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A FUNCTION GENERATOR AND POTENTIOSTAT-GALVANOSTAT FOR ELECTROANALYTICAL EXPERIMENTS AND EVALUATION OF SQUARE WAVE VOLTAMMETRY MODE OF OPERATION

by 7214

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Introduction

Present work in electroanalytical research requires an instrument with capabilities of performing a wide variety of electrochemical functions. Additionally, electroanalytical research also demands that the conversion of the instrument from one electrochemical technique to another be made rapidly and, preferably, by means of a single switch. Although several multipurpose instruments have been reported in the literature which are relatively easy to transform from a potentiostatic to a galvanostatic mode of operation (1-3), a multipurpose instrument has not been described which incorporates a function generator that (1) provides all necessary waveforms, (2) responds during the experiment to the cell potential, an integral timing circuit, and manual controls, and (3) terminates the experiment after a predetermined number of half cycles.

The instrument described here is intended for chronoamperometric, cyclic voltammetric, chronocoulometric, square wave voltammetric, and cyclic chronopotentiometric studies, as well as for normal polarography and stripping analysis. Important features include: (1) rapid change from one circuit configuration to the next by means of a single switch; (2) a timing circuit for control of chronoamperometric and chronopotentiometric experiments; (3) a counting circuit which terminates the electrochemical experiment after a predetermined number of half cycles; (4) independently controlled amplitudes of the anodic and cathodic potential steps for double potential step chronoamperometric experiments; (5) anodic and cathodic currents which may be varied independently

for use in current reversal chronopotentiometric studies of follow-up chemical reactions; (6) triangular wave and staircase function generators for cyclic voltammetric and square wave voltammetric studies, respectively; (7) electronic switching of the function generators; and (8) positive feedback capability for correction of uncompensated iR in a potentiostatic mode of operation.

Potentiostat-Galvanostat

Plate 1 is a simplified schematic of the three-electrode potentiostat-galvanostat and incorporates modified versions of circuits originally given by Smith(4) and Shain(1). Selection among the several modes of operation (square wave voltammetry, cyclic voltammetry, chronoamperometry, standby, and cyclic chronopotentiometry) is made by the master control switch, S1. With the master control switch in a potentiostatic mode of operation (positions 1 through 3), the potential between the working and the reference electrodes is determined by the several voltages introduced in parallel to the control amplifier (OA1) and by the values of the resistors in the bridge network. Compensation of ohmic potential loss between the working and reference electrodes (uncompensated iR) is effected by the positive feedback loop from the current follower (OA3) to the control amplifier. Although the buffer amplifier (OA4) in the positive feedback circuit can be eliminated in a minimum-amplifier circuit, its presence greatly facilitates computation of the uncompensated resistance, thus permitting rapid readjustment of the potentio-

PLATE 1

Three-Electrode Potentiostat-Galvanostat

0A1, 0A3, 119A (Analog Devices); 0A2, 0A4, LM210 (National); S1, 12p5t, shorting; S2, S3, spdt, toggle; S4, S7, spdt, center off, toggle; S5, 3pdt, toggle; S6, dp11t, shorting; D1-2, IN5240; C1, 56pf; C2, 10^{-3}uf; C3, 0.01 uf; R1-3, R20, R27, 10KΩ; R4-5, R17, R12-13, R28, 100KΩ; R6-7, R18, 50KΩ; R14, 1MΩ; R15, 500KΩ; R16, 200KΩ; R19, 20KΩ; R21, 5KΩ; R22, 2KΩ; R23, 1KΩ; R24, 500Ω; R25-26, 10KΩ 10-turn potentiometer; R10-11, 500Ω, 10-turn potentiometer; R8-9, 1KΩ, trimpot; R29-31, 10KΩ, 5%. Unless otherwise noted, all fixed resistors are 1% tolerance. Not shown in the figure are the power supply connections and the biasing networks for the operation amplifiers.

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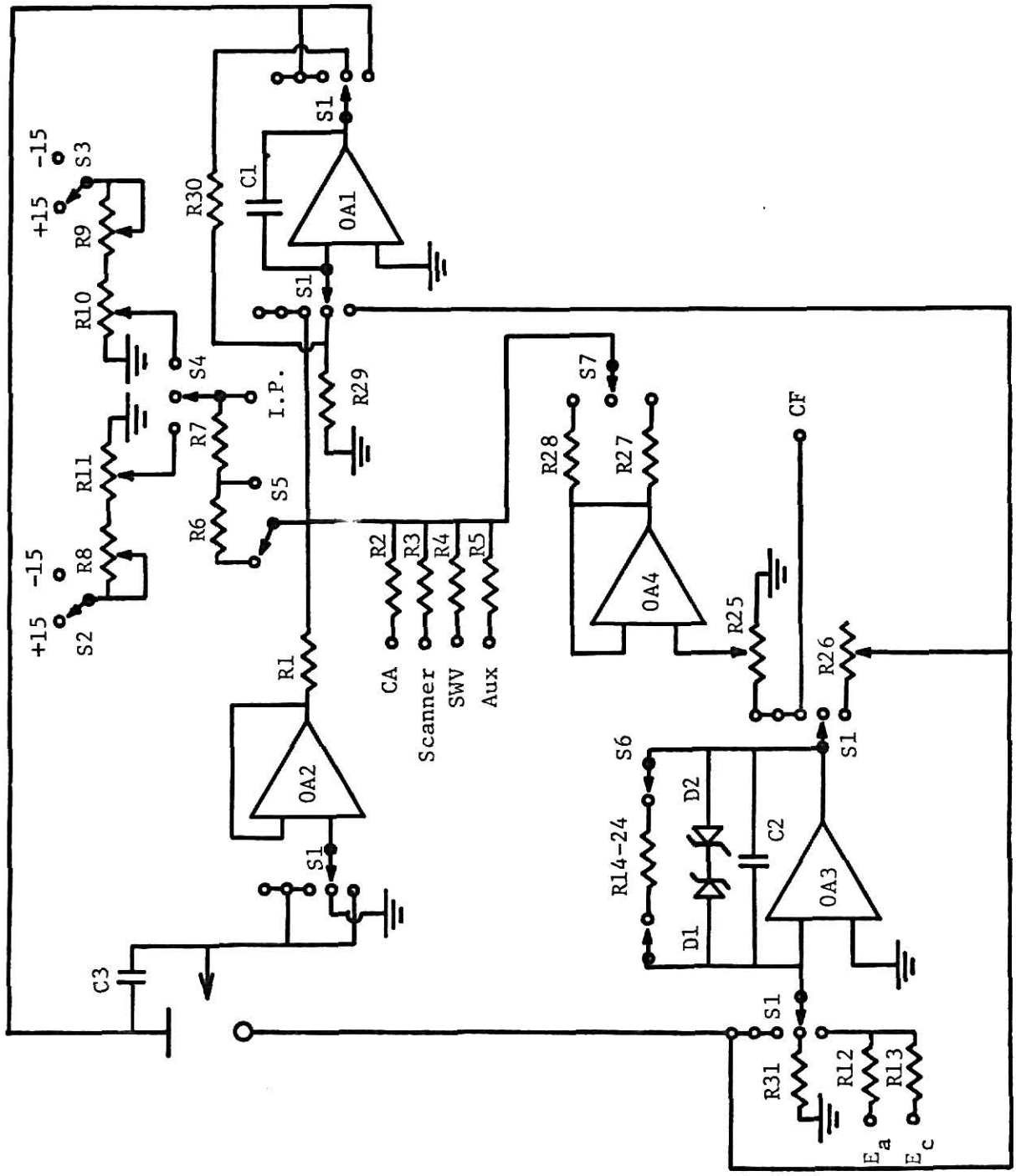
PLATE 1


+15
-15
S3
R9
R10
S4
R11
R8
S2
R30
C1
S1
OA1
R29
I.P.
R7
S5
R6
R2
R3
R4
R5
CA
Scanner
SWV
Aux
R1
OA2
C3
S7
R28
R27
OA4
CF
R25
R26
S6
R14-24
D2
D1
C2
OA3
R31
R12
R13
E_a
E_c

meter setting (R25) when the current range resistor (R14-24) is varied. The output bound across the current follower allows full current output when the output voltage of this amplifier exceeds 10 volts(5). This modification is especially necessary in chronoamperometric and square wave voltammetric studies because of the large, transient current requirements which are encountered when the electrode potential is changed abruptly. Placement of capacitors C1-3 for the stabilization of the potentiostat under conditions of 100% iR compensation follows the suggestions of Brown, Smith and Booman(6).

With the master control switch in the galvanostatic mode (position 5), amplifier OA3 now functions as an adder. Current through the cell is determined by the sum of the voltages applied to the input resistors of the adder (R12-13), the ratio of the feedback resistor (R14-24) to the input resistors, and the resistance of the potentiometer (R26) between the adder (OA3) and the working electrode. The circuit is most useful for current reversal chronopotentiometry. Unequal current programming, which is especially advantageous in homogeneous kinetic studies(7), can be obtained readily by varying the ratio of the applied voltages, E_a and E_c (vide infra).

Control Logic

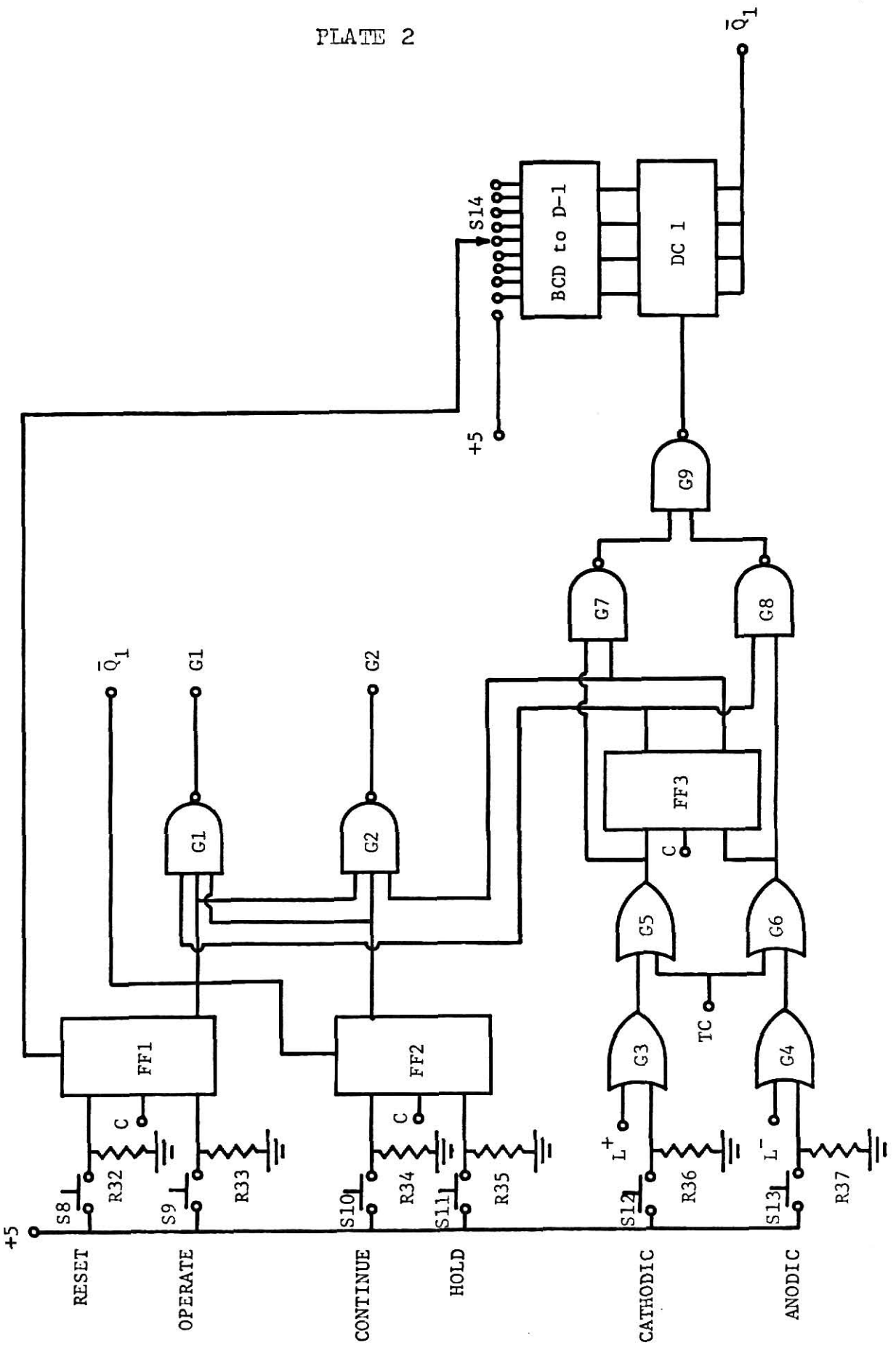
The control of the function generator is provided by the circuit shown Plate 2. The control logic determines whether the electrochemical experiment should proceed in an anodic or in a cathodic direction, provides a means of temporarily interrupting

PLATE 2

Control Logic

FF1, FF2, FF3, 1/2 MC853P; G1-2, 1/3 MC863P; G3-6, 1/4 MC1809P; G7-9, 1/4 MC849P; DC 1, MC838P; BCD to D1, MC7442P; S8-13, spst, Grayhill 40-1; S14, spl0t; R32-37, 470 Ω, 5%.

PLATE 2


$\bar{Q}_1$
S14
BCD to D-1
DC 1
+5
G9
G7
G8
$\bar{Q}_1$
G1
G2
FF3
C
G1
G2
G5
G6
TC
FF1
FF2
G3
G4
C
C
L^+
L^-
+5
S8
R32
S9
R33
S10
R34
S11
R35
S12
R36
S13
R37
RESET
OPERATE
CONTINUE
HOLD
CATHODIC
ANODIC

an experiment, counts the number of half cycles, and finally, resets the instrument to a prescribed set of initial conditions after the electrochemical experiment has been completed. The logic elements are all DTL and TTL integrated circuits where a logical "1" corresponds to +5V and a logical "0" corresponds to 0V.

The explanation for the operation of the control logic assumes that the instrument is initially in the RESET condition; i.e., $\bar{Q}_1$ of flip-flop 1 (FF1) is a logical "0". RESET directly sets a logical "1" at Q_2, thereby placing FF2 in the CONTINUE mode of operation. In addition, the logical "0" at $\bar{Q}_1$ places the outputs of NAND gates G1 and G2 high, causing the anodic and cathodic voltage generators to be inhibited (vide infra).

Initiation of the electrochemical experiment is made by the application of a logical "1" (OPERATE) to the K input of FF1. On the clock pulse, the logical "1" is transferred to the inputs of gates G1 and G2. Depending upon the state of FF3, the output from one of the triple NAND gates (G1 or G2) will be a logical "0" while the output of the other gate will remain a logical "1". Thus, in the OPERATE condition the state of FF3, whether anodic or cathodic, will determine which one of the voltage generators will be enabled and which one will be inhibited.

An interrupt in the electrochemical experiment occurs when a logical "1" appears at the K input of FF2 (HOLD). Since this causes Q_2 to become a logical "0", outputs of both G1 and G2 will be a logical "1". As previously discussed, this condition turns both the anodic and the cathodic voltage generators off. The

experiment can be continued, with no change in direction, by the application of a logical "1" (CONTINUE) to the J input of FF2.

The direction of the electrochemical experiment, either anodic or cathodic, is controlled by OR gates G3-6 and FF3. The presentation of a logical "1" either to the complementary input or simultaneously to both the J and K inputs of FF3 causes a logical "1" to appear at the complementary output on the next clock pulse. The change in state of FF3 causes a corresponding change in state in the anodic and the cathodic control gates, G1 and G2, which in turn cause the anodic voltage generator to be switched on and the cathodic voltage generator to be switched off or vice versa.

The presentation of a logical "1" to the inputs of OR gates G3-6 can be achieved manually by switches S12 and S13, by the anodic and cathodic voltage limit detectors, or by the timing circuit. The direction of the electrochemical experiment can be changed either by the timing circuit or by manual control as long as the cell potential is between the selected voltage limits. The voltage limit detection circuit, shown in Plate 3, consists of an adder (OA5) and two comparators (OA6 and 7). The anodic and cathodic limits can be varied independently by potentiometers R48 and R57 and, if desired, may be both set on the same side of the initial potential by switches S15 and S16. The only restriction is that the cathodic voltage limit must <u>always</u> be negative with respect to the anodic voltage limit. Switch S17 varies the gain of the adder, thereby providing maximum voltage limits of ± 1, ± 2, and ± 4 V when the absolute magnitude of the

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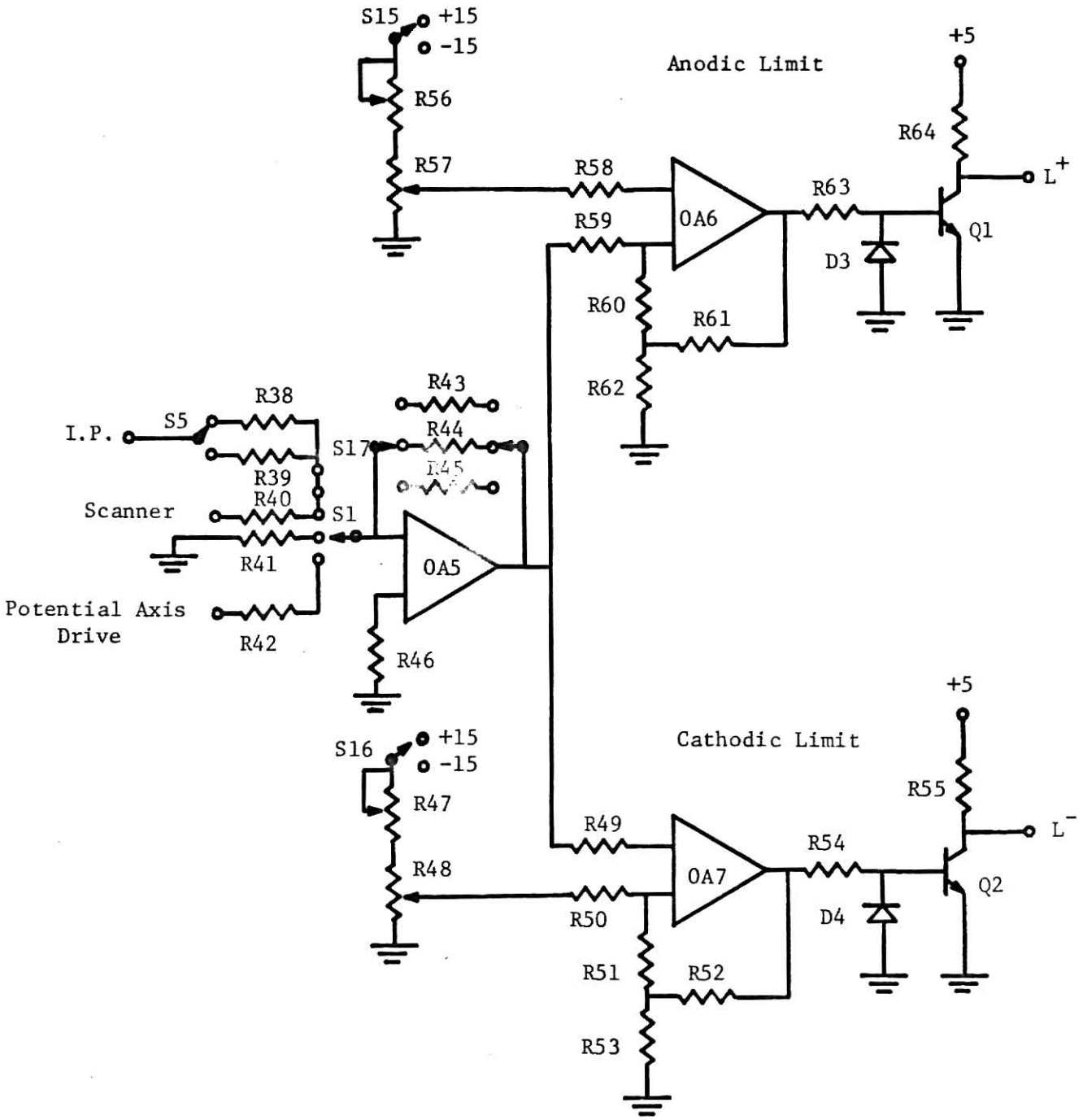
ILLEGIBLE

PLATE 3

Voltage Limit Detection

OA5-7, MC1741CP; S15-16, spdt, toggle; S17, dp3t, shorting;
1-2, MPS6513; D3-4, IN457A; R40-43, R49-52, R58-61, 100KΩ;
38, 1MΩ; R39, 500KΩ; R44, 50KΩ; R45, 25KΩ; R46, 27KΩ, 5%;
53, R62, 180Ω, 5%; R54, R63, 2.7KΩ, 5%; R55, R64, 4.7KΩ,
%, R47, R56, 50KΩ trimpot; R48, R57, 1KΩ, 10-turn potentiometer.
ot shown in the figure are the power supply connections and the
iasing networks for the operational amplifiers.

PLATE 3


S15
+15
-15
R56
R57
R58
Anodic Limit
+5
R64
L+
R63
R59
OA6
Q1
D3
R60
R61
R62
R43
R38
S5
I.P.
R44
S17
R45
R39
R40
Scanner
S1
R41
OA5
Potential Axis Drive
R42
R46
S16
+15
-15
R47
R48
Cathodic Limit
+5
R55
L-
R49
R54
OA7
Q2
D4
R50
R51
R52
R53

voltage drop across R48 and R57 is 2.0 and 0.5V, respectively.

It should be emphasized that the voltage applied to the comparators is from an adder such as OA5 rather than from the voltage follower, OA2. The use of a separate adder obviates the problem which a varying amount of positive feedback would have on the switching limits if the output from the voltage follower were used.

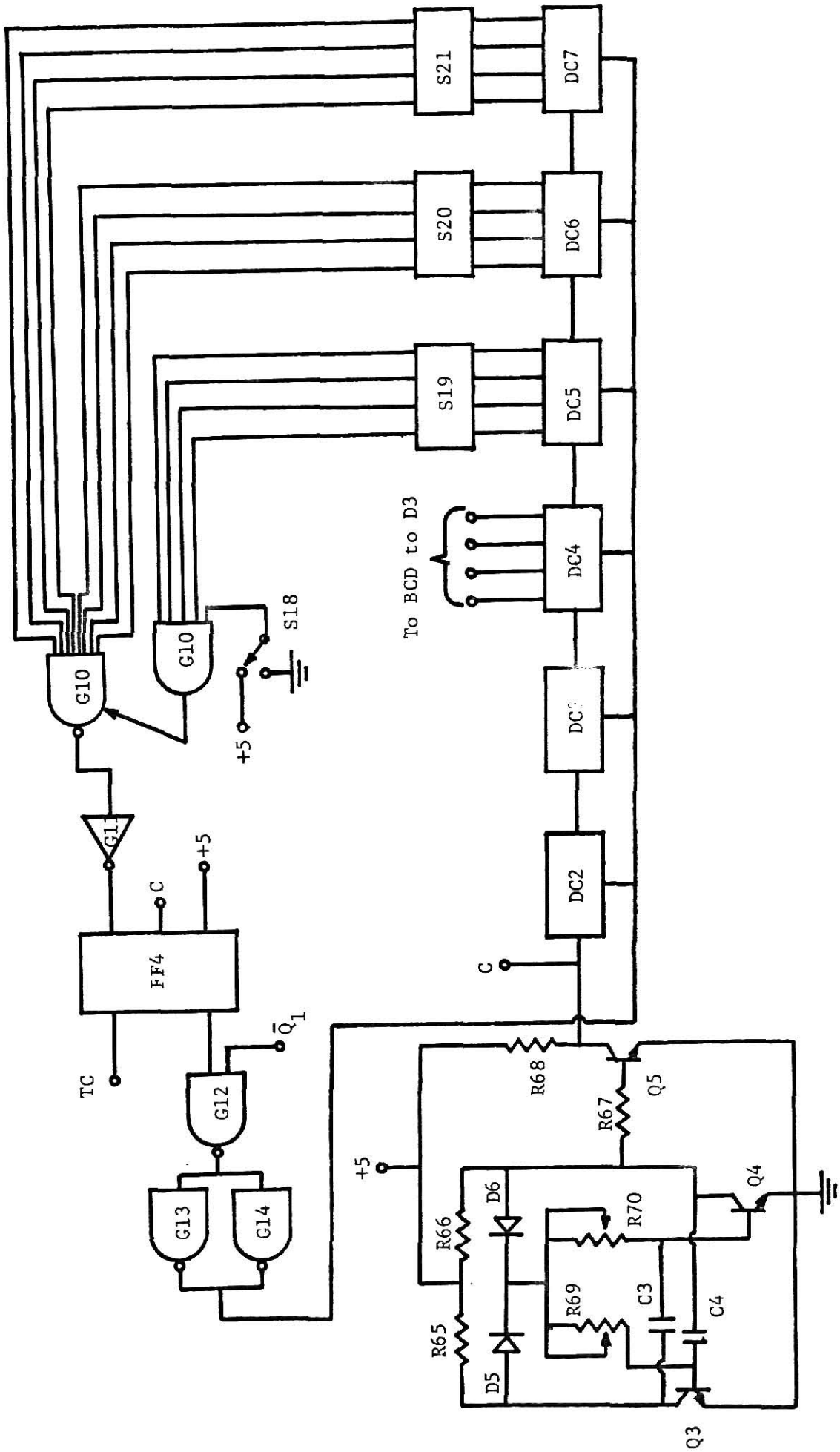
In normal operation, the potential difference between the reference and working electrodes is at some value between the anodic and cathodic voltage limits. Since both comparators are saturated at their positive limits in this condition, the outputs of transistors Q1 and Q2 are a logical "0". When a voltage limit is attained, the output from the appropriate comparator is clamped near ground by either D1 or D2, which results in the appearance of a logical "1" at the DTL interface. As seen previously, the presentation of a logical "1" to the complementary input of FF3 by G3 or G4 causes the outputs of FF3 to change state with a concomitant change in the operation of the anodic and cathodic voltage generators.

The switching of the anodic and cathodic voltage generators for chronopotentiometric and chronoamperometric studies is achieved by the timing circuit shown in Plate 4. The 100 KHz clock is counted down by six series-wired decade counters. The outputs of the last three decade counters are decoded on 4pl0t switches which serve to select the half-cycle duration. The minimum half-cycle duration which may be selected from the combination of switch settings is 10 msec while other values of

PLATE 4

Timing Circuit

G11-14, 1/4 MC857P; G10, MC1803P and MC833P; DC2-7, MC838P; Q3-5, MPS6513; FF4, 1/2 MC853P; D5-6, IN457A; S18, spdt, toggle; S19-21, 4p10t; C4-5, 220pf; R65-67, 10KΩ, 5%; R68, 4.7KΩ, 5%; R69-70, 20KΩ, trimpot.


S21
DC7
S20
DC6
S19
DC5
To BCD to D3
DC4
S18
G10
G10
+5
G1
C
+5
FF4
TC
$\bar{Q}_1$
G12
G13
G14
C
DC2
R68
R67
Q5
+5
D6
R66
R70
Q4
R69
C3
C4
R65
D5
Q3

time may be selected in increments of 10 msec up to a maximum of 9.99 sec. When G10 is enabled by S18 and the predetermined count is attained on the decade counters, each input to expanded gate G10 is presented with a logical "1". The logical "1" is then transmitted to FF4 which changes state on the next clock pulse. The logical "1" now at Q_4 effects the reset of the decade counters to a count of zero via power NAND gates G12-14 and toggles FF3, causing the anodic and cathodic voltage generators to change state. The counting process can then either be repeated as many as eight more times before the experiment is terminated or may be allowed to continue indefinitely (S14).

Chronoamperometric, chronopotentiometric, and cyclic voltammetric studies frequently require that an experiment contain an exact number of half cycles. For example, it is often desired in cyclic voltammetry that exactly two full cycles be recorded. Although manual control is possible if the duration of the experiment is several seconds, studies of shorter duration require both a counter to count the number of half cycles and a means to terminate the experiment. The circuit to perform this function consists of gates G7-9, FF3, a decade counter, and a BCD to D decoder (Plate 2).

The presentation of a logical "1" either to G3 or G4 by either the voltage limit detection circuit or switches S12 and S13 or to G5 and G6 concurrently by the timing circuit causes a logical "1" to be presented to NAND gate G7 or G8. The logical "1", which remains at the input of the NAND gate until FF3 changes state, is then transmitted via NAND gate G9 to the decade counter.

Operator selection of the number of half cycles (SELECT COUNT) is made by S14. The "1" to "0" transition which occurs when the counter reaches the predetermined count causes an immediate override of the synchronous inputs of FF1 and a change in states of Q_1 and $\bar{Q}_1$. The logical "0" which is now present at $\bar{Q}_1$ causes the anodic and cathodic voltage generators to be turned off (via NAND gates G1 and G2) and resets the decade counter to zero in preparation for the next experiment.

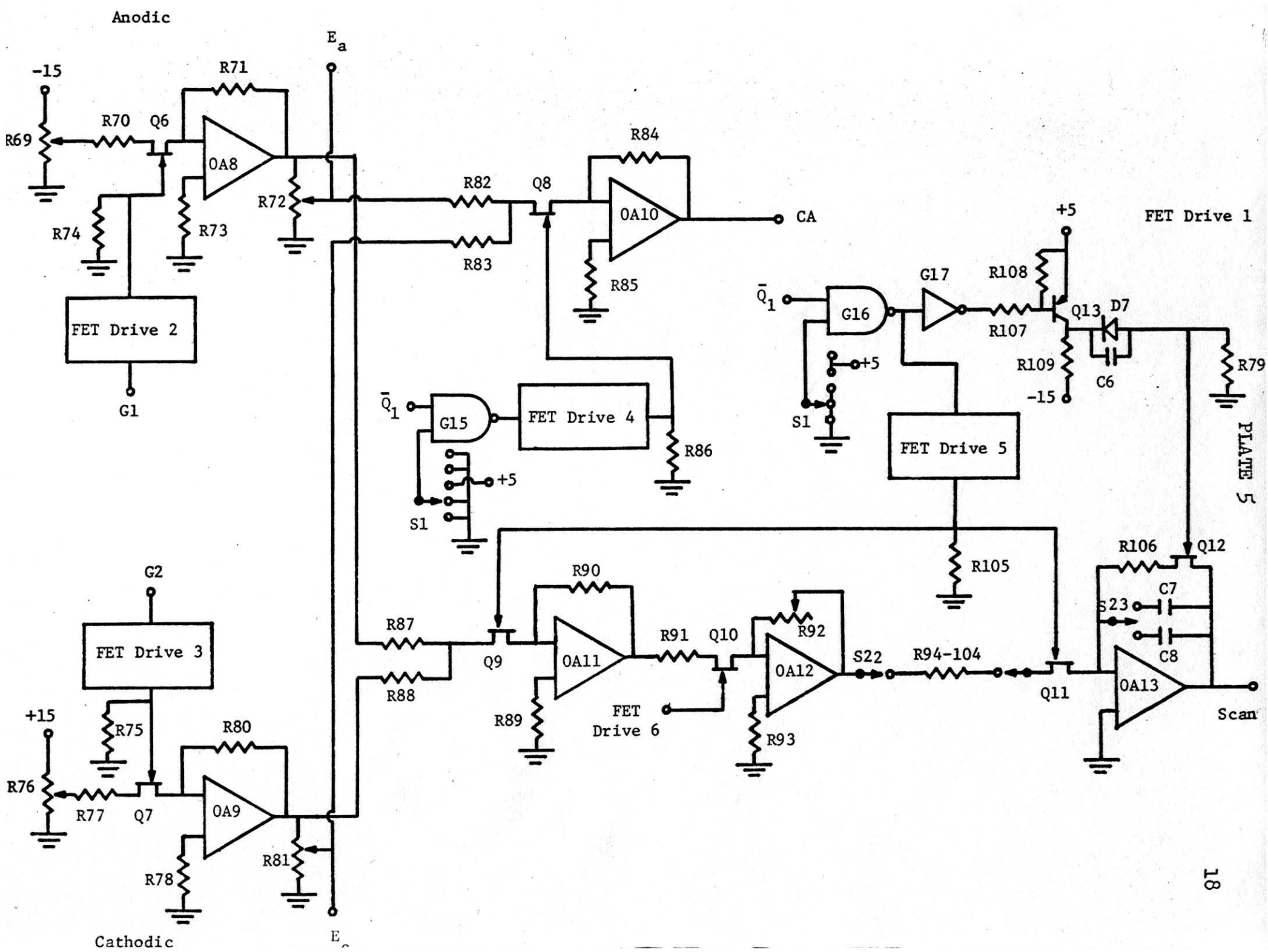
Function Generator

The function generator shown schematically in Plate 5 consists of the anodic (OA8) and cathodic (OA9) voltage generators, two adders (OA10 and 11), an inverter (OA12), and an analog integrator (OA13). When the control logic is in the RESET condition, the outputs of G1 and G2 of the control logic circuit are a logical "1", which cause FET drivers 2 and 3 to switch FETs Q6 and Q7 to the inverting inputs of the voltage generators off. Since the off resistance of the FET switch is extremely large compared to the 1K resistance in the feedback loops of the voltage generators, the gain of both amplifiers will be zero and the output from operational amplifiers 8-13 will each be 0.000V. When the control logic is switched to the OPERATE condition, one or the other of the FET switches will be turned on, changing the gain of that operational amplifier from zero to a value near unity. The outputs of the anodic and cathodic voltage generators are subsequently adjusted to -1.000 and +1.000V, respectively, by trimpots R69 and R76.

PLATE 5

Function Generator

Q6-12, 2N4860; Q13, MPS3703; OA8-12, MC17141CP; OA13, 40J (Analog Devices); D7, 1N914; G15-17, 1/4 MC849P; S22, dp11t; S23, spdt, toggle; C6, 56pf; C7, 10 uf, polystyrene; C8, 0.1 uf, polystyrene, matched with C7; R70-71, R77, R80, R87-88, R90-91, 10KΩ, 1%; R82-83, R104, 100KΩ, 1%; R94, 10MΩ, 1%; R95, 5MΩ, 1%; R96, 3.33 MΩ, 1%; R97, 2MΩ, 1%; R98, 1.43 MΩ, 1%; R99, 1MΩ, 1%; R100, 500KΩ, 1%; R101, 333KΩ, 1%; R102, R84, 200KΩ, 1%; R103, 143KΩ, 1%; R69, R76, 2KΩ, trimpot; R72, R81, 10-turn potentiometer, 1KΩ; R92, 20KΩ, trimpot; R74-75, R86, R105, 100KΩ, 5%; R73, R78, R93, 4.7KΩ, 5%; R89, 3.3KΩ, 5%; R85, 43KΩ, 5%, R79, 1MΩ, 5%; R107-109, 10KΩ, 5%. FET Drives 2-5 are identical to FET Drive 1. Not shown in this figure are the power supply connections and the biasing networks for the operational amplifiers and the gates.


Anodic
E_a
-15
R71
R69
R70
Q6
0A8
R72
R74
R73
R82
Q8
R84
0A10
CA
R83
R85
FET Drive 2
G1
$\bar{Q}_1$
G15
FET Drive 4
R86
+5
S1
FET Drive 1
+5
G17
R108
$\bar{Q}_1$
G16
R107
Q13
D7
R109
C6
-15
S1
FET Drive 5
R79
PLATE 5
R105
R106
Q12
G2
R90
C7
S23
FET Drive 3
R87
R91
Q10
R92
C8
Q9
0A11
0A12
S22
R94-104
Q11
0A13
Scan
R88
R89
FET
Drive 6
R93
+15
R75
R80
R76
R77
Q7
0A9
R81
R78
Cathodic
E_c
18

Potentiometers R72 and R81 serve to determine the magnitudes of the potential steps in a chronoamperometric experiment as well as to determine the anodic and cathodic currents in cyclic chronopotentiometry. Consider first the chronopotentiometric mode of operation. If it is assumed that the gain of the adder amplifier (OA3) in Plate 1 is unity, then the cell currents are given simply by the voltage settings on potentiometers R72 and R81 and the value of the resistance (R26) between the output of OA3 and the working electrode. There are two distinct advantages of this particular generator. First, the cathodic and anodic currents can be varied independently, thus facilitating current reversal chronopotentiometric studies of homogeneous chemical reactions. And second, since the cell current is switched electronically, the deleterious effect which would be observed if the auxiliary and working electrode were shorted momentarily by a mechanical switch is avoided(8,9).

In order to perform a single or double potential step chronoamperometric experiment, NAND gate G15 must first be enabled by the master control switch, S1. Thus, when FF1 of the control logic is placed in the OPERATE condition ($\bar{Q}_1$ = "1"), the FET switch to OA10 will be turned on, allowing a voltage other than zero to appear at the output of the operational amplifier. Since the gain of the operational amplifier is 2.000 in this particular circuit, the magnitudes of the anodic and cathodic potential steps can be varied separately by potentiometers R72 and R81 from 0 to $\pm$ 2 volts.

The enabling of G16 by the master control switch allows one

to perform a cyclic voltammetric experiment. With the control logic in the OPERATE condition, the FET switches to the inputs of operational amplifiers OA11-13 are turned on, while the FET switch in parallel with the capacitor in the feedback loop of the analog integrator is turned off. As long as the control logic remains in the OPERATE and the CONTINUE conditions, an output voltage of + or - 1.000V is provided by either the cathodic or the anodic voltage generator, respectively. The voltages from the generators are summed by OA11 and adjusted slightly by OA12 to correct for deviations of the two matched integrating capacitors from their nominal values. Scan rates varying from 0.01 to 100 V/sec in 22 steps can be obtained by the appropriate selection of input resistor (S22) and integrating capacitor (S23). Although this range of scan rates is adequate for our studies, the circuit can be readily modified to obtain virtually any scan rate which may be desired.

The scan may also be interrupted and the integrator voltage held at any desired point by the presentation of a logical "1" to the K input of FF2. As seen previously, the HOLD condition causes the anodic and cathodic voltage generators to be inhibited, but does not alter the condition of the FET switches on amplifiers 11-13. The scan can be restarted from the point of interruption by the presentation of a logical "1" to the J input of FF2 by S10. At the completion of the cyclic voltammetric experiment, the control logic is switched from the OPERATE to the RESET condition. This change in condition causes the FET switches to the inputs of OA11-13 to be turned off and the FET switch in parallel to the

integrator capacitor (C7 or 8) to be turned on, thereby resetting the output of OA13 to zero in preparation for the next experiment.

Square Wave Voltammetry

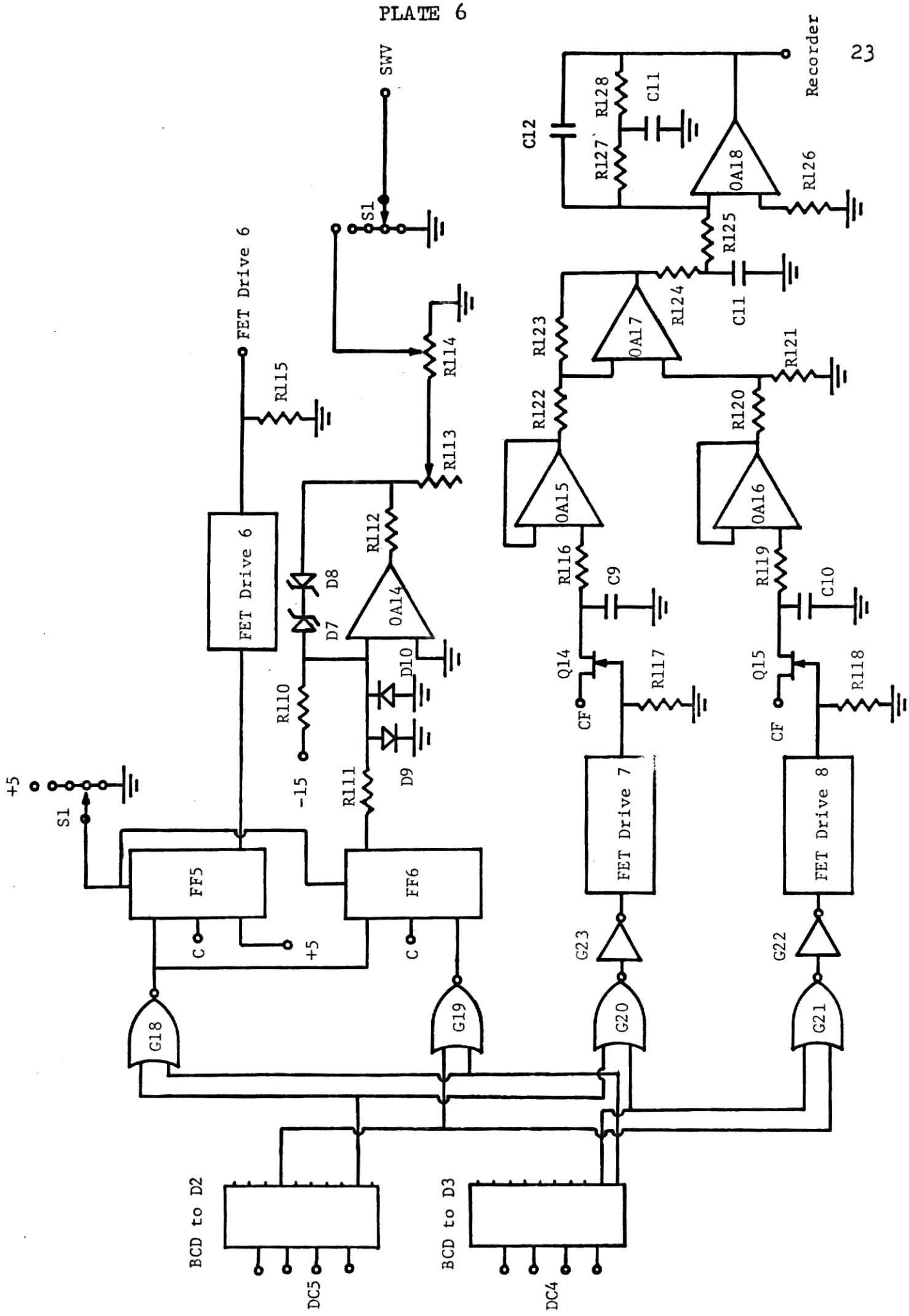
The theory of square wave voltammetry and its analytical application have been reported recently by Ramaley and Krause(5, 10). The demonstrated sensitivity of this technique, its excellent resolution, and its applicability to all stationary electrode surfaces suggest that square wave voltammetry will probably be the most useful of the several electrochemical methods for multicomponent and trace analysis studies.

The square wave generator, current measuring circuits, and the additional logic required to perform this function are shown in Plate 6. The staircase potential generator, which will be discussed first, utilizes the triangular wave generator of Plate 5, the timing circuit of Plate 4, the control logic of Plate 2, and the BCD to D decoders, NOR gate G18, and FF5 of Plate 6. Upon initiation of the square wave voltammetric experiment, count from decade counters 4 and 5 is decoded by the two BCD to D decoders of Plate 6. When the count from these decoders is "10", NOR gate G18 is presented with a logical "0" at both inputs. FF5, which has its synchronous inputs overridden in all modes of operation except square wave voltammetry, toggles on the next clock pulse, placing a logical "1" and a logical "0" at Q_5 and $\bar{Q}_5$, respectively. Since a logical "0" at $\bar{Q}_5$ will turn on the FET switch to the input of operational amplifier OA12 of Plate 5, the

PLATE 6

Square Wave Voltammetry

BCD to D2, BCD to D3, MC7442P; OA14, OA17-18, MC1741CP; OA15-16, LM210 (National); G18-21, 1/4 MC1810P; G22-23, 1/6 MC836P; Q14-15, 2N4860; D7-8, IN5240B; D9-10, IN194; FF5-6, 1/2 MC853P; C9-10, 1 uf, polycarbonate; C11, 1 uf; C12, 0.5 uf; R110, 1MΩ; R112, R116, R119, 2KΩ; R111, R115, R117-118, 100KΩ; R120-R123, 10KΩ, 1%; R124, R125, 220KΩ; R126, 270KΩ; R127, 300KΩ; R128, 470KΩ; R113, 20KΩ, trimpot; R114, 500Ω, 10-turn potentiometer. All fixed resistors are 5% tolerance unless otherwise noted. The power supply connections and biasing networks for the operational amplifiers are not shown.


SWV
S1
FET Drive 6
R115
R114
R113
R112
D8
D7
OA14
D10
D9
R110
R111
-15
+5
S1
FF5
FF6
C
+5
C
G18
G19
BCD to D2
DC5
BCD to D3
DC4
FET Drive 6
C12
R128
C11
R127
OA18
R126
Recorder
R125
R124
C11
R123
OA17
R121
R122
R120
OA15
OA16
R116
C9
R119
C10
Q14
R117
CF
Q15
R118
CF
FET Drive 7
FET Drive 8
G23
G22
G20
G21

triangular wave generator will operate only until the count of "11" appears on the decoders. The result is a staircase waveform with a frequency of 10 Hz and a potential-step size which is dependent upon the sweep rate of the triangular wave generator.

The connections between the decoders and the NOR gates are selected to give a logical "1" at the outputs of G18 and G19 on counts of "10" and "60", respectively. Thus, on these counts, FF6 changes state, causing OA14 to alternately switch from one 10V limit to the other. The voltage resulting from this 10Hz oscillator is then attentuated by potentiometer R113 so that the square wave amplitude across R114 is exactly one volt. Since the 100 K resistor (R4) in the bridge network of the control amplifier causes the signal to be attenuated by another factor of 10, any potential between 0 and 100 mv may be selected by potentiometer R114 for the square wave amplitude.

Measurement of the square wave current occurs one millisecond after each change in the square wave potential. Thus, on counts of "11" and "61" from the decoders, the FET switches to the two sample-and-hold amplifiers (OA15-16) are alternately switched on for exactly one msec to measure the output voltage of the current follower. The difference in output voltage of the two sample-and-hold amplifiers is then measured by the differential amplifier, OA17, filtered, and recorded by an x-y recorder.

Potential-Axis Drive, Time-Base, and Integrator Circuits

Since the output of the voltage follower in the potentiostatic mode is a function of the cell current, a separate ampli-

fier (Plate 7a) is required to present the corrected potential of the reference electrode for recording. The gain of the adder (OA19) which serves this purpose can be varied by S24.

The circuit of Plate 7b provides a time-based voltage for the drive of the x-y recorder for chronoamperometric, chronopotentiometric, and chronocoulometric studies. The rate of the voltage sweep may be varied in a 1-2-5-10 sequence, or turned off entirely by selector switch S25. The time base is activated by switching Q16 off with the application of a logical "1" to the FET driver circuit by $\bar{Q}_1$ (OPERATE). The time base is reset to zero in preparation for the next experiment upon the receipt of the RESET command at FF1 of the control logic.

A similar circuit (Plate 7c) is used for integration of the current in chronocoulometric studies. With S26 in the operate condition, the analog integrator is activated by switching Q17 off. Integration of the signal from the current follower continues until the RESET command is given to the control logic by either the SELECT COUNT circuit of the control logic or manually via S8 to the J input of FF1.

Power Supplies

The ± 15V power supply, a Philbrick Model PR-300R, is rated at 300 ma with a stability of 0.01% and a maximum noise and ripple of 250 uV, p-p. This supply serves as the source of all reference voltages in the instrument. The 5V power supply for the DTL and the TTL integrated circuits was constructed with a LM209K (National Semiconductor) as the voltage regulating element (11).

PLATE 7

(A)

Potential-Axis Drive

OA19, MC1741CP; S24, dp3t, shorting; R129, 1MΩ; R130, 500KΩ; R131-134, 100KΩ; R135, 50KΩ; R136, 25KΩ; R137, 25KΩ, 5%. All fixed resistors are 1% tolerance unless otherwise noted. Power supply and bias network connections to OA19 are not shown.

(B)

Time Base

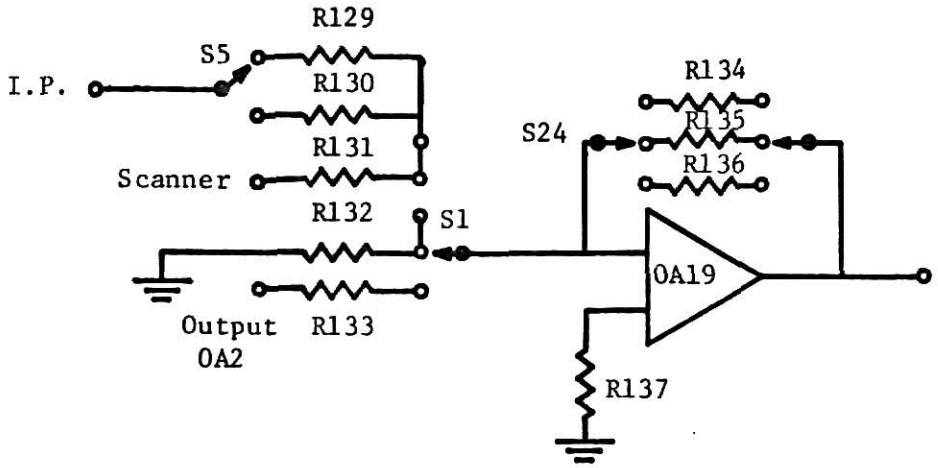
OA20, 40J (Analog Devices); Q16, 2N4860; S25, dp5t; R138, 20KΩ, 5%; R139, 500Ω, trimpot; R140, 1MΩ, 5%; R141, 1MΩ; R142, 500KΩ; R143, 200KΩ; R144, 100KΩ; R145, 1KΩ, 5%; C13, 1 uf, polystyrene. All fixed resistors are 1% tolerance unless otherwise noted. Power supply and bias network connections to OA20 are not shown.

(C)

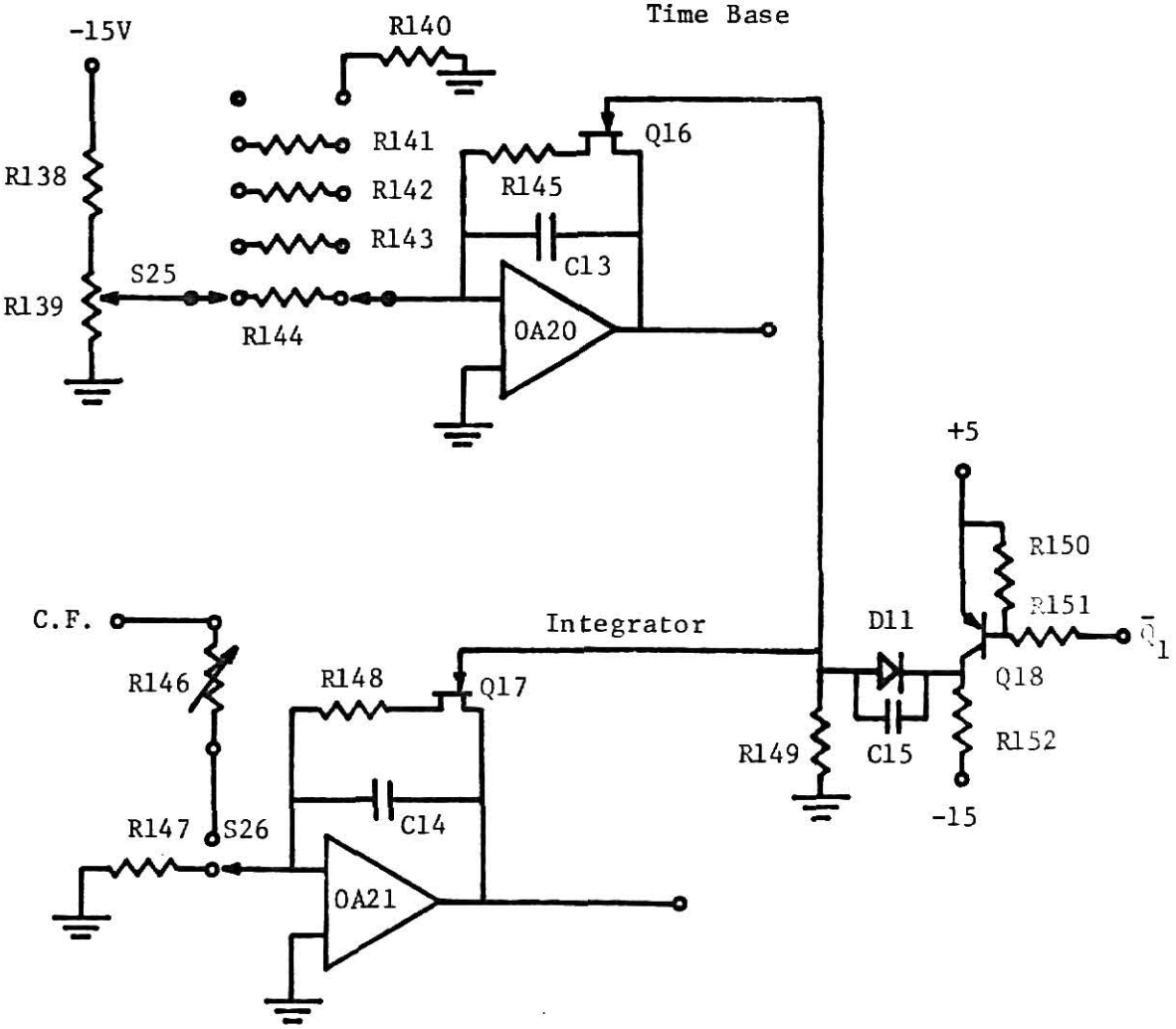
Integrator

OA21, 40J; Q17, 2N4860; Q18, MPS3703; D11, IN914; C14, 1 uf, polystyrene; C15, 56pf; S26, spdt; R146, Heath EUW-30; R147-148, 1KΩ, 5%; R150-152, 10KΩ, 5%; R149, 100KΩ, 5%. Power supply and bias network connections to OA21 are not shown.

Potential-Axis Drive



Time Base



The 165V power supply for the integral lighted swithces (S8-13) is noncritical.

Evaluation of Square Wave Voltammetry

The development of square wave polarography by Barker(12,13) has become well established as an analytical technique, especially in trace analysis. This technique has had applied to it the multitude of modifications and adaptations as has any instrumental technique. The theory of pulse polarography has recently been summarized by Burge(14).

Ramaley and Krause presented both theory (10) and experimental data (5) that indicate very significant improvements by summing a square wave potential and a staircase potential to yield a staircase-square-wave. They propose that the electroanalytical method be called square wave voltammetry (SWV). Square wave voltammetry has been shown to offer the advantages of square wave polarography and yet may be accomplished in much shorter periods of analysis time.

Among the additional advantages of square wave voltammetry are: (1) increased sensitivity, (2) shorter analysis time, and (3) the ability to use stationary electrodes. Since one is no longer restricted exclusively to the dropping mercury electrode, a large number of oxidation studies which were previously precluded because of the ease of mercury oxidation are now feasible on solid electrode surfaces. Also, electrode noise such as has become encountered due to mercury streaming through the capillary is avoided.

Experimental

The previously discussed instrument incorporates many desirable features such as the three-electrode system, bound output current follower amplifier, and sample-and-hold measuring circuits. The output of the sample-and-hold circuits is measured differentially, the differential output passed through a 1 Hz filter amplifier and displayed by an x-y recorder.

The electrode systems utilize the saturated calomel electrode (SCE) as the reference electrode, a hanging mercury drop (HMDE), a platinum button or carbon paste as the working electrode, and a platinum wire or a carbon rod as the auxiliary electrode. The saturated calomel electrode (15) and carbon paste electrode (16) were prepared as given by Adams and the hanging mercury drop electrode was prepared according to Shain(17).

All chemicals used were reagent grade, without purification, and solutions were prepared using water distilled from alkaline-permanganate. Nitrogen used for deaeration was standard grade, water-pumped gas without additional treatment.

Comparison of Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV)

A stock solution of 10^{-3}M o-dianisidine was prepared in 1M H_2SO_4 and a cyclic voltammogram was run to determine the reversibility of the electrochemical couple. As can be seen from Plate 8, the difference between $E_{p,a}$ and $E_{p,c}$ is approximately 27-28 mv, which compares favorably with the theoretical value of

28 mv for a two-electron reversible process (18)

The instrument was changed to the square wave voltammetry mode and a square wave voltammogram (Plate 9) obtained with the same solution. The curve obtained indicates that there is approximately a sixty fold increase in sensitivity from the measuring technique alone.

Peak Current as a Function of Pulse Amplitude

The purpose of the next experiment was to obtain square wave voltammograms from one concentration of o-dianisidine solution while varying the potential step. Parry and Osteryoung(19) presented a theoretical derivation that indicates when $\Delta E/2$ becomes very large with respect to RT/nF the equation for the limiting current is reduced simply to the Cottrell expression. The peak differential current should remain constant with any further increase in pulse amplitude.

Data were taken at 10, 20, 40, 50, 60, and 80 mv steps. Plate 10 shows the experimental points of the differential peak current (i_p) plotted as a function of pulse amplitude. Under the experimental conditions $\Delta E/2$ approaches RT/nF at about 15-20 mv.

Effect of Pulse Amplitude on Peak Half Width

The peak half width ($W_{\frac{1}{2}}$) shall be defined as the width of the peak at one half its maximum height. The value of $W_{\frac{1}{2}}$ was determined for each of the above pulse amplitudes and plotted as a function of pulse amplitude (Plate 11). Extrapolation of this

PLATE 8

Cyclic Voltammogram of 10^{-3}M

o-dianisidine in 1M H_2SO_4

Scan rate -0.05V/sec; carbon paste working electrode.

PLATE 8

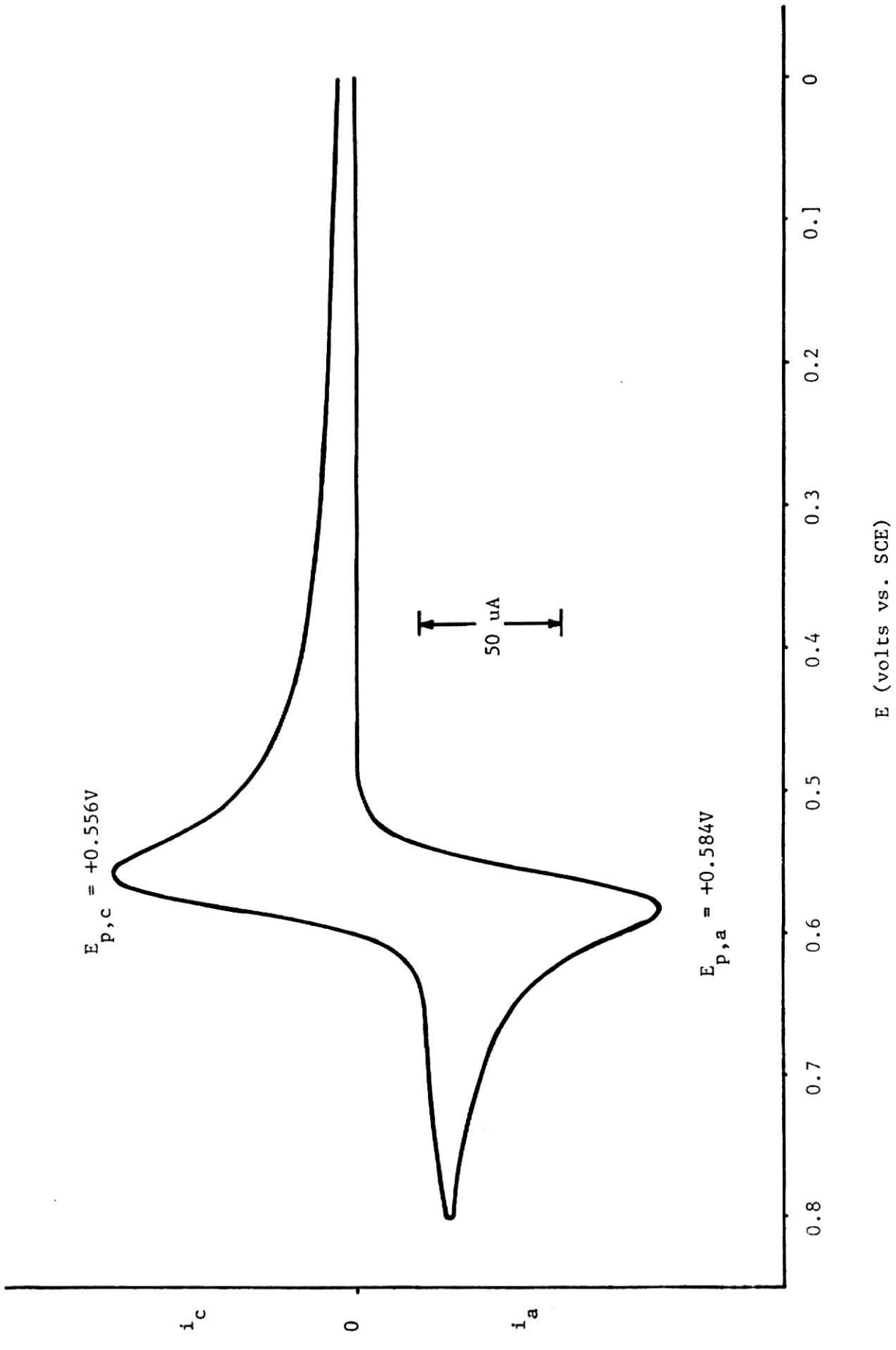

$E_{p,c}$ = +0.556V
$E_{p,a}$ = +0.584V
50 uA
i_c
0
i_a
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
E (volts vs. SCE)

PLATE 9

Square Wave Voltammogram of 10^{-3}M

o-dianisidine in 1M H_2SO_4

Scan rate - 0.002V/sec; carbon paste working electrod

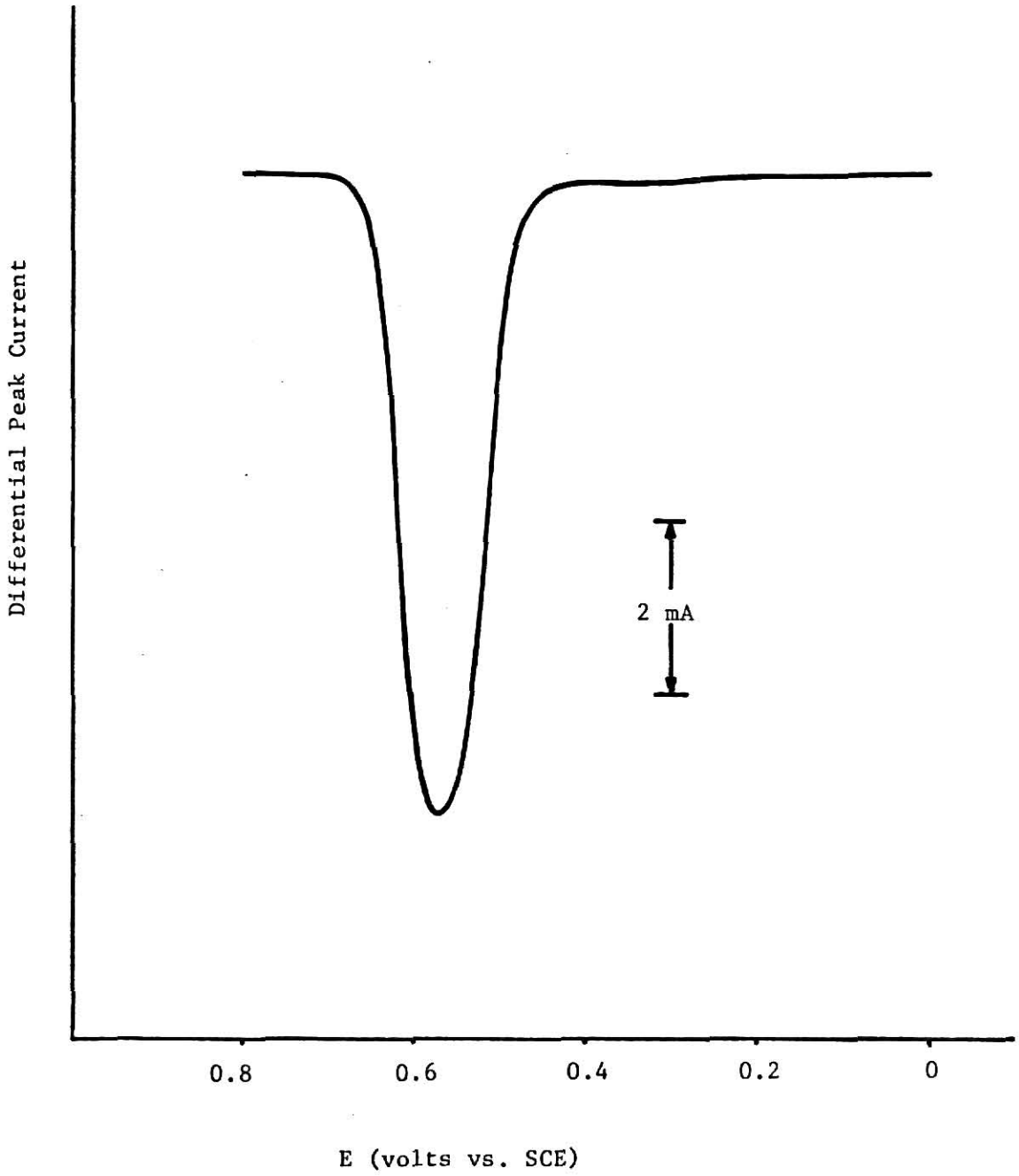
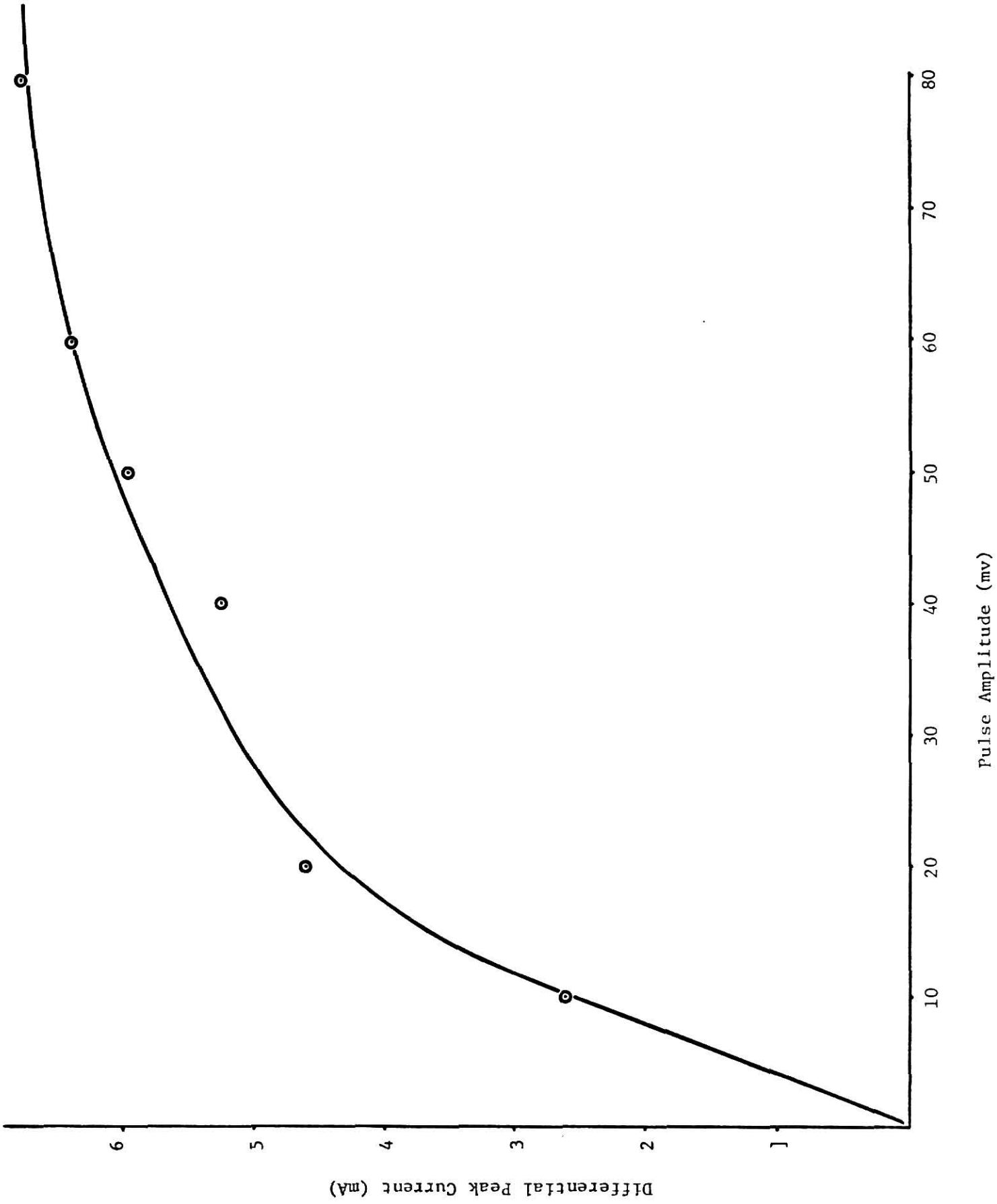

Differential Peak Current
2 mA
0.8
0.6
0.4
0.2
0
E (volts vs. SCE)

PLATE 10

Differential Peak Current as a Function of Pulse Amplitude for Solution 10^{-3}M o-dianisidine in 1M H_2SO_4

pulse(mv)	i_p(mA)
10	2.62
20	4.60
40	5.24
50	5.96
60	6.40
80	6.78

PLATE 10


Differential Peak Current (mA)
1
2
3
4
5
6
10
20
30
40
50
60
70
80
Pulse Amplitude (mv)

curve indiates that the minimum $W_{\frac{1}{2}}$ attainable is approximately 45 mv which is in agreement with the theory presented by Parry and Osteryoung. The expression for the peak half width, which is valid only for small pulse amplitudes, is $W_{\frac{1}{2}} = 3.52\ RT/nF$. Thus, at 25°C the equation gives peak half widths of 90, 45, and 30 mv for one, two, and three electron processes, respectively. It should be clear then that the peaks of two one-electron processes separated by 100 mv in $E_{\frac{1}{2}}$ cannot be completely resolved by any polarographic technique while with two or three electron processes whose difference in $E_{\frac{1}{2}}$ is 100 mv are resolvable.

The above should also indicate many desirable features of an instrument with a variable pulse amplitude, mainly the ability to permit the optimum selection of pulse amplitude for each analytical situation. It is highly desirable that experimental conditions be optimized to obtain maximum sensitivity yet retain adequate resolution.

Total Current as a Function of Pulse Amplitude

Since large pulse amplitudes were seen to result in broadening of the peak it is intuitively obvious that a better correlation could be made with total differential current plotted as a function of pulse amplitude. The result of such a plot is as expected (Plate 12). It can be easily seen now that since the peak current approaches some maximum with increasing pulse amplitude, then there must be considerable peak broadening with increasing pulse amplitude. This effect will inherently lead to loss of

PLATE 11

Plot of Peak Half Width ($W_{\frac{1}{2}}$) as a Function of Pulse Amplitude

pulse(mv)	$W_{\frac{1}{2}}$(mv)
10	50
20	55
40	88
50	105
60	125
80	168

Dashed curve calculated for a two-electron process, values taken from Parry and Osteryoung(19).

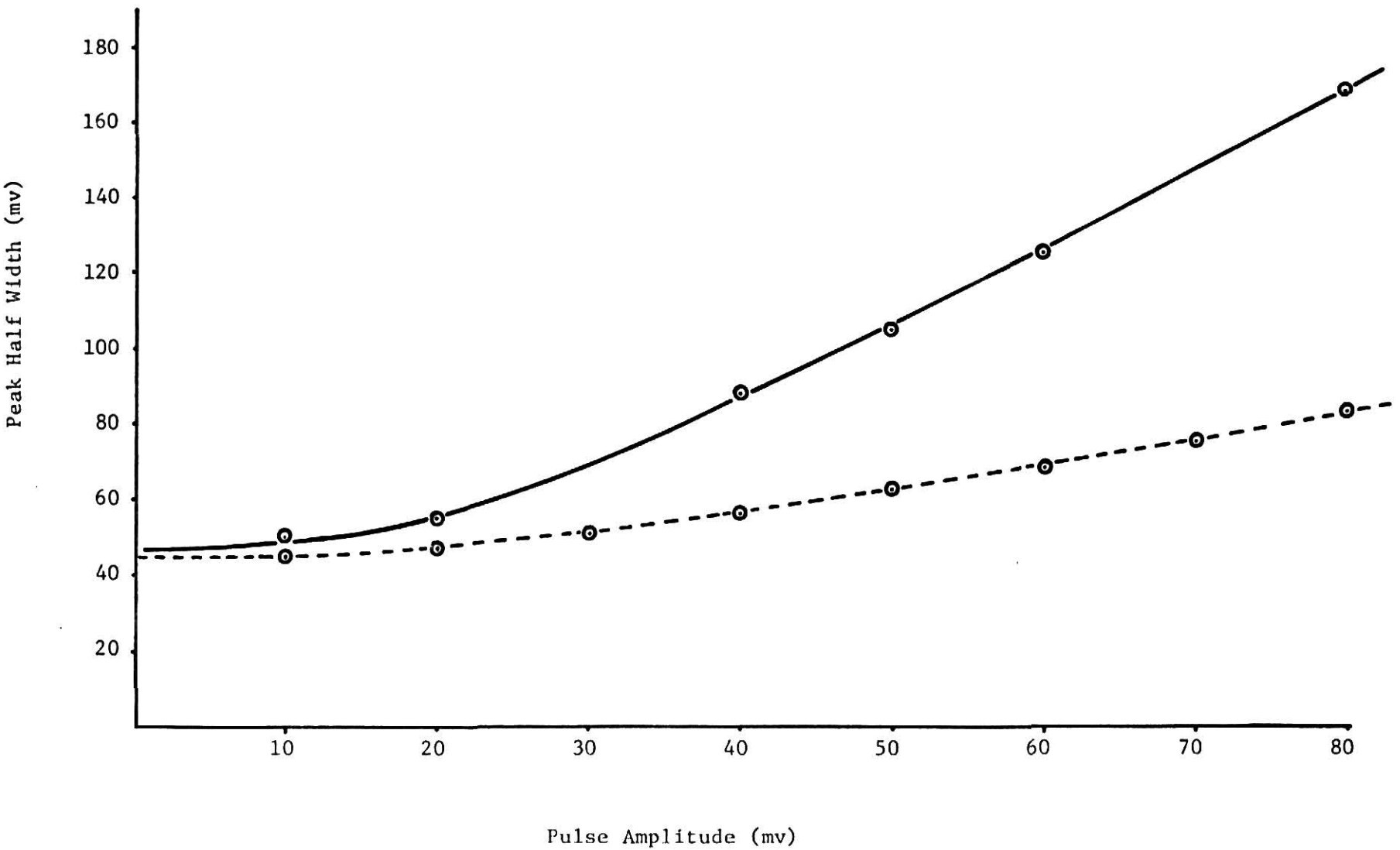

Peak Half Width (mv)
180
160
140
120
100
80
60
40
20
10
20
30
40
50
60
70
80
Pulse Amplitude (mv)

PLATE 11

resolution for multi-component waves if not checked. Thus, one needs to select the pulse amplitude that yields maximum peak current while maintaining the optimum peak width for the system of interest.

Linearity, Reproducibility and Sensitivity of SWV

As with any analytical technique, to be of significant value, the signal response must vary predictably with a change in concentration of the species being measured. Plate 13 shows data obtained by square wave voltammetry (50mv pulse amplitude) for two orders of magnitude dilution of o-dianisidine (10^{-3} to 10^{-5}M). Reproducibility of peak current for successive runs of the same solution was found to be within experimentally acceptable limits.

Attempts to run cadmium reduction waves quantitatively were not successful due to what was believed to be impurities in the reagent chemicals and/or the water pumped nitrogen used for deaeration. Waves were obtainable at the 100 ppb (10^{-6}M) and 50 ppb (5×10^{-7}M) levels (Plate 14) which indicates that this technique should compare favorably with stripping techniques (20) on the basis of sensitivity with both modes limited by purity of reagents. Krause and Ramaley(5) present detection limits of 1.1×10^{-7}M, 4.7×10^{-8}M (4.7 ppb Cd^{2+}), and 2.5×10^{-8}M for 1, 2, and 3 electron processes, respectively, of amalgam-forming metals. In addition, square wave voltammetry is much more desirable an analytical technique because: (1) there are fewer critical parameters that must be controlled and (2) the time of analysis is much shorter.

PLATE 12

Total Differential Current as a Function of Pulse Amplitude for Solution 10^{-3}M o-dianisidine in 1M H_2SO_4

pulse(mv)	area(sq. mm.)
10	189
20	376
40	648
50	860
60	1,040
80	1,290

PLATE 12

Peak Area in sq. mm.
200
400
600
800
1,000
1,200
10
20
30
40
50
60
70
80
Pulse Amplitude (mv)

PLATE 13

Linearity - Differential Peak Current as a Function of Concentration for Solutions of o-dianisidine in 1M H_2SO_4 with 50 mv Pulse Amplitude (10^{-3}M to 10^{-5}M)

conc. M	i_p(mA)
1.09×10^{-3}	6.04
2.18×10^{-4}	1.24
1.09×10^{-4}	0.719
2.18×10^{-5}	0.180
1.09×10^{-5}	0.100

PLATE 13

Differential Peak Current (mA)
1
2
3
4
5
6
Concentration (x 10^{-5}M)
10
20
30
40
50
60
70
80
90
100
110

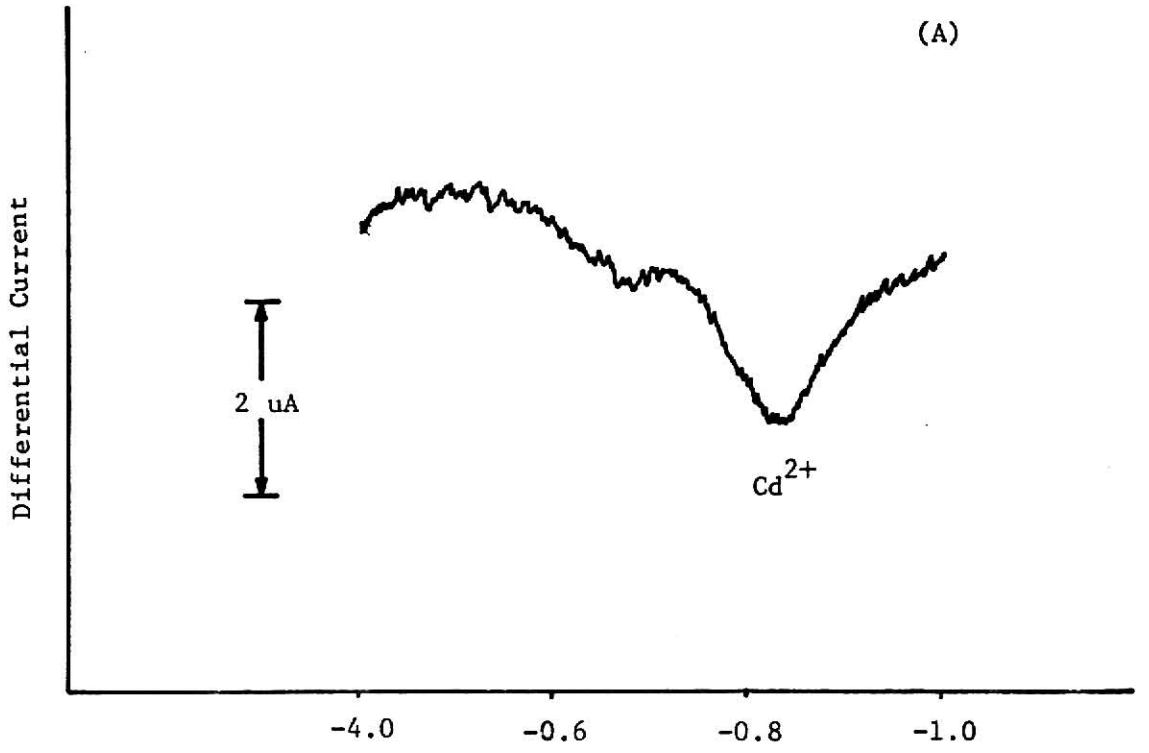
PLATE 14

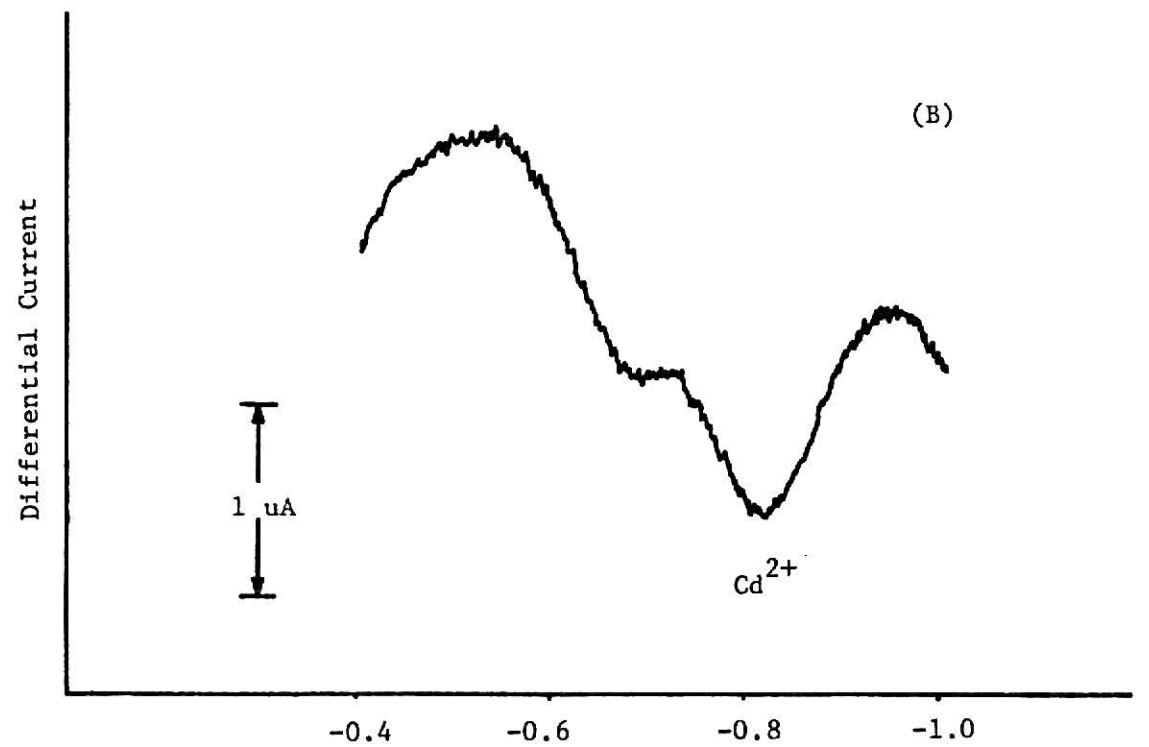
Square Wave Voltammogram of:

A) 10^{-6} (100 ppb) Cd^{2+} in 0.1M NH_3 + 0.1M NH_4Cl

B) 5×10^{-7}M (50 ppb) Cd^{2+} in 0.1M NH_3 + 0.1M NH_4Cl

Hanging mercury drop working electrode; saturated calomel reference electrode; platinum wire auxiliary electrode.


(A)
Differential Current
2 uA
Cd^{2+}
-4.0
-0.6
-0.8
-1.0
E (volts vs. SCE)


(B)
Differential Current
1 uA
Cd^{2+}
-0.4
-0.6
-0.8
-1.0
E (volts vs. SCE)

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VITA

The author was born in Hiawatha, Kansas, on January 30, 1942. He attended Vance Elementary School in Bethel, Kansas, and Bonner Springs High School where he graduated a member of the National Honor Society in 1960. He attended Baker University, Baldwin, Kansas, and received a B. A. in Chemistry August, 1964, from Kansas State Teachers College, Emporia, Kansas.

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The author was married to Sharon J. Ingram on September 16, 1963 in Bonner Springs, Kansas. There are three children: Jeffrey Scott born November 5, 1965; Michael Keith, born December 29, 1966; and Heather Lyn, born August 4, 1968.

A FUNCTION GENERATOR AND POTENTIOSTAT-GALVANOSTAT FOR ELECTROANALYTICAL EXPERIMENTS AND EVALUATION OF SQUARE WAVE VOLTAMMETRY MODE OF OPERATION

by

HARVEY K. HUNDLEY

B.A. in Chemistry, Kansas State Teachers College, 1964

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1971

ABSTRACT

The multipurpose instrument described is intended for chronoamperometric, chronocoulometric, cyclic voltammetric, cyclic chronopotentiometric, square wave voltammetric, polarographic and stripping analysis studies. The three-electrode potentiostat-galvanostat incorporates a function generator that (1) provides all necessary waveforms, (2) responds during the experiment to the cell potential, an integral timing circuit, and external controls, and (3) resets the instrument to the initial conditions after a selected number of half cycles has been completed.

The square wave voltammetric mode of operation was evaluated by experimentally investigating (1) differential peak current as a function of pulse amplitude, (2) effect of pulse amplitude on peak broadening, (3) total current as a function of pulse amplitude, and (4) linearity, reproducibility, and sensitivity. All experiments demonstrated the value of this technique as an excellent analytical tool and showed good agreement with theory and previously published articles.