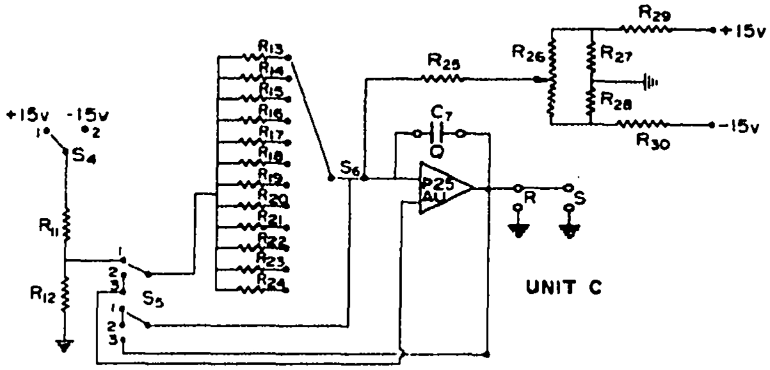

Fig. 6. Ramp generator (unit C). S_5, double-pole 3-position shorting; S_6, single-pole 11-position shorting; R_{13}, 100K; R_{14}, 200K; R_{15}, 500K; R_{16}, 1M; R_{17}, 2M; R_{18}, 5M; R_{19}, 7.5M; R_{20}, 10M; R_{21}, 15M; R_{22}, 20M; R_{23}, 50M; R_{24}, open position for insertion of another suitable resistor; R_{25}, 70K; R_{26}, 25-turn 0.5K trimpot; R_{27}, R_{28}, 22K; R_{29}, R_{30}, 50K; C_7, 1.00 μF (±1%, Southern Electronics, Burbank, Calif., Model PC 105G2APL, 200 V d.c.).

(Fig. 6). By variation of the input resistance with switch S_6, eleven scan rates between 2 and 1000 mV/sec can be generated. A 1.0-mF polystyrene capacitor is used in feedback. The polarity of the output signal is selected by means of a switch S_4. Switch S_3 selects the mode of the integrator to either sweep, hold or reset. The output of the ramp generator is monitored continuously with a (+10)-0-(−10) V d.c. meter (Eberbach Corp. Model 301-57).

The performance of the ramp generator was generally very satisfactory, although the minimum drift attainable, ±0.2 mV/sec, became significant for studies requiring very low scan rates, *e.g.*, 2 or 5 mV/sec. However, when an X-Y recorder is used, slight variations of sweep rate are not important. When the performance of the ramp generator becomes critical, a Philbrick P2 amplifier could be used instead of the P25AU.

Full-wave precision rectifier (units D and E)

A full-wave precision rectifier, based on HOWE's design[9], utilized two Philbrick P65AU amplifiers (Fig. 3). The unit performed well and the output could be fed directly to one axis of an X-Y recorder.

The damping capacitor, C_{11}, tended to cause the output on the recorder to be attenuated by a factor of 1.93, although this was a linear effect over the normal current ranges expected and could easily be corrected. Without the damping capacitor, the current oscillations on the recorder became very large and considerable noise was seen.

Reference electrode follower (unit F)

Because of their high imput impedance and stability, Philbrick P25AU amplifiers were employed in the reference electrode follower, which monitors the potential difference between the reference and working electrodes. The follower was wired in the conventional unity gain, non-inverting mode (Fig. 3).

Control amplifier (unit G)

The control amplifier is based on a Philbrick P65AU amplifier. Five identical sets of input jacks are provided so that several signals can be introduced and summed simultaneously (Fig. 3). The state of control of the output of the control amplifier is monitored by means of a (+10)-0-(−10)-V d.c. meter (Eberbach Corp. Model 301-57).

Current booster (unit H)

The current booster amplifier is a Philbrick P66A amplifier, which has a maximum output of ±20 mA at ±10 V without external resistors and ±100 mA at ±10 V with appropriate externally connected resistors[10].

Voltage booster (unit I)

In order to achieve high voltage outputs in the control amplifier loop, provision is made for the use of a Philbrick P6154 voltage booster amplifier capable of ±10 mA at ±100 V. By means of switch S_7, the current booster or voltage booster can be switched into the circuit or, as is usual, the unit can be used without any booster amplifiers.

In order to prevent the control amplifier from reaching its output limits when the counter and reference electrode leads are disconnected, provision is made by means of switch S_8, for shorting the two electrodes together internally.

Current amplifier (unit J)

A Philbrick P65AU amplifier is used in the inverting mode to convert the current flowing at the working electrode into a proportionate voltage which can be fed to a recorder. By means of the feedback resistor (switch S_{11}), the amplification of the current could be altered to the extent that 1 μA flowing at the working electrode could be converted to 1, 10, 100 or 1000 mV.

In order to eliminate high-frequency noise when the unit is used as an alternating current polarograph, it is necessary to have a small damping capacitance across the amplifier. Generally, a 0.001-mF capacitor was preferred since this did not attenuate the a.c. signals to any appreciable extent.

Operating procedure

Depending upon the operation required, various units are connected together by means of coaxial cable. Thus, for d.c. polarography and voltammetry and for cyclic voltammetry, units B, C, and F to J are used, although booster units H and I are not needed for most purposes.

For controlled potential electrolysis, units B, F, G, and H or I would normally be required.

For alternating current polarography, units A to G are required.

Clearly, by suitable patchcording or, preferably, construction of alternative mini-boxes, many other operations can be performed, *e.g.*, *cf.* references 1–6 and 11.

All voltammograms and polarograms during the testing and subsequent use of the instrument were recorded satisfactorily on either a Moseley Model 135 or Model 7001A X-Y recorder.

INSTRUMENT PERFORMANCE

Inorganic system

The iron(III)/iron(II) system in 0.25 *M* oxalic acid–0.25 *M* potassium oxalate solution (pH 2.65), which is generally considered to be reversible at the dropping mercury electrode, was examined to evaluate the performance of the instrument. Polarography (d.c.) at the dropping mercury electrode (DME) gave the same results as a Sargent Model XXI polarograph. Linear sweep and cyclic voltammetry at the

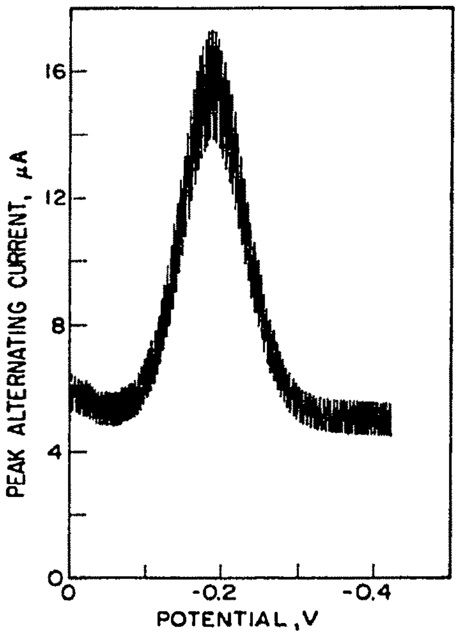

Fig. 7. Alternating current polarogram of 1 m*M* iron(III) in oxalate background (pH 2.65). Frequency: 50 Hz; amplitude: 30 mV peak-to-peak; scan rate: 2 mV/sec. Potential is *vs.* SCE.

pyrolytic graphite electrode (PGE) and the hanging mercury drop electrode (HMDE) gave results identical to those obtained with a cyclic voltammetry unit based on the original DeFord designs[11], which utilized vacuum-tube operational amplifiers.

Alternating current polarography at the DME was as expected for a reversible system as evidenced by (1) the linear relationship between the peak current and the amplitude of the alternating signal over the range of 4–40 mV peak-to-peak voltage at 50 Hz, (2) the invariance of the peak current with the height of the mercury column, (3) the linear relationship between the peak current and the square root of the applied frequency between 15 and 64 Hz, followed by a region at higher frequencies where the current rapidly decreased with increasing frequency, and (4) the linear peak current–concentration curve at 50 Hz and the 10-mV peak-to-peak amplitude over the concentration range 0.1–1 mM. A typical a.c. polarogram is shown in Fig. 7.

The observed alternating current was lower than that predicted theoretically[12], primarily because of the uncompensated capillary resistance of the dropping mercury electrode. By means of recently published circuits[13], it should be possible to reduce substantially the effects of the series resistance.

The unit is capable of performing only fundamental harmonic a.c. polarography, although it would be possible—by increasing the number of operational amplifiers—to extend the unit to perform second and third harmonic a.c. polarography[5].

Organic system

Purine, which gives two 2-electron waves at the dropping mercury electrode

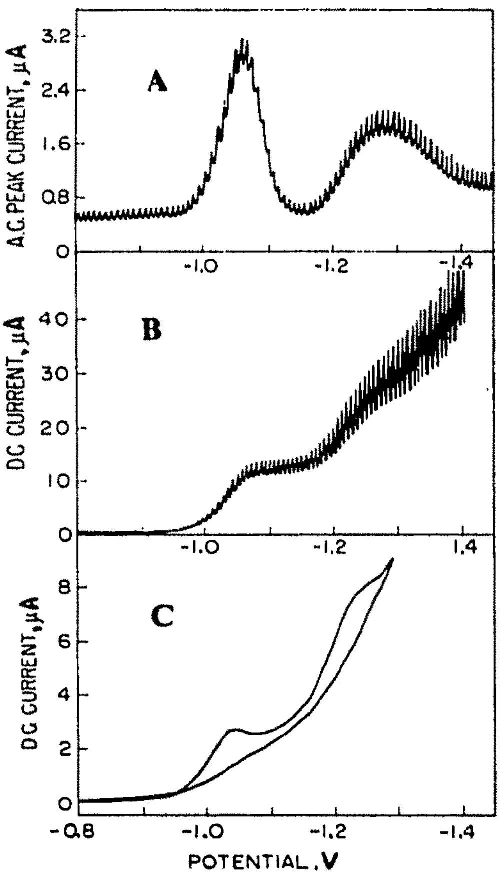

Fig. 8. Response of purine in pH 4.1 aqueous acetate buffer solution (ionic strength: 0.5 M). (A) Alternating current polarography at DME; d.c. scan rate, 2 mV/sec; a.c. amplitude, 10 mV peak-to-peak; frequency, 50 Hz; 2 mM purine. (B) D.C. polarography at DME; scan or polarization rate, 2 mV/sec; 2 mM purine. (C) Cyclic voltammetry at hanging mercury drop electrode; scan rate, 20 mV/sec; 0.5 mM purine. Potential is *vs.* SCE.

in acidic solution with some catalytic hydrogen evolution accompanying the second wave[14], was examined in 0.5 *M* acetate buffer solution of pH 4.1. Curves obtained on polarography at the DME, cyclic voltammetry at the hanging mercury drop electrode, and alternating current polarography at the DME are shown in Fig. 8.

The polarographic data agree with those previously reported for a Leeds & Northrup Type E Electro-Chemograph[14]; the cyclic voltammetric and a.c. polarographic data agree with those obtained with separate units based on vacuum-tube operational amplifiers[15].

Of special significance from the analytical viewpoint is the definition of the second purine wave on a.c. polarography as compared to that on d.c. polarography.

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SUMMARY

A relatively inexpensive unit based upon solid-state operational amplifiers is described; its modular design makes it an extremely versatile instrument for many electrochemical techniques, *e.g.*, normal direct current polarography and linear sweep voltammetry, cyclic voltammetry, alternating current polarography, and coulometry and electrolysis at controlled electrode potential. It can be readily adapted to many other functions.

RÉSUMÉ

Une unité modulaire solide relativement peu coûteuse est décrite constituant un instrument extrêmement versatile pour de nombreuses techniques électrochimiques: polarographie à courant direct normal et voltammétrie à balayage linéaire, voltammétrie cyclique, polarographie à courant alternatif, coulométrie et électrolyse à potentiel contrôlé. Cet appareil peut être facilement adapté à plusieurs autres usages.

ZUSAMMENFASSUNG

Es wird eine relativ kleine Verstärkereinheit, welche sich für zahlreiche elektrochemische Techniken wie z.B. die Polarographie, Voltametrie, Coulometrie und für die Elektrolyse eignet, beschrieben. Sie kann ebenso schnell zahlreichen anderen Funktionen angepasst werden.

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