



3 1293 10747 7014



This is to certify that the

thesis entitled

A GENERAL PURPOSE ELECTROANALYTICAL
SYSTEM BASED ON A MICROCOMPUTER
CONTROLLED COULOSTATIC GENERATOR

presented by

Spyros Emmanouel Hourdakis

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date August 8, 1978



OVERDUE FINES ARE 25¢ PER DAY
PER ITEM

Return to book drop to remove
this checkout from your record.

MSU

FEB 12 1966

9 580 7401 0

A GENERAL PURPOSE ELECTROANALYTICAL SYSTEM
BASED ON A MICROCOMPUTER CONTROLLED
COULOSTATIC GENERATOR

By

Spyros Emmanouel Hourdakis

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1978

G109120

ABSTRACT

A GENERAL PURPOSE ELECTROANALYTICAL SYSTEM BASED ON A MICROCOMPUTER CONTROLLED COULOSTATIC GENERATOR

By

Spyros Emmanouel Hourdakis

A microcomputer controlled and operated electrochemical analysis system has been developed and, in its polarographic mode, it has been shown to be more sensitive than polarography in the determination of cadmium. The system consists of an electrochemical reaction cell, a digitally controlled charge generator for adding charge to the working electrode, a voltage measurement system to monitor the working electrode potential, and a multimicrocomputer system, as the control logic, to control the operation of the charge generator and the voltage measurement system. The central part of the new electrochemical system is the charge generator. A new charge generator has been developed which uses the charge injection technique to add charge pulses into the electrochemical cell. The characteristics of the charge generator were studied and its operation is discussed in detail.

The function of the charge generator is the injection

of charges into the cell and the function of the voltage measurement system is the monitoring of the potential of the working electrode. The control logic determines how these two simple functions are employed in any given experiment. Using a computer instead of hardware logic as the control logic, an extra flexibility is added to the electrochemical system. The system can be operated in many electrochemical polarization modes, where the charge, current, or potential must be measured or controlled, without modification of the instrument hardware. The multimicrocomputer system consists of three independent microcomputers and each one of them is responsible for a specific task. One microcomputer coordinates the operation of the other microcomputers so that the system works as one functional unit. The advantages of the multimicrocomputer system over the single microcomputer, for real-time control of the instrument, are the speed, the modularity, and the convenience of the programming of the system.

The electrochemical system was applied in the polarographic determination of cadmium. The sensitivity of the system was limited to 0.5 μM cadmium.

ACKNOWLEDGMENTS

I wish to express my deep appreciation to Professor C. G. Enke for his guidance, encouragement and friendship throughout my work at Michigan State University. Thanks are given to Professor M. Weaver for his helpful suggestions as second reader.

Gratitude is also extended to the Department of Chemistry, Michigan State University and the Office of Naval Research for financial support.

I would like to thank all the members of the laboratory of Dr. C. G. Enke for their friendship, and assistance during our association. I especially thank Dr. T. V. Atkinson, Dr. T. Last, Dr. J. E. Hornshuh, and E. Carlson.

Special thanks to our friends in the U.S.A., who contributed to render our stay in this country a pleasant and unique experience.

TABLE OF CONTENTS

Chapter	Page
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER 1 - Introduction	1
A. Coulostatic Polarization Technique	4
B. A Microcomputer Controlled Coulostatic Generator	6
CHAPTER 2 - Operation of the Coulostatic Generator	12
A. Introduction	13
B. Constant Electrode Potential	20
C. Electrode Potential as a Function of Time	33
D. Effect of the Supporting Electrolyte	45
E. Implementation of the Coulostatic Generator in the Basic Polarization Techniques	50
1. Controlled Potential Experiments	50
2. Controlled Current Experiments	51
CHAPTER 3 - Polarographic Measurements Using the Microcomputer Controlled Coulostatic Generator	53
A. Introduction	54
B. Determination of Cd^{2+}	58
C. Selectivity	79

Chapter	Page
CHAPTER 4 - Description of the System	
Hardware.	89
A. Pulse Generator	90
1. Digital-to-Analog Converter	91
2. Switches and Charging Amplifier	93
3. The Interface Logic	95
B. Voltage Measurement System.	97
C. The Real-Time Clock	102
CHAPTER 5 - Multimicrocomputer System	
Architecture.	105
A. Introduction.	106
B. Multiprocessor System	108
C. Multiprocessor Control of the Electrochemical System.	111
1. Coordinator micro	113
2. Slave 2 micro	113
3. Slave 1 micro	117
CHAPTER 6 - Communication in a Distributed Intelligence System	120
A. Introduction.	121
B. Description of the System	124
C. The Minicomputer Side of the Link	129
D. The Micro I/O Port.	133
E. The Communicator.	138
F. Operation	143
APPENDIX A - Converse Library for the Micro- computer System	146
APPENDIX B - Data Analysis Programs	167

Chapter	Page
APPENDIX C - Microcomputer to Minicomputer Communication Programs.	174
REFERENCES.	181

LIST OF TABLES

Table		Page
1	Diffusion limited current of various concentrations of Cd^{2+} in 0.1 M KCl as supporting electrolyte.	68
2	Diffusion limited current of various concentrations of Cd^{2+} in 0.1 M KCl as supporting electrolyte. DELAY = 5000 msec.	81
3	Log $[(i_d - i)/i]$ as a function of the electrode potential for two different runs	85
4	Memory map of the coordinator.	114
5	Memory map of slave 2.	116
6	Memory map of slave 1.	118
7	Converse library for operation of the electrochemical system	146

LIST OF FIGURES

Figure	Page
1 Block diagram of the electrochemical system	10
2 Block diagram of the coulostatic generator.	15
3 Flow chart of the program CELLT5. First part	21
4 Flow chart of the program CELLT5. Second part.	22
5 The electrode potential as a func- tion of time. Controlled potential = 0 mV	28
6 The electrode potential as a func- tion of time. Controlled potential = -1500 mV	30
7 The electrode potential as a func- tion of time. Controlled potential = -1500 mV, TEXP = 3000 msec	32
8 Flow chart of the program SCANV. First part.. . . .	35
9 Flow chart of the program SCANV. Second part.	36
10 Flow chart of the program SCANV. Third part	37

Figure		Page
11	Software generated ramps	42
12	The actual ramp applied to the cell as a function of the theoretical ramp. DVSTEP = 50 mV.	43
13	The actual ramp applied to the cell as a function of the theoretical ramp. DVSTEP = 10 mV.	44
14	The electrode potential as a function of time. Controlled potential = 0 mV. Supporting electrolyte 1×10^{-4} M KCl. . .	46
15	The electrode potential as a func- tion of time. Controlled potential = -1500 mV. Supporting electrolyte 1×10^{-4} M KCl	47
16	The actual ramp applied to the cell as a function of the theoretical ramp for three different solutions of KCl as supporting electrolyte (Plot 1 0.1 M KCl, Plot 2 0.001 M KCl, Plot 3, 0.0001 M KCl)	49
17	Flow chart of the program POLAR1. First part	59
18	Flow chart of the program POLAR1. Second part.	60

Figure		Page
19	Flow chart of the program POLAR1.	
	Third part..	61
20	Polarogram of a 0.1 M KCl solution (1), 5×10^{-4} M Cd^{2+} in 0.1 M KCl solution (2), 1×10^{-3} M Cd^{2+} in 0.1 M KCl solution (3)	65
21	Polarogram of a 0.1 M KCl solution (1), 5×10^{-5} Cd^{2+} in 0.1 M KCl solution (2), 1×10^{-4} Cd^{2+} in 0.1 M KCl solution (3)	66
22	Polarogram of a 0.1 M KCl solution (1), 5×10^{-6} Cd^{2+} in 0.1 M KCl solution (2), 1×10^{-5} Cd^{2+} in 0.1 M KCl solution (3)	67
23	The working curve for Cd^{2+} determina- tion	69
24	Plot of $\text{Log } I_d$ versus $\text{Log } C$ for Cd^{2+} determination.	70
25	Polarogram of 0.1 KCl solution at two different periods of the drop life: DELAY = 100 msec (1), DELAY = 5000 msec (2).	72
26	Polarogram of a 5×10^{-6} M Cd^{2+} in 0.1 M KCl solution at different periods of the drop life, and the corresponding	

	polarograms of a blank solution.	
	DELAY = 100 msec (1,2), DELAY =	
	5000 msec (3,4).	77
27	Polarogram of a 0.1 M KCl solution	
	(1), 1×10^{-6} M Cd^{2+} in 0.1 M KCl	
	solution (2), 5×10^{-6} M Cd^{2+} in 0.1	
	M KCl solution (3), 1×10^{-5} M Cd^{2+}	
	in 0.1 M KCl solution (4). DELAY	
	= 5000 msec.	78
28	Polarogram of a 0.1 M KCl solution	
	(1), and a 5×10^{-7} M Cd^{2+} in 0.1	
	M KCl solution. DELAY = 5000 msec	80
29	The working curve for Cd^{2+} determina-	
	tion at DELAY = 5000 msec.	82
30	Plot of Log I_d versus Log C for	
	Cd^{2+} determination at DELAY = 5000	
	msec	83
31	Polarograms of a 1×10^{-4} M Cd^{2+}	
	in 0.1 M KCl solution obtained with	
	different run parameters. For Plot 1	
	VPULSE = -300 mV, VINITIAL = -400 mV,	
	VFINAL = -900 mV, DVSTEP = 20 mV,	
	DELAY = 100 msec. For plot 2 VPULSE	
	= -300 mV, VINITIAL = -500 mV, VFINAL	
	= -900 mV, DVSTEP = 15 mV, DELAY =	
	100 msec	84

Figure		Page
32	Log $[(i_d - i)/i]$ versus E for two dif-	
	ferent scans	87
33	Polarogram of a 1×10^{-4} M Cd^{2+} ,	
	1×10^{-4} M Zn^{2+} , 1×10^{-4} M Ni^{2+}	
	in 0.1 M KCl solution.	88
34	Digital-to-Analog converter. Bi-	
	polar operation.	92
35	Switches and charging amplifier.	94
36	Charge Generator interface logic	96
37	Analog-to-Digital converter.	98
38	A/D converter interface logic.	99
39	Real-time clock.	103
40	Block diagram of the multimicro-	
	computer system.	109
41	Multiprocessor control of the	
	electrochemical system	112
42	Operations of a dedicated computer	123
43	Operations of an "high intelligence"	
	computer system.	125
44	Block diagram of an hierarchical	
	system	128
45	Block diagram of the MDB-1710 and	
	the external I/O port.	130
46	Block diagram of the micro I/O	
	port	134

Figure		Page
47	Block diagram of the micro- computer peripherals	139

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Polarography has been used as an analytical technique since Heyrovsky discovered that the current measured at a dropping mercury electrode (DME), which is maintained at a particular potential, is related to the concentration of the electroactive species present in the solution in which the DME and the reference electrodes are immersed. Even with the use of a three electrode system (DME, a reference and counter electrode) which reduces the error due to the IR drop in the cell, classical DC polarography has a serious defect which sets a limit on the sensitivity of this technique. The theory assumes that the current in the cell is the diffusion controlled Faradaic current. But the actual current that one measures contains contributions from a number of other sources. The problem of distinguishing the current of interest from the currents due to other phenomena is the problem that the "modern" electroanalytical techniques try to solve (1, 2, 3, 4, 5, 6).

The result of the effort of the development of the modern electroanalytical methods were new polarographic instrument designs which provide lower noise levels and better performance. A basic element in the development

of the new polarographic instruments and new electro-analytical techniques is the use of operational amplifiers. The use of operational amplifiers in the development of new polarographic instruments has been studied by a number of workers and there are many articles, reviews, and books on the theory and applications of operational amplifiers in electrochemistry (7, 8, 9, 10, 11). Operational amplifier circuits can be used to generate a wide variety of voltage signals and, as signal detectors, to sample the output signals from an electrochemical experiment and provide these signals in a form suitable for measurement. Several instruments have been developed which can perform a variety of electrochemical techniques: linear sweep polarography, chronopotentiometry, cyclic voltammetry, chronoamperometry, cyclic chronoamperometry, square wave voltammetry and polarography, and pulse polarography (12, 13, 14, 15, 16, 17).

These instruments are generally developed around a potentiostat (or galvanostat) which is a controller circuit that maintains the potential (or current) at the working electrode equal to some signal-generator potential, which may be a constant voltage or a time varying signal. In its fundamental operation the controller reacts to the difference between the actual and the desired potentials through a negative feedback circuit in such a way as to reduce the difference to zero. In the potentiostat,

the electrochemical cell is part of a closed circuit in which the current is continually controlled in order to keep the potential difference between the working electrode and the reference electrode equal to the desired value.

A. Coulostatic Polarization Technique

In the early 1960's P. Delahay published a series of papers in which he described the theory and applications of a new method, the coulostatic polarization method (18-23). The method was originally developed for studies of adsorption phenomena and electrode processes, but it proved useful for trace analysis as well.

The basic principle of the coulostatic method is the very rapid addition of charge to the working electrode of an electrochemical cell to bring its potential to a new value at which there is a Faradaic current. The cell is at open circuit after the addition of the charge and the Faradaic current is entirely supplied by discharge of the double layer capacitance. The potential tends to change toward its initial value as the double layer capacitance is progressively discharged. The potential-time variation is measured after the addition of the charge and is related to the concentration of the substances involved in the electrode reaction. The double layer charging current problem which limits the usefulness of most

polarographic methods in trace analysis is avoided in the coulometric technique. The voltage measurements are made when no net current passes through the cell which eliminates the effects of the solution resistance during the measurements, and permits lower concentrations of supporting electrolyte.

Despite the above characteristics and advantages which make the coulometric polarization technique an attractive technique for analytical applications, only a small number of applications of this method have been reported (21,23). This is due to the lack of selectivity of this method and the relative inconvenience of the hanging mercury drop electrode compared to the dropping mercury electrode, and the difficult interpretation of the data.

Recently a number of new coulometric methods have been developed which improve the selectivity of the coulometric method (24-28). These methods use a dropping mercury electrode, and the potential decay curves are measured and plotted as a function of the applied potential. This plot allows both quantitative and qualitative analysis of mixtures of electroactive species.

The early instruments used for the coulometric technique included a potentiometer with which the potential of the working electrode was set at the foot of the current - potential curve for the analyzed electroactive

species, a coulostat by which a known quantity of charge was supplied to the cell and a circuit for sampling and reading the cell voltage. The coulostat injects the charge to the working electrode via a small capacitor charged to a very high voltage (19,30,31). In a more recent coulostatic instrument the potentiometer has been replaced by a potentiostat and the small charging capacitor by an operational amplifier circuit which acts as a constant current source (28). This system works as follows: Towards the end of the drop life, when the change of the area of the dropping mercury electrode is minimal, the ramp voltage is disconnected from the cell and a coulostatic pulse is applied to the system. This pulse of charge changes the potential of the cell to a new value. The cell potential is allowed to decay at open circuit for a predetermined period of time. In the next step the same procedure is repeated for a higher electrode potential.

B. A Microcomputer Controlled Coulostatic Generator

Although the potentiostat offers a very accurate way of controlling the potential of a working electrode to follow a number of different excitation forms, its electro-analytical use has some limitations: A net current passes through the cell, which requires the presence of relatively high concentration of supporting electrolyte to avoid IR drop errors in the controlled potential, and the

total current passing through the cell is the sum of the Faradaic current and the double layer charging current which limits the sensitivity to the Faradaic component.

On the other hand, the traditional coulometric technique has the disadvantages that the potential of the working electrode is not constant during the whole time of the experiment, and in most cases the measured variations of the electrode potential are larger than the desired resolution.

Also, the time required for a measurable potential variation is not constant. Despite these limitations, the coulometric technique has a number of advantages: The potential of the working electrode is measured when no current is passing through the cell; the current is not measured but determined by the controlled addition of charge; the charge is quantized, i.e., digital; and the double layer capacitance of the working electrode is accessible in real time and in real systems.

The charge injection technique, which is used in the coulometric method to change the potential of the working electrode to a desired value, can be used as well to maintain the electrode potential at a desired value. In this way the charge injection technique combines the advantages of the coulometer and the potentiostat.

The idea of controlling the potential of the working electrode by injection of charges has been used by

Goldsworthy and Clem to develop the so called "Bipolar Digipotentiograter" (29). This system uses the charge injection technique to maintain a control potential and simultaneously serves as a current-to-digital converter. The system applies small pulses of constant coulombic content to the working electrode as often as necessary to keep its potential at a desired value. The construction and operation of the bipolar digipotentiogrator is based on dedicated hardwired logic.

Instead of the dedicated hardwired logic, a micro-computer can be used to control and operate a coulостatic generator which uses the charge injection method to control the potential of the working electrode. Such a coulостatic generator is the heart of the electroanalytical system described in this thesis.

Computers have been used in the development of modern automated instruments in order to increase the efficiency and the flexibility of the instruments. The dedicated computer, i.e., the computer which is directly interfaced to the instrument and to the experiment, operates the instrument, collects data, performs data analysis, and makes decisions regarding the course of the experiment. Minicomputers have been used extensively, during the past years, as dedicated computers to develop new instruments and new analytical techniques. The minicomputer with its powerful library, its fast response

time, and its ability to manipulate large amounts of data, is almost ideal for automation and on-line use. The disadvantage of the use of the minicomputer as a dedicated computer is its cost.

Some years ago the microprocessor, a single integrated circuit chip containing at least 75% of the power of the central processor part of a computer, appeared on the market. The microprocessor can be used, with the aid of some support chips (memory, counters, input-output registers, buffers), to build a microcomputer as part of any instrument. The dedicated computer used in this system is a multimicrocomputer system that has been developed in our laboratory and which substitutes for the minicomputer in the control and the operation of the instrument.

Figure 1 shows a block diagram of the system which consists of: an electrochemical reaction cell with working, reference, and counter electrodes, a pulse generator for adding charge to the cell, a voltage measurement system to monitor the working electrode potential, a microcomputer to control the operation of the system, and a device for operator-system communication.

The basic principle of the operation of this system, when controlling the potential of a dropping mercury electrode, is the rapid addition of charge to the working electrode to bring its potential to a desired value and to control the electrode potential at this value. The

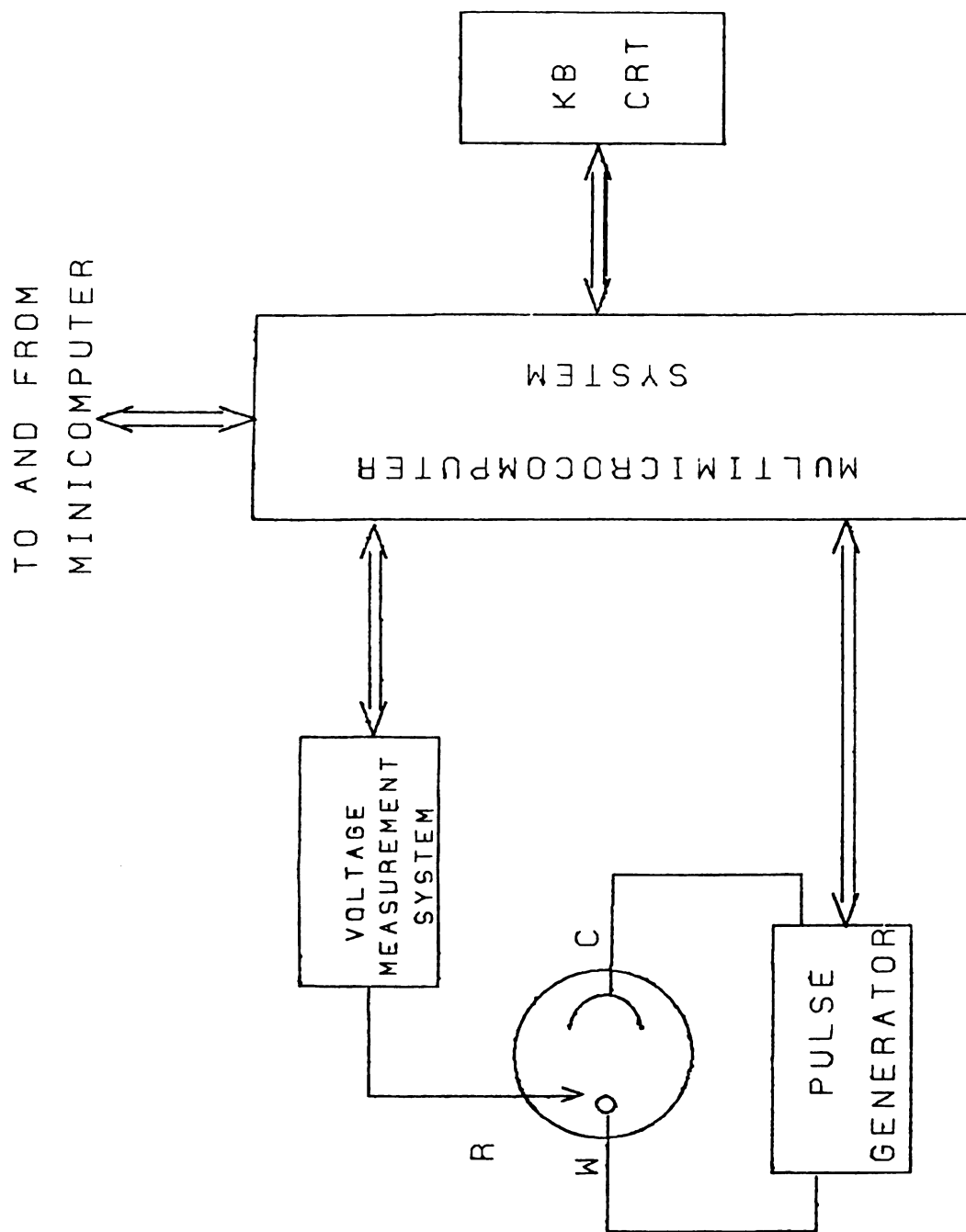


Figure 1. Block diagram of the electrochemical system. R , W , and C are the reference, working, and counter electrodes, KB and CRT are a keyboard/cathode ray tube terminal.

instrument monitors the electrode potential between the addition of charges. If there is a deviation of the electrode from the desired potential, the computer commands the pulse generator to add more charge to the electrode to restore its potential to the desired value. In the next drop a new series of charge pulses is added to the working electrode to bring its potential to a new, higher, value. The same procedure is repeated until the end of the scan (desired range of controlled potentials).

The pulse generator and the voltage measurement system can perform only two very simple operations on the electrochemical cell: add charge to the working electrode, and measure the potential of the working electrode. The use of the microcomputer as the control element of the operation of the system gives an extra dimension of flexibility in the system which is not found in conventional instruments. The operator has the ability, by programming, to determine how the simple operations of the pulse generator and the voltage measurement system are to be used in order to perform an experiment, and he can program the system to produce and apply any complex potential waveform to the electrochemical cell. This flexibility of the system permits the operator to choose and apply the electrochemical technique which gives the best response for the investigated chemical system.

CHAPTER 2

OPERATION OF THE COULOSTATIC GENERATOR

CHAPTER 2

OPERATION OF THE COULOSTATIC GENERATOR

A. Introduction

The interface between a dropping mercury electrode (DME) and an aqueous solution of an electrolyte, behaves like an electrical capacitor in that it is capable of storing electric charge. If the so called double layer capacitor is in an open circuit and no electric charge is added to it, the potential across the capacitor will remain constant and equal to the potential of zero charge (PZC). In the presence of electroactive species in the solution, the potential across the interface will be equal to a value at which no Faradaic reaction will occur (or the Faradaic current will be equal and opposite to the charging current). If an electric charge is injected to the double layer capacitor, the potential across the interface will change by a value $\Delta E = q/C_{dl}$ where $\Delta E = E_1 - E_{PZC}$ (the difference between the potential of zero charge and the new potential), q is the amount of charge injected to the double layer and C_{dl} is the double layer capacitance. In an open circuit, the potential of the double layer capacitor will not remain constant but it will tend to return to an equilibrium value.

There are two processes by which the potential across the electrode-solution interface will be changed: the double layer capacitance changes as the area of the DME changes, and the double layer capacitor is discharged by any electrochemical reaction taking place across the interface.

In order to keep the potential of the electrode constant some charge must be added to the double layer capacitor to compensate for the effect of the growth of the drop and the discharge due to the Faradaic reaction ($q_{\text{total}} = q_{\text{charging}} + q_{\text{Faradaic}}$). The total charge can be positive or negative. For reductions, the Faradaic "charge" is negative but the "charging" charge can be either positive or negative depending upon which side of the electrocapillary maximum (PZC) the desired potential lies.

A coulостatic generator able to inject charge pulses to the working electrode in order to maintain its potential equal to a desired value is shown in Figure 2. The coulостatic generator consists of a Digital-to-Analog Converter (DAC), an inverter (A1), a set of FET switches SW1, SW2, SWi, a set of small capacitors C1, C2, Ci, an operational amplifier (A2) to provide the necessary charge pulses to the cell, and a microcomputer to control and operate the DAC and the switches. The voltage measurement system, which is used to monitor the potential of the reference

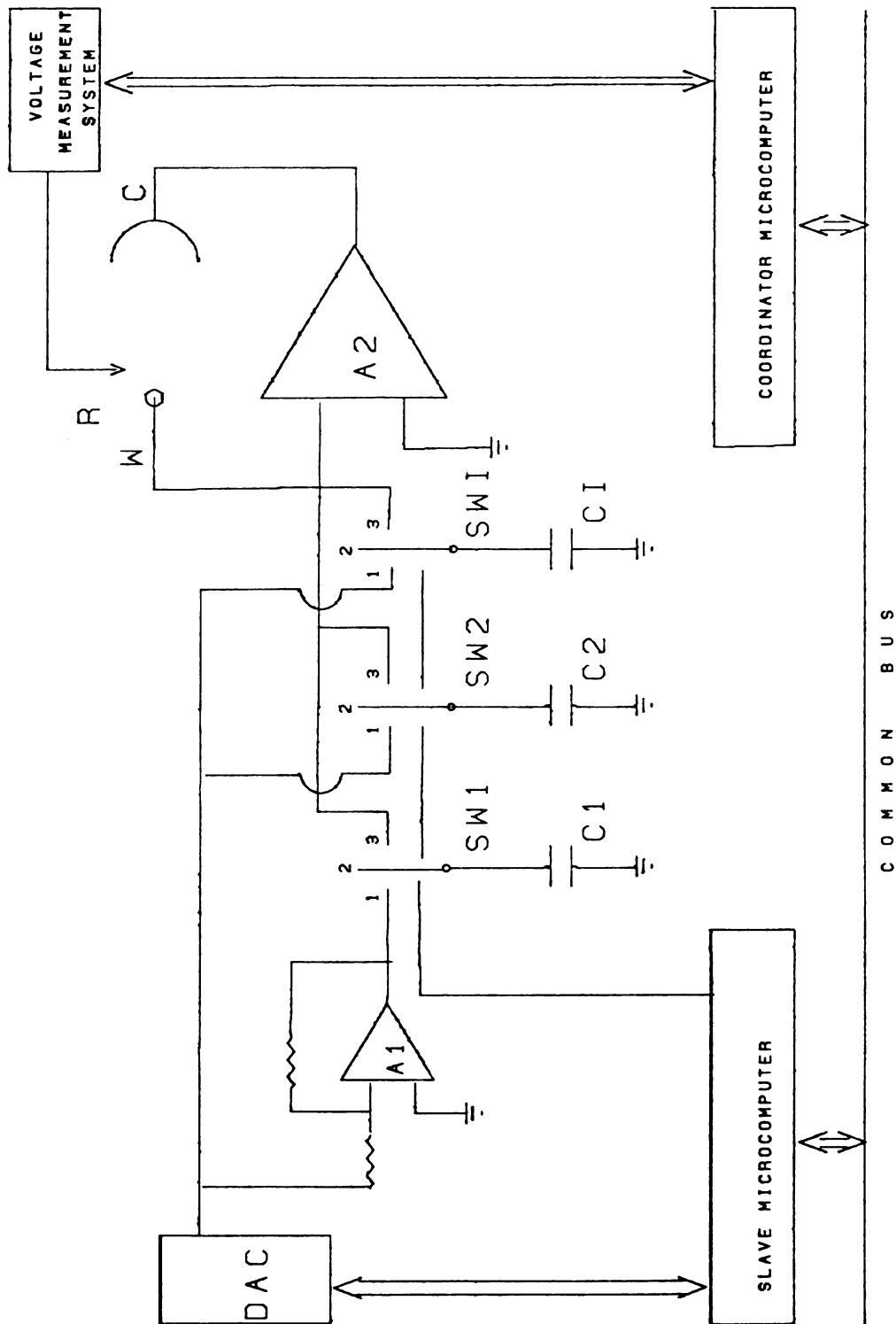


Figure 2. Block diagram of the coulостatic generator.

electrode with respect to the working electrode, is shown in the same block diagram. The voltage measurement system is controlled by a different microcomputer, the coordinator, which is connected with the slave microcomputer through the common bus, and which coordinates the operation of the system.

The cell used throughout this study was a three electrode cell with a dropping mercury electrode (DME) as a working electrode, a cylinder of platinum gauze for the counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The DME was made from a 6 to 12 second capillary and the height of the mercury was adjusted to give a 9.0 second drop time. The cell also includes a glass bubbler through which nitrogen was passed to expel the oxygen from the solution. During an experiment, the bubbler was raised above the solution so the nitrogen continued to flow over the top of the solution. The nitrogen was bubbled through the 250 ml gas washing bottles containing vanadous chloride solution and heavily amalgamated zinc, and through distilled water before it entered the cell.

The operation of the pulse generator is as follows: the slave microcomputer loads the DAC with a 10 bit word. The selected output voltage of the DAC, V_{DAC} , is connected through the inverter A1 and switch SW1 to capacitor C1, or through any switch SWI to the corresponding capacitor

CI. This produces a precise charge $q = CI V_{DAC}$ which is stored in the selected capacitor. In order to inject the charge to the cell, the slave microcomputer switches the appropriate switch to position 3. The operational amplifier, A2, senses a difference in the voltage between the positive and negative input and through the negative feedback, which contains the counter and the working electrode, tries to eliminate this difference by forcing an opposite charge through the counter electrode. The result of this operation of the amplifier is that the charge stored in the charging capacitor is quickly transferred to the working electrode of the electrochemical cell. The amount of charge that the pulse generator injects to the cell depends on the selected output voltage of the DAC and on the selected charging capacitor. Inverter A1 provides the same output voltage but opposite in sign from the DAC, i.e., $-V_{DAC}$. So in order to inject charge of identical magnitude but opposite sign, the slave microcomputer does not have to load the DAC with a different word but it simply selects the appropriate switch. The design details of the electronic components of the pulse generator and the voltage measurement system are given in Chapter 4. In the present form, the coulometric generator uses two charging capacitors C1 and C2 with capacitance 0.001 μF and 0.01 μF respectively. Capacitor C2 is used to inject negative charge to the

cell and capacitor C1 is used to inject positive charge.

The pulse generator injects charge to the cell and the voltage measurement system monitors the potential of the working electrode. The control logic determines how these two simple operations must be used in order to control the potential of the working electrode at a desired value. A multimicrocomputer system was used as the control logic. The multimicrocomputer system was developed jointly with James E. Hornshuh (32) and Erik M. Carlson (33) and was used for real-time control of the pulse generator and the voltage measurement system. Details of the computer architecture and its operation are given in Chapter 5.

Since all the instrument control and the data acquisition functions are under computer control, an operating software system was developed which was based on the use of the CONVERS-M software system (33). CONVERS-M is a new dynamic programming technique which allows the operator to create his own commands, and which is designed to operate in the multimicrocomputer system. The new commands are subroutines written in assembly language. Once these subroutines have been written and entered in the system software library they can be called up and executed in one of two ways: the name of the subroutine can be entered at the terminal for immediate execution or the subroutine name can be included in another software

routine as a line of code. Thus the operator can create his own specific subroutines to operate and control his instrument and use these subroutines as a line of code in a more sophisticated routine to perform an experiment. Each microcomputer has its own subroutine library and it operates independently from the other microcomputers of the system. The coordinator coordinates the operation of the slaves and regulates when and which subroutine must be executed in each slave so that the total operation of the system becomes a unified function. This programming technique allows the maximum operating speed of the system since a number of different tasks can be performed at the same time. Appendix A includes listings of the basic programs used during this work. Appendix A also includes the name and the function of the subroutines used during this work. For the purpose of the discussion in this chapter we can consider the multimicrocomputer system as a unified operational unit and that the execution of any program is the continuous execution of instructions.

In order to understand the operation of the coulometric generator and to study its characteristics, two cases will be examined: the potential of the DME is constant, and the potential of the DME is a function of time.

B. Constant Electrode Potential

Although the coulостatic generator has the ability to control the electrode potential at positive and negative values versus the SCE, only the negative values will be examined.

The flow chart of the program used to maintain the potential of the DME at a constant value is shown in Figures 3 and 4. The program starts with an initial dialog to obtain the values of the run parameters. The program displays the name of the parameters and their default values on the CRT. The operator can change the value of any parameter by entering the name of the parameter and its new value. The computer checks the validity of each entry and updates the CRT display. If an illegal parameter or value is entered, the computer ignores the last entry and reads out a question mark and waits for a new entry. A new value for any parameter becomes the new default value.

The significance and the legal values for the run parameters are as follow:

VPULSE : It determines the output voltage of the DAC, and the voltage at which the charging capacitor will be charged. VPULSE can be varied from -5 mV to -2500 mV.

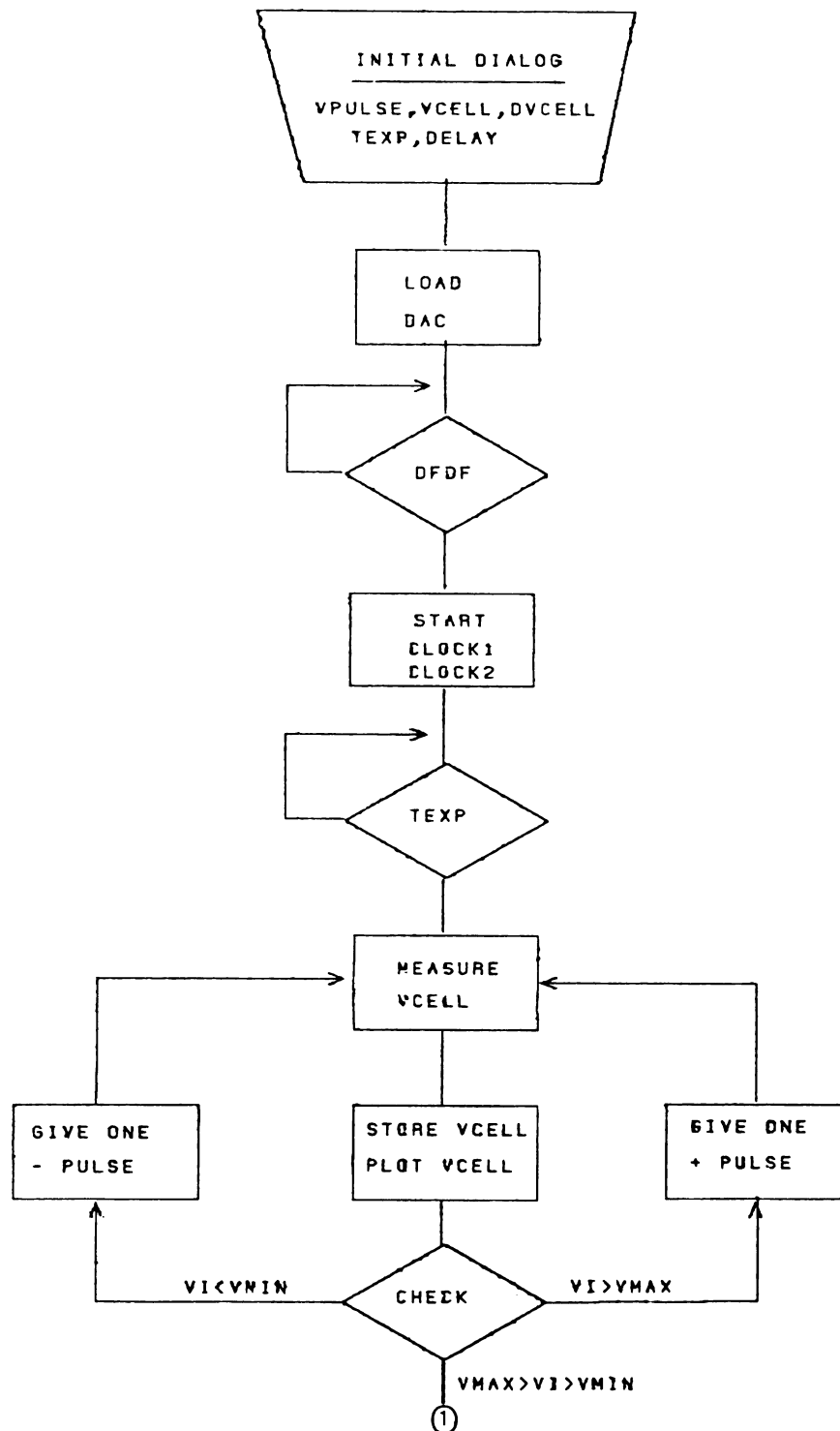


Figure 3. Flow chart of the program CELLT5. First part.

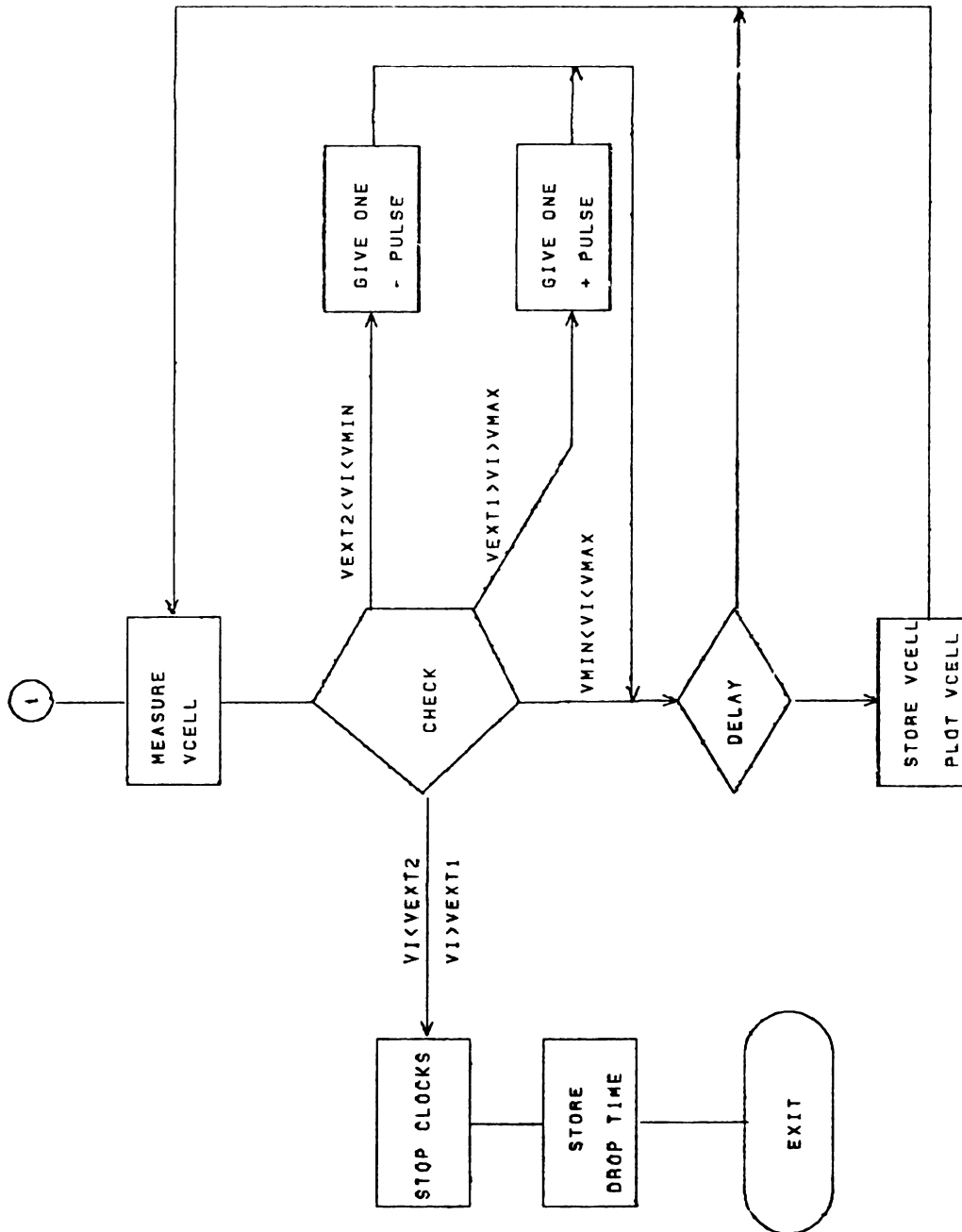


Figure 4. Flow chart of the program CELLT5. Second part.

- VCELL : It determines the potential of the DME vs S.C.E. at which the working electrode must be kept. VCELL can be varied from 0 mV to -2500 mV vs S.C.E.
- DVCELL : For each VCELL the computer assigns two new values to it. $V_{MAX} = V_{CELL} + DV_{CELL}$ and $V_{MIN} = V_{CELL} - DV_{CELL}$. V_{MAX} and V_{MIN} are the permissible limits between which the electrode potential must lie. DVCELL can be varied from 2 mV to 2500 mV.
- TEXP : It determines the time, after the beginning of the drop, at which the system will start to control the electrode potential. Its value can be from 0 msec to 36000 msec. It has been observed that the control of the electrode potential very early in the drop life is not accurate. The rate at which the double layer capacitance of the DME is changing, at the early life of the drop, is very big and the coulostatic generator cannot control the electrode potential accurately during that period. Some time after the beginning of the drop the rate at which the double layer capacitance is changing is much smaller and the control of the electrode potential becomes more accurate. 100 msec has been found to be the

minimum value of TEXP for consistently accurate control of the electrode potential.

DELAY : After TEXP msec from the beginning of the new drop the coulstatic generator will start monitoring the electrode potential, and will try to bring it to VCELL by injecting charge to the working electrode. Each value of the electrode potential that the computer measures will be stored in the memory and it can be plotted on the CRT. After the electrode potential reaches the desired value, the computer continues to monitor the electrode potential and injects, if it is necessary, more charge to the working electrode to maintain its potential constant. From that time until the end of the drop, the computer stores and plots only the nth measured electrode potential value. So a 200 value for the DELAY parameter means that after the electrode potential reaches the desired value only the 200th measured value will be stored and plotted.

A special character ($\uparrow$ C) terminates the dialog and the computer starts the experiment.

In order to coordinate the operation of the coulstatic generator with the beginning of a new drop and to measure the exact time of the drop life, a software drop fall

detector was used to detect the drop fall. The basic principle of the software drop fall detector is that at the instant of the drop fall there is a sudden and large change in the electrode potential, which is due to the fact that the drop carries away all the charge that has been stored in the double layer capacitor. If the measurement of the electrode potential was made prior to any addition of charge, the potential of the new drop will be more positive than the previous one. If the measurement was made after the addition of the charge pulse, the potential of the new drop will be more negative or more positive since the double layer capacitance of the new drop is much smaller than the double layer capacitance of the previous drop. Two new values (VEXT1, VEXT2) must be assigned to each electrode potential to be used as "out-of-control" limits so that the program can detect the drop fall. The initial dialog assigns these two values to each VCELL. The value ± 100 mV has been found to be the best value to define VEXT1, and VEXT2 ($VEXT1 = VCELL + 100$ mV, $VEXT2 = VCELL - 100$ mV).

The DFDF program is a similar subroutine to the program described in Figure 3. The only difference is that DFDF does not store or plot the measured values of the electrode potential.

After the detection of the drop fall and the beginning of the new drop, the computer starts two real-time clocks.

Clock 1 measures the time of the drop life. Clock 2 measures the delay time of the drop life. When $t = T_{EXP}$, Clock 2 sets a flag to indicate that the delay time has elapsed and that the operation of the control system must start. The rest of the program controls the addition of charge pulses to the cell, stores the measured values in the memory and plots these values on the CRT. When the drop falls, the program stops the clocks, reads and stores in memory the time of the drop life, and returns to the calling program.

The drop time and the number of points that have been acquired can be displayed on the CRT by entering the name of the subroutine WRITE1 in the keyboard. Also the operator can store the acquired data on a floppy disk by entering the name of the subroutine SAVE1 in the keyboard. Prior to storing the data on disc, SAVE1 allows the operator to write in the file name and any file header text from the keyboard. Although the acquired electrode potential information can be processed locally by the micro, stored information is usually transmitted to the minicomputer for final processing. The communication link between the microcomputer and the minicomputer allows bidirectional transfer of information between the two computers. Details of the communication link architecture and its operation are given in Chapter 6.

The final processing of the data is performed on the

minicomputer to take advantage of the computational ability of the minicomputer and to use the mini's peripherals and especially its graphical capabilities. All the data plots included in this thesis have been created using an extremely powerful plotting program (MULPLT) written by T. V. Atkinson (34).

A typical plot of the electrode potential versus time obtained with the program described in this section is shown in Figure 5. The run parameters for this plot are: VPULSE = -300 mV, VCELL = 0 mV, DVCELL = 4 mV, TEXP = 100 msec and DELAY = 200. The number of points are 200 and the drop time is 8406 msec. The data were obtained from a solution of 1×10^{-3} M Cd^{2+} in 0.1 M KCl. Oxygen was expelled from the solution by passing nitrogen through the solution for 5 minutes. The first measured value of the electrode potential was more negative than VCELL so the pulse generator started injecting positive pulses to the working electrode in order to bring its potential between VMAX and VMIN. 110 pulses have been added to the cell to bring the electrode potential to the desired value. After that point (B) one point every 200 measurements was stored in the memory and plotted on the CRT until the end of the drop (C). The total number of points is 34910 and the time of the experiment is 8306 msec. This corresponds to an data acquisition rate of ~ 4.2 kHz (~ 238 μsec /point period). VCELL was reached in 26 msec

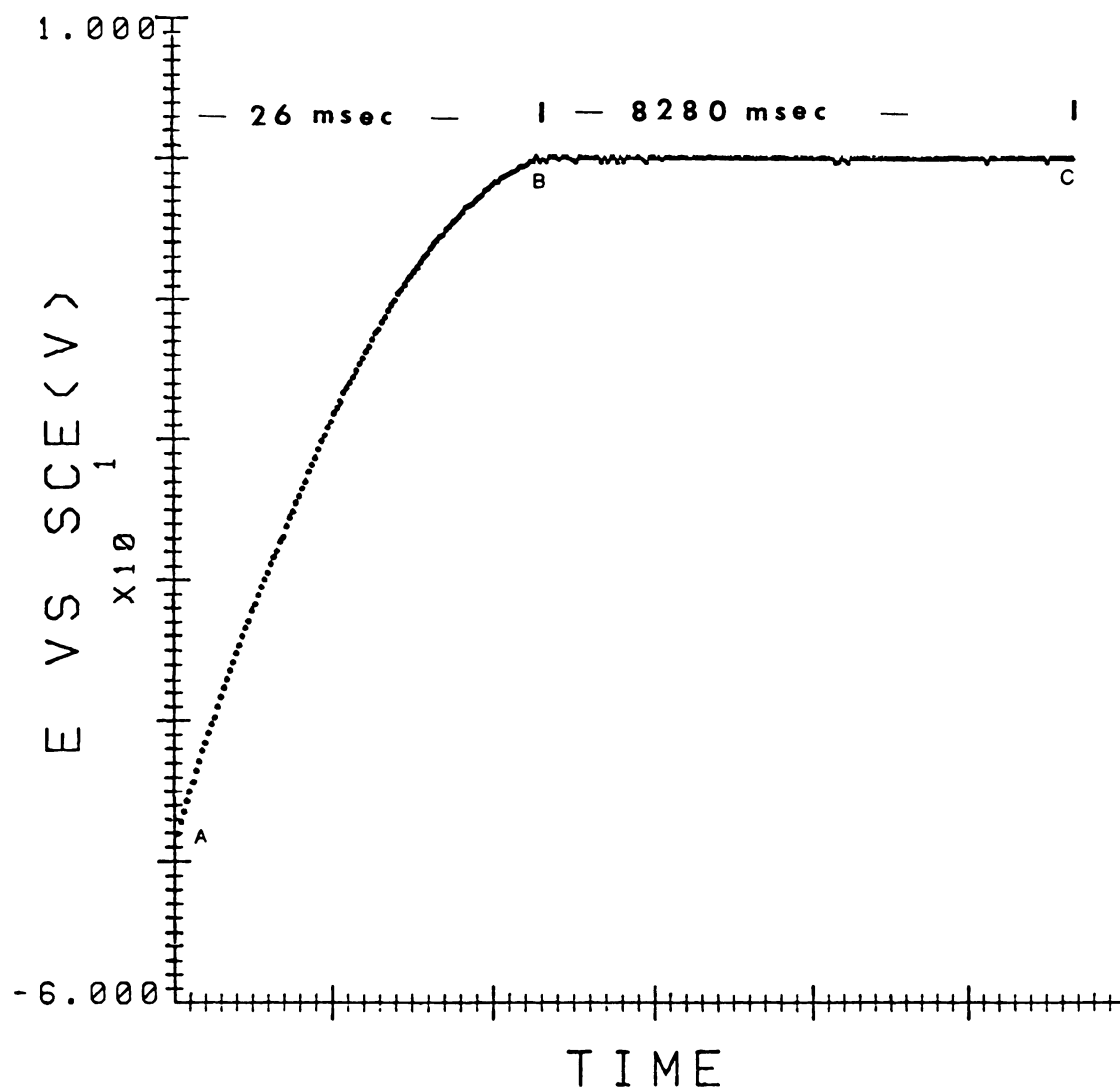


Figure 5. The electrode potential as a function of time.
Controlled potential = 0 mV.

and for the rest of the drop life, 8280 msec, the potential remained constant between 0 mV and -5 mV.

Figure 6 shows a plot of the electrode potential versus time obtained with the same program and using the same solution. The run parameters are: VPULSE = -300 mV, UCELL = -1500 mV, DVCELL = 4 mV, TEXP = 100 msec, DELAY = 200. The number of points are 22622 and the drop time is 7354 msec. The data acquisition rate is ~ 3.1 kHz (~ 321 μ sec)/point period). The difference in the data acquisition rates is due to the fact that in the first case (Figure 5) the coulstatic generator was injecting positive pulses only. In the second case (Figure 6), the coulstatic generator probably had to give both positive and negative pulses in order to keep the electrode potential constant after point B. VCELL was reached in 7 msec and for the rest of the drop life (7247 μ sec) the electrode potential remained constant at -1500 ± 10 mV.

In the early part of the plot shown in Figure 6 a small curvature is observed. In order to observe the electrode potential variations at the initial part of this plot, and to understand the cause of the curvature, a new scan was made using the same solution and the same program but with different values of the run parameters. The run parameters are: VPULSE = -1500 mV, VCELL = -1500 mV, DVCELL = 4 mV, TEXP = 3000 msec, DELAY = 200. The

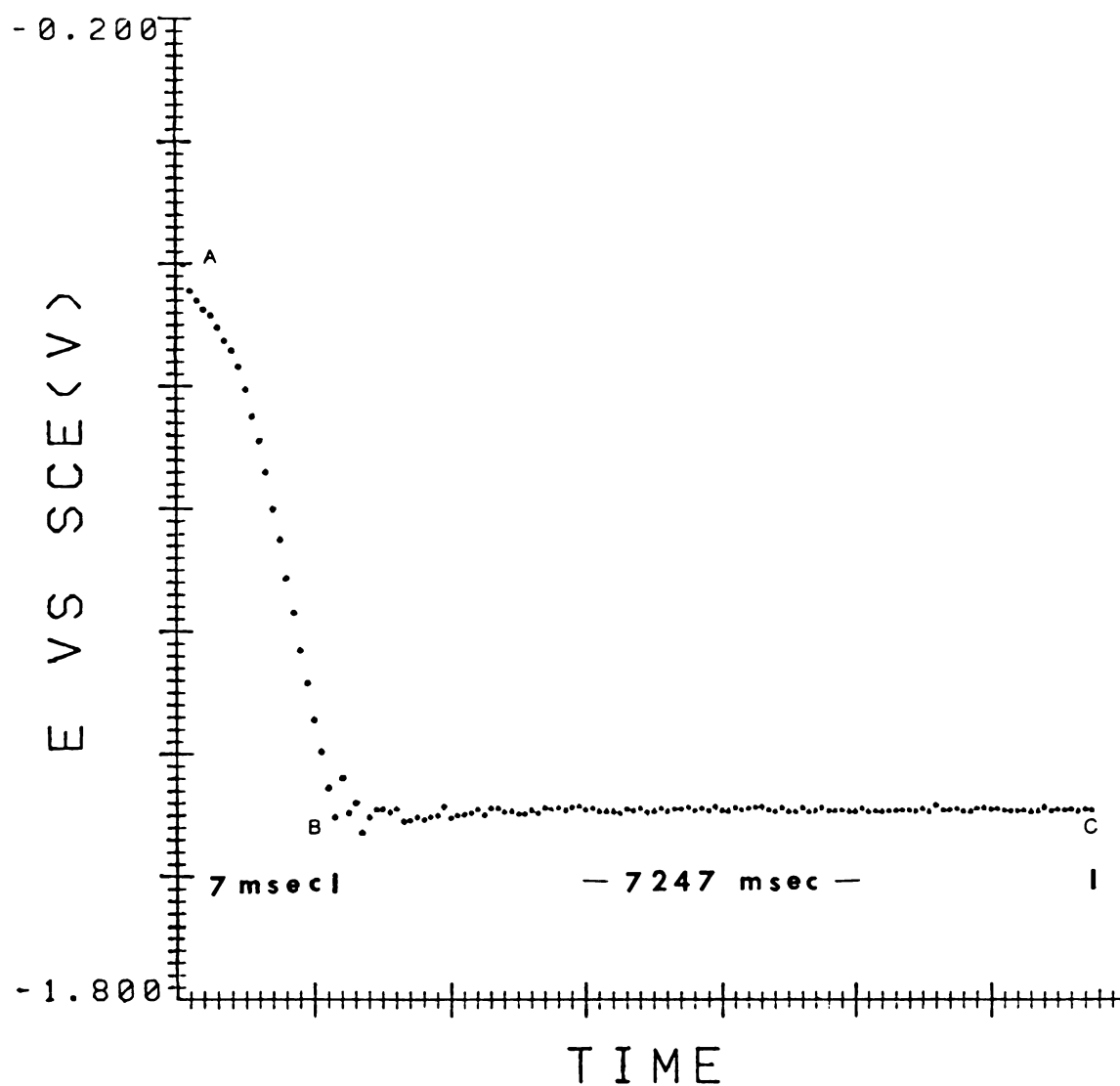


Figure 6. The electrode potential as a function of time.
Controlled potential = -1500 mV.

result is shown in Figure 7, plot I. The beginning of the experiment was moved to a different period of the drop life ($T_{EXP} = 3000$ msec), at which time the double layer capacitance of the working electrode is larger and the rate of change of the double layer capacitance is smaller. The value of V_{PULSE} had to be increased to -1500 mV in order to have a good control of the electrode potential. The presence of some electroactive species in the solution is obvious from this plot (1×10^{-3} Cd^{2+} in this case). The shape of this plot can be explained as follows: Prior to any addition of charge, the electrode potential is at some equilibrium value at which no Faradaic reaction occurs. After the addition of one charge pulse, the electrode potential is moved to a new value. Initially, all the charge injected to the working electrode per pulse is used to charge the double layer capacitor and change its potential to a new value. After a certain value of the electrode potential, a Faradaic reaction (the reduction of Cd^{++}) starts. After that electrode potential, the charge that is injected to the DME is used not only to charge the double layer capacitor but also to supply the necessary Faradaic current for the reduction. The change of the electrode potential per charge addition is smaller now. As the electrode potential moves to more negative values, the Faradaic reaction rate increases until it reaches its diffusion limited value (point B). After

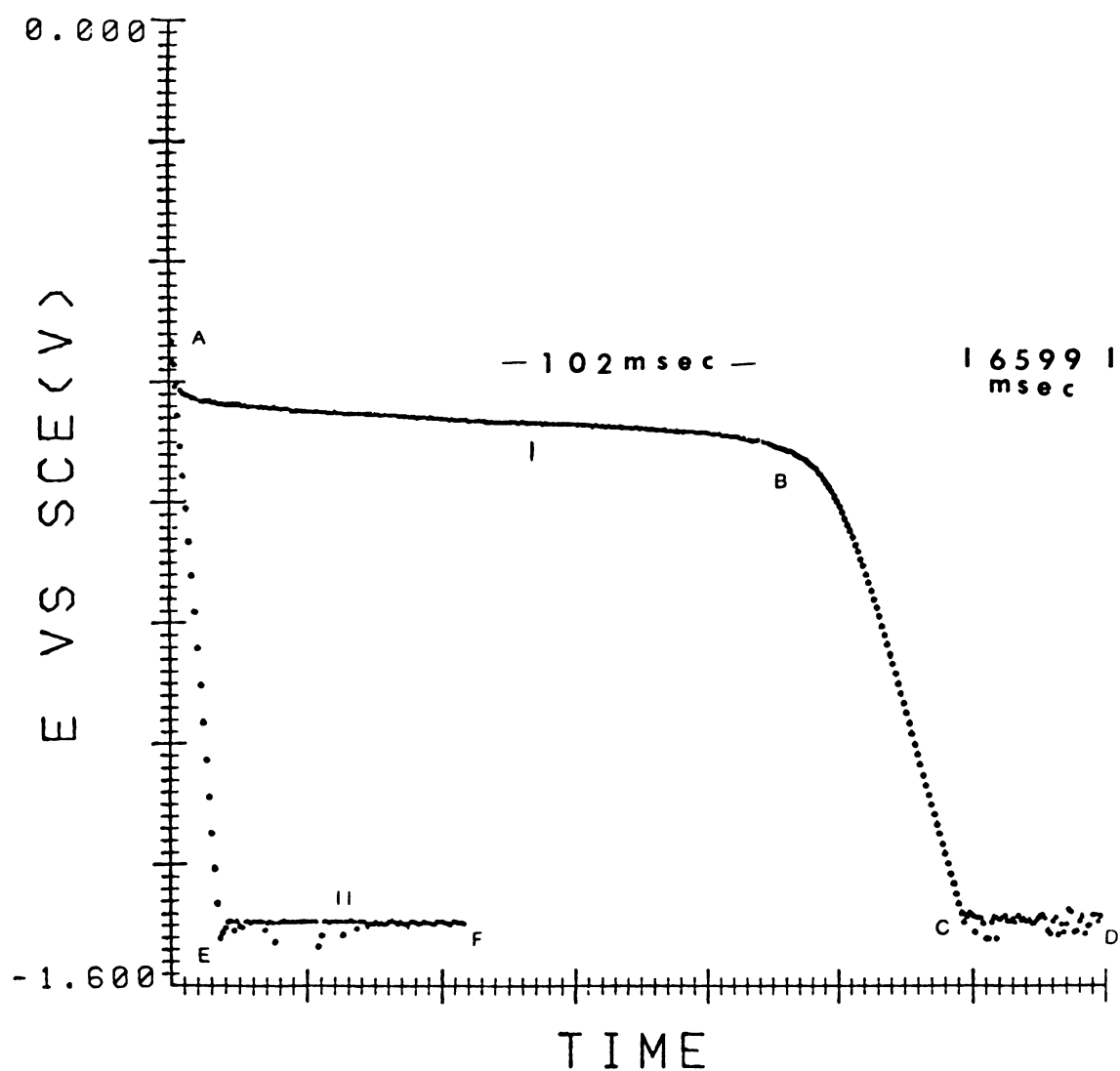


Figure 7. The electrode potential as a function of time. Controlled potential = -1500 mV, TEXP = 3000 msec.

that point, the "Faradaic charge", the charge that must be added to the cell in order to keep the Faradaic reaction at its diffusion limited value, is constant, so the effect of the "Faradaic charge" on the potential variation after the addition of each pulse is constant. The additional charge, also constant, charges the double layer capacitor along the almost linear transition from point B to point C.

The potential variation, as a function of time, in a blank solution containing the supporting electrolyte only (0.1 M KCl), is shown in Figure 7, Plot II. The run parameters for Plot II are the same as in Plot I.

The above method is a form of chronopotentiometry on a DME. Although the electrode area is changing with time, the above method can be used in a manner similar to chronopotentiometry for analysis.

C. Electrode Potential as a Function of Time

In the previous section, the method of controlling the potential of the DME at a fixed, constant value was discussed, and some examples of the operation of the coulometric generator were given. In this section, the discussion will be extended to more complex potential excitation waveforms.

A number of different potential excitation forms have been used in electrochemistry in order to perturb the

equilibrium of chemical system. The response of the chemical system to these voltage waveforms has been used for quantitative and qualitative analysis. In the conventional electrochemical system, the potential excitation waveform is generated by dedicated hardwired logic. To change the excitation waveform, some changes must be made to the hardware logic of the system. The data acquisition system is also controlled by dedicated hardwired logic in the conventional electrochemical systems, and in order to change it, some changes must be made to the hardware logic of the system. In the automated electrochemical system, in which the operation of the system is under computer control, the potential excitation waveforms are generated by the software logic. The same hardware logic is used to generate any potential excitation waveform simply by changing the control program. The same flexibility is offered for data acquisition in the automated electrochemical systems. The same hardware logic can be used in different ways, determined by the software logic. The coulостatic generator described here offers this flexibility.

In order to illustrate the method used to generate and apply, to the electrochemical cell, any potential excitation waveform, one example will be studied, i.e., the generation of a ramp.

Figures 8, 9 and 10 show the flow chart of the program

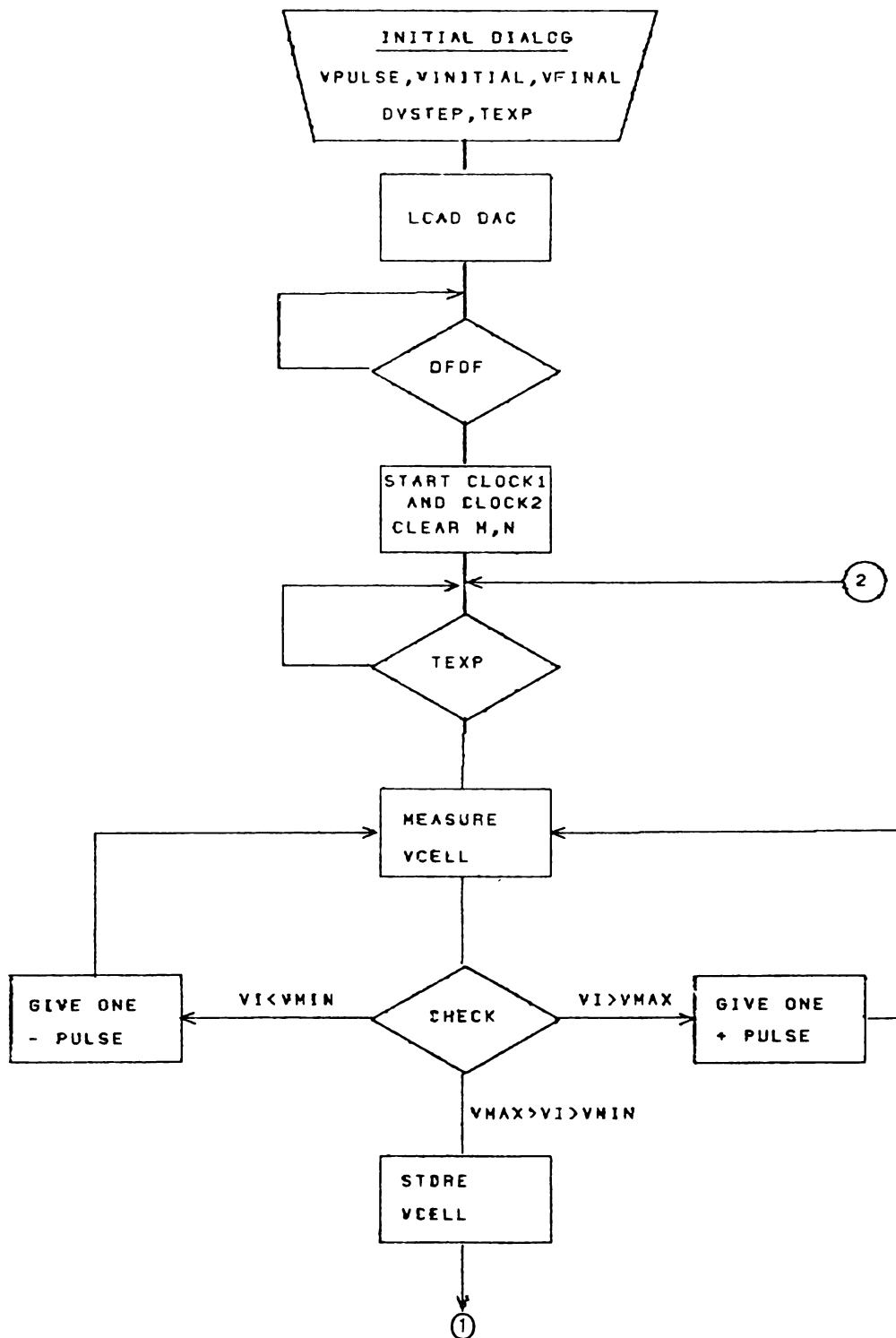


Figure 8. Flow chart of the program SCANV. First part.

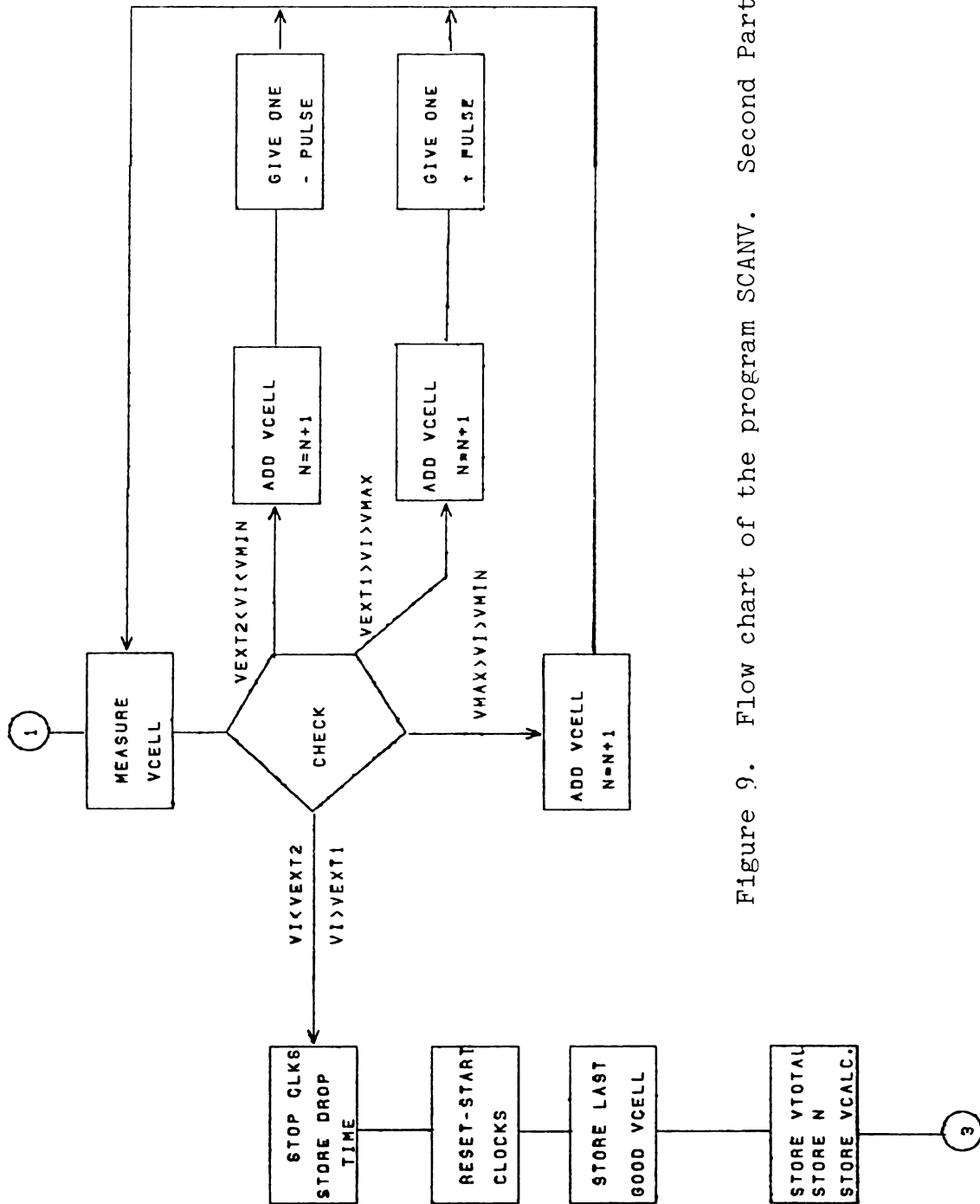


Figure 9. Flow chart of the program SCANV. Second Part.

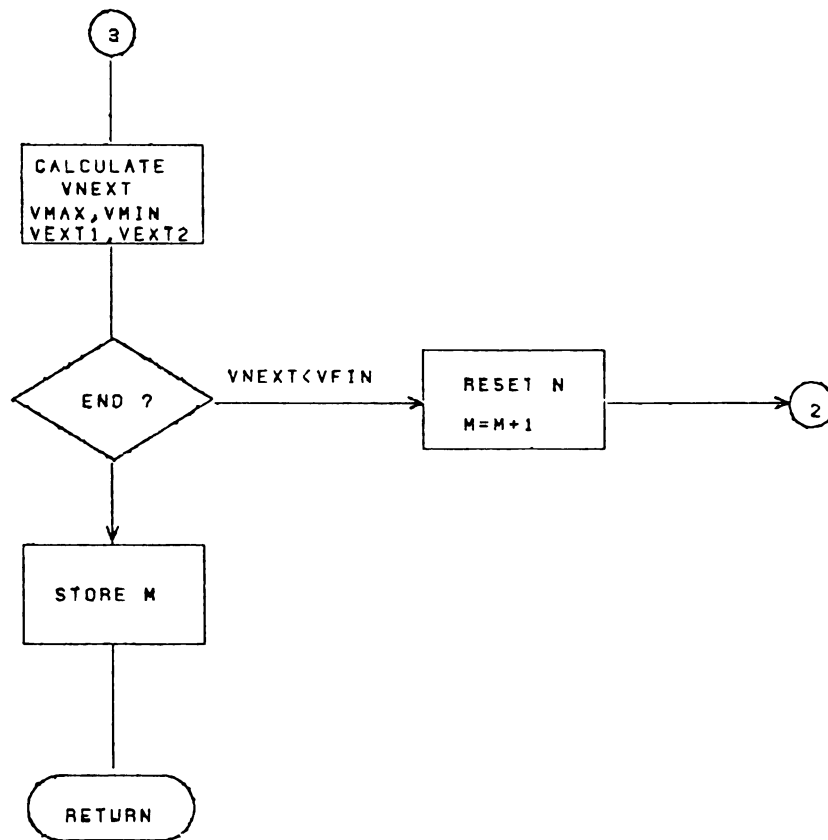


Figure 10. Flow chart of the program SCANV. Third part.

used to generate and apply a ramp to the electrochemical cell. The program starts with an initial dialog to obtain the values of the run parameters. This initial dialog is similar to the initial dialog described in Section B and the same discussion applies to it. The significance and the legal values for the run parameters are as follows:

VPULSE : Again VPULSE determines the output voltage of the DAC. Its value can be varied from -5 mV to -2500 mV. VPULSE determines the amount of charge that the pulse generator injects to the cell per charge pulse. For negative pulses $q_- = VPULSE \times 0.001 \mu F$ and for positive pulses $q_+ = VPULSE \times 0.001 \mu F$. The amount of charge that the pulse generator must inject to the cell per pulse in order to keep the electrode potential constant depends on the concentration of the supporting electrolyte, the concentration of the electroactive species, the desired electrode potential, and the time of the experiment. In order to find the optimum value for VPULSE the operator can run the program described in Section B and observe the effect of VPULSE on the accuracy of the potential control for the particular potential range of interest and solution. Once the optimum

value for VPULSE has been found it can be used from then on for all solutions of similar composition.

- VINITIAL : Determines the starting value of the ramp.
Its value can be from 0 mV to -2500 mV.
- VFINAL : Determines the final value of the ramp.
Its value can be from 0 mV to -2500 mV.
- DVSTEP : It determines the difference of the electrode potential between drops. Its value can be from 2 mV to 2500 mV.
- TEXP : It has the same significance as in Section B.

The initial dialog calculates VMAX, VMIN, VEXT1, and VEXT2 for the first value of the electrode potential (VINITIAL). To calculate VMAX and VMIN the value 4 mV is used, and for VEXT1, VEXT2, the value 100 mV is used. To start the experiment, a special character must be entered from the keyboard ($\uparrow$ C). After the detection of the drop fall, the computer starts the two real-time clocks and clears the two 16-bit software counters; COUNTER 1, and COUNTER 2. After TEXP has elapsed, the computer measures the electrode potential and if it is not equal to VINITIAL it asks the pulse generator to inject positive or negative pulses in order to bring the electrode potential to VINITIAL. When the electrode potential reaches the desired value, the computer stores this first

"good" value and continues to control the addition of the charge pulses in order to maintain the electrode potential constant. Each measured potential value that is not beyond the two extreme values VEXT1 and VEXT2, is added to a 32-bit software buffer and the number of measurements is increased by one. When the program detects the drop fall, it stops the clocks and stores the drop time. Then it resets and restarts the clocks. In the few following steps the program stores some information concerning this drop. In the following steps the program calculates the potential which the next drop must be and checks this value to see if this is the end of the scan. If VNEXT < VFINAL the program stores VNEXT and calculates the new values for VMAX, VMIN, VEXT1, VEXT2, and jumps to the TEXP timing loop. If VNEXT > VFINAL the program stores the number of drops (M) and returns to the calling program. After the end of the scan the operator can store the acquired data on a floppy disk by entering the name of the subroutine SAVE2 in the keyboard. The stored information is transmitted to the minicomputer for final processing and final plotting. A listing of the programs used in the minicomputer for data processing is given in Appendix B. The stored information includes: the number of drops (M), the first "good" and the last "good" electrode potential values for each drop, the sum of all "good" values and the number of measurements (N) for each drop, the

theoretical value of the electrode potential for each drop, and the drop time for each drop.

Figure 11 shows three software generated ramps. In this figure the calculated values of the electrode potential are plotted as a function of time. The run parameters for Plot 1 are: VPULSE = -200 mV, VINITIAL = 0 mV, VFINAL = -1000 mV, DVSTEP = 100 mV, and TEXP = 100 msec. For plot 2 and plot 3 the run parameters are the same as before except DVSTEP which has the value 50 mV and 10 mV respectively. The sweep speed for ramp 1 is 0.656 V/min, for ramp 2 is 0.342 V/min and for ramp 3 is 0.0728 V/min.

Figure 12 and 13 show the agreement between the theoretical ramp, generated by the program, and the actual ramp applied to the cell by the system. In these plots the average values of the electrode potential have been plotted against the calculated potential values. The data were obtained from a solution of 1×10^{-3} M Cd^{2+} in 0.1 M KCl. Nitrogen was passed through the solution for 5 minutes before the experiment. For the plot in Figure 12 the run parameters are VPULSE = -300 mV, VINITIAL = 0 mV, VFINAL = -1000 mV, DVSTEP = 50 mV, and TEXP = 100 msec. For the plot in Figure 13 the run parameters are: VPULSE = -300 mV, VINITIAL = 0 mV, VFINAL = -1000 mV, DVSTEP = 10 mV, and TEXP = 100 msec.

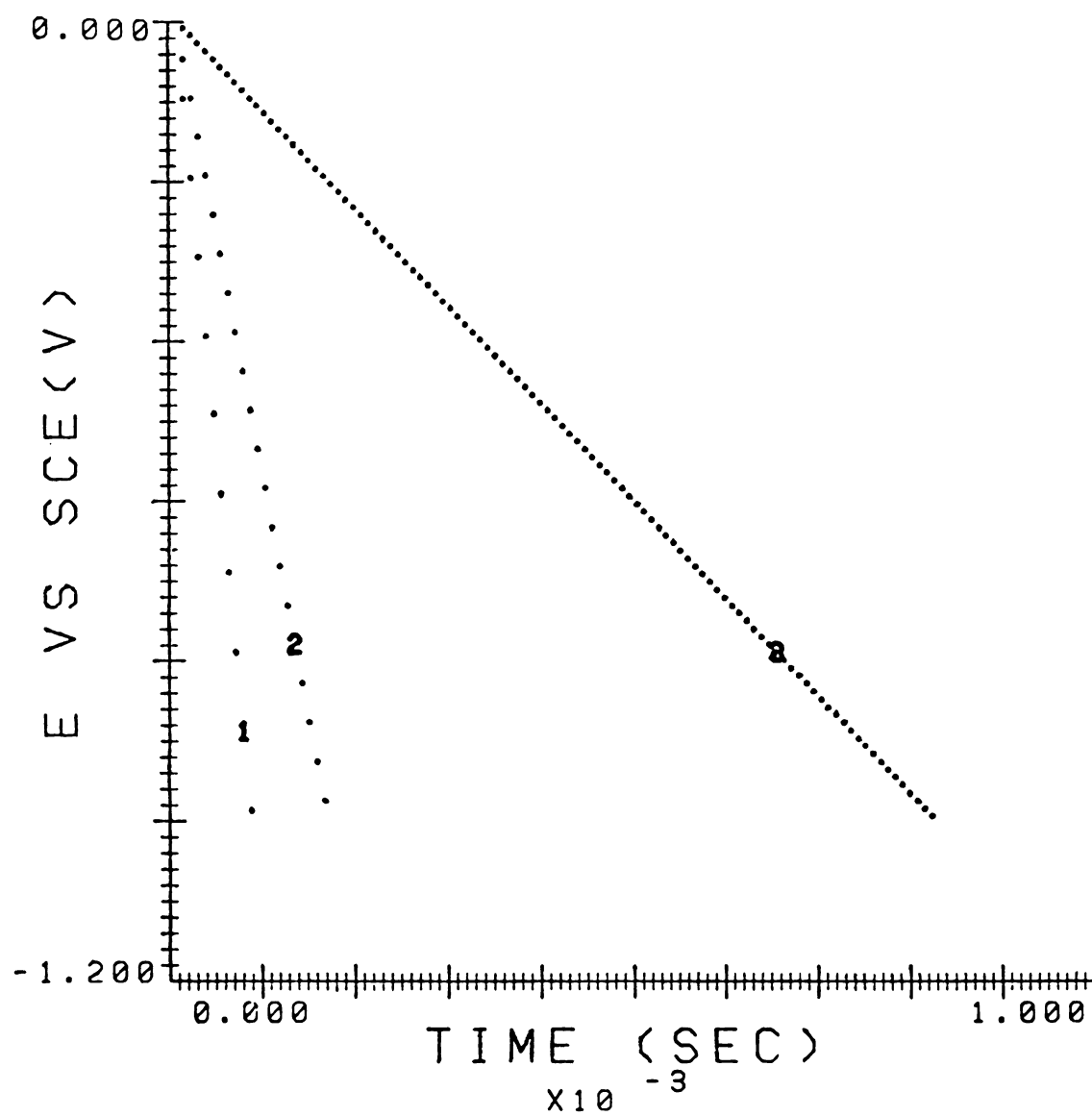


Figure 11. Software generated ramps.

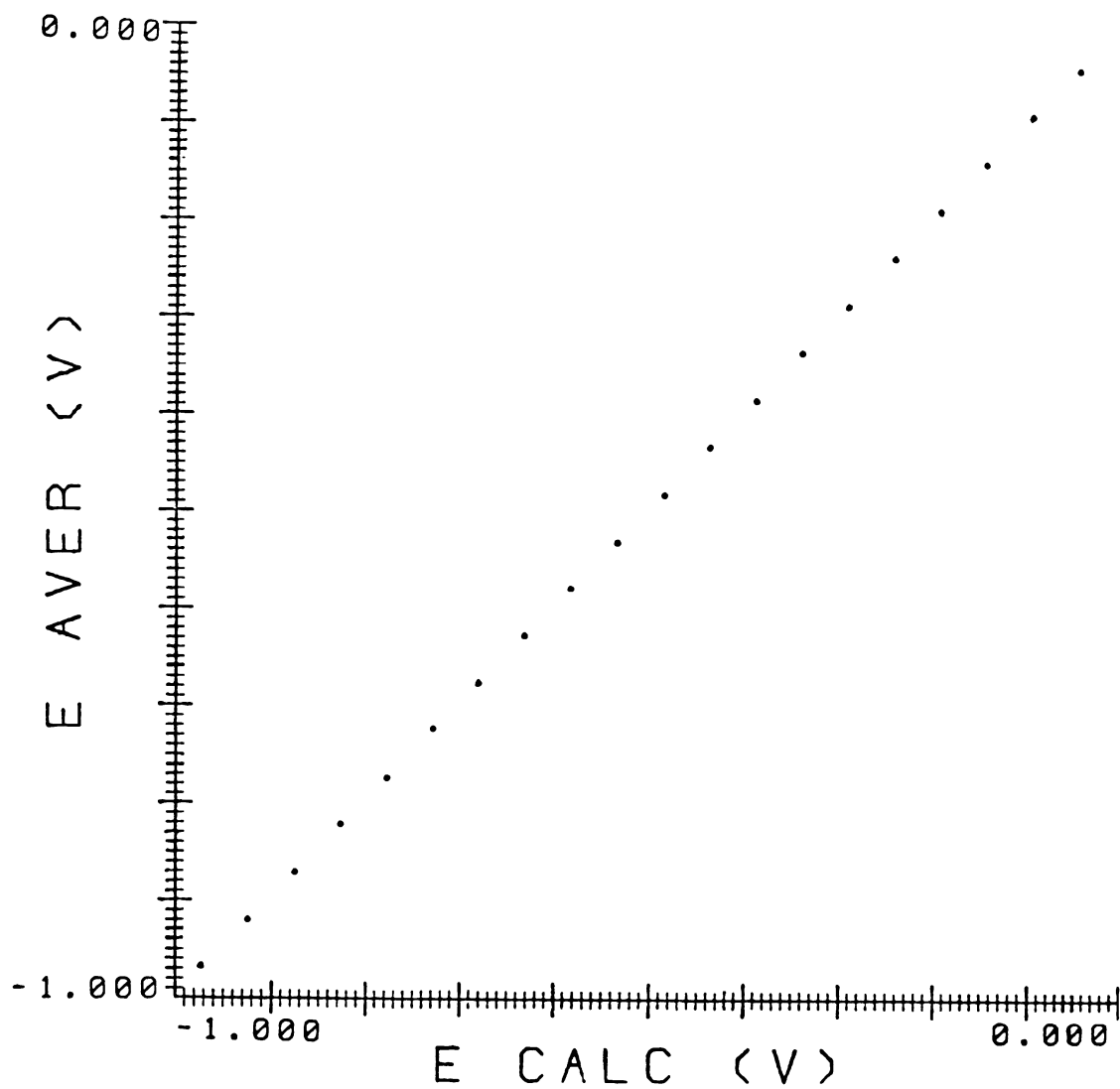


Figure 12. The actual ramp applied to the cell as a function of the theoretical ramp. DVSTEP = 50 mV.

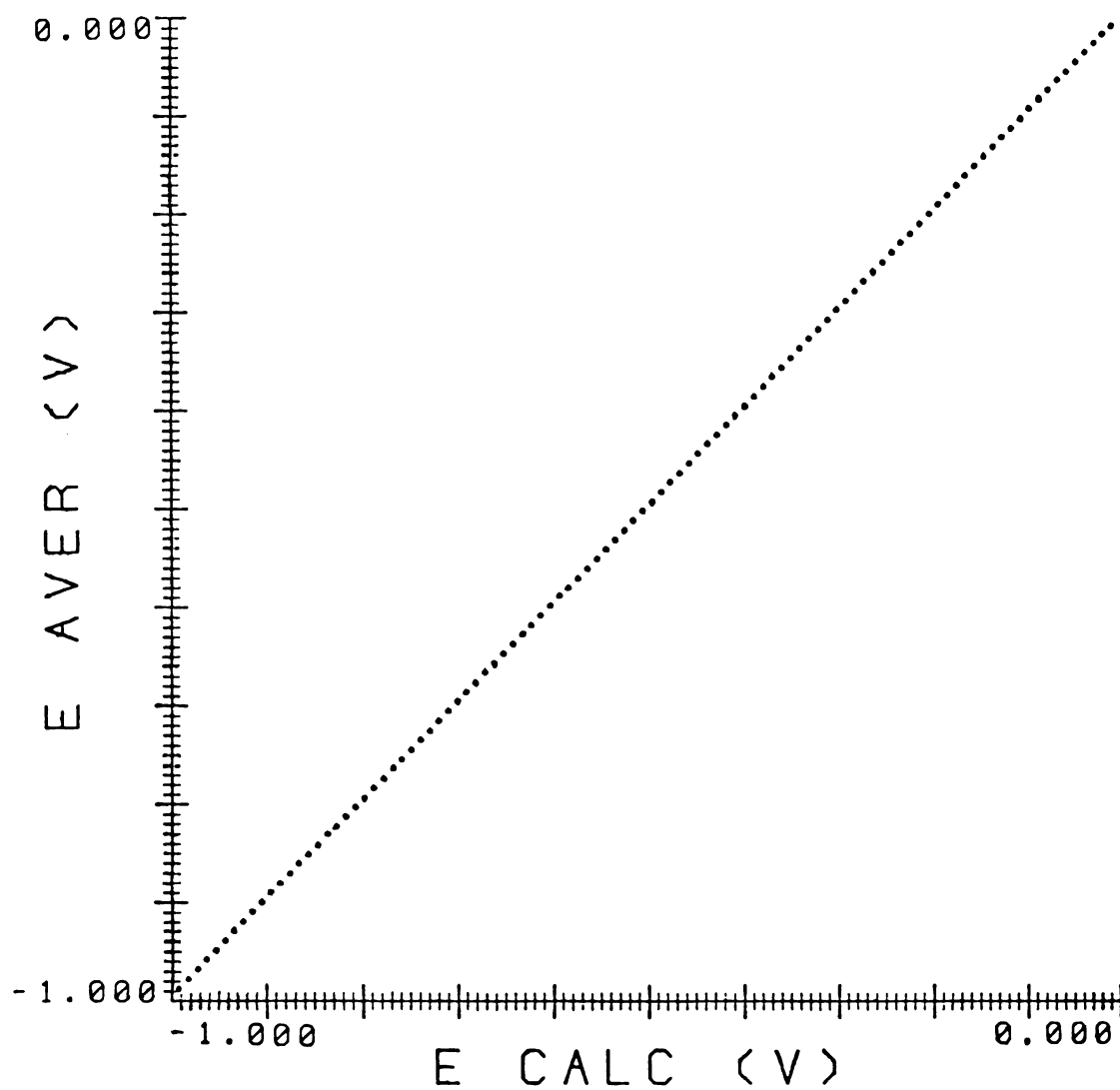


Figure 12. The actual ramp applied to the cell as a function of the theoretical ramp. DVSTEP = 50 mV.

D. Effect of the Supporting Electrolyte

In the two previous sections the methods used to generate simple and complex potential excitation forms were discussed, the effects of the run parameters were studied and some examples of the data obtained from real solution were given. All these test solutions contained 0.1 M KCl as supporting electrolyte. In this section, the effect of the supporting electrolyte on the performance of the coulometric generator will be discussed.

Since the electrochemical cell is in an open circuit and all potential measurements are made when no net current is passing through the cell, the performance of the coulometric generator should not be affected by the concentration of the supporting electrolyte. A set of solutions with different concentrations of supporting electrolyte were prepared and the test programs described in Section B and Section C were used to observe the performance of the coulometric generator. The data obtained from these tests indicate that the characteristics of the coulometric generator are not affected by the concentration of the supporting electrolyte. Concentrations as low as 0.001 M KCl may be used with no appreciable effect.

Figures 14 and 15 show the electrode potential variations as a function of time. These data were obtained from a solution of 1×10^{-4} M Cd^{2+} in 0.0001 M KCl as supporting electrolyte using the test program CELLT5

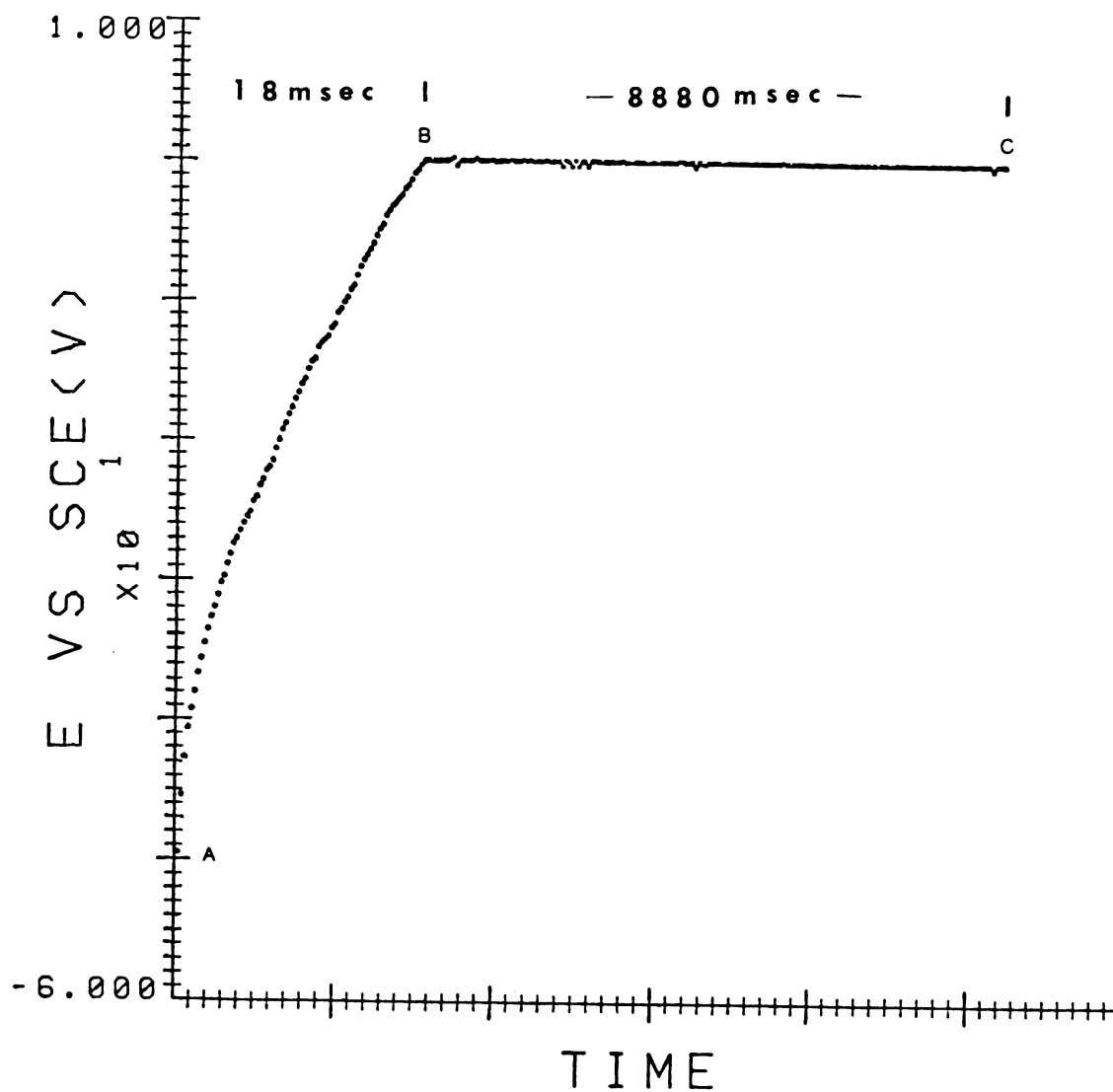


Figure 14. The electrode potential as a function of time. Controlled potential = 0 mV. Supporting electrolyte 1×10^{-4} M KCl.

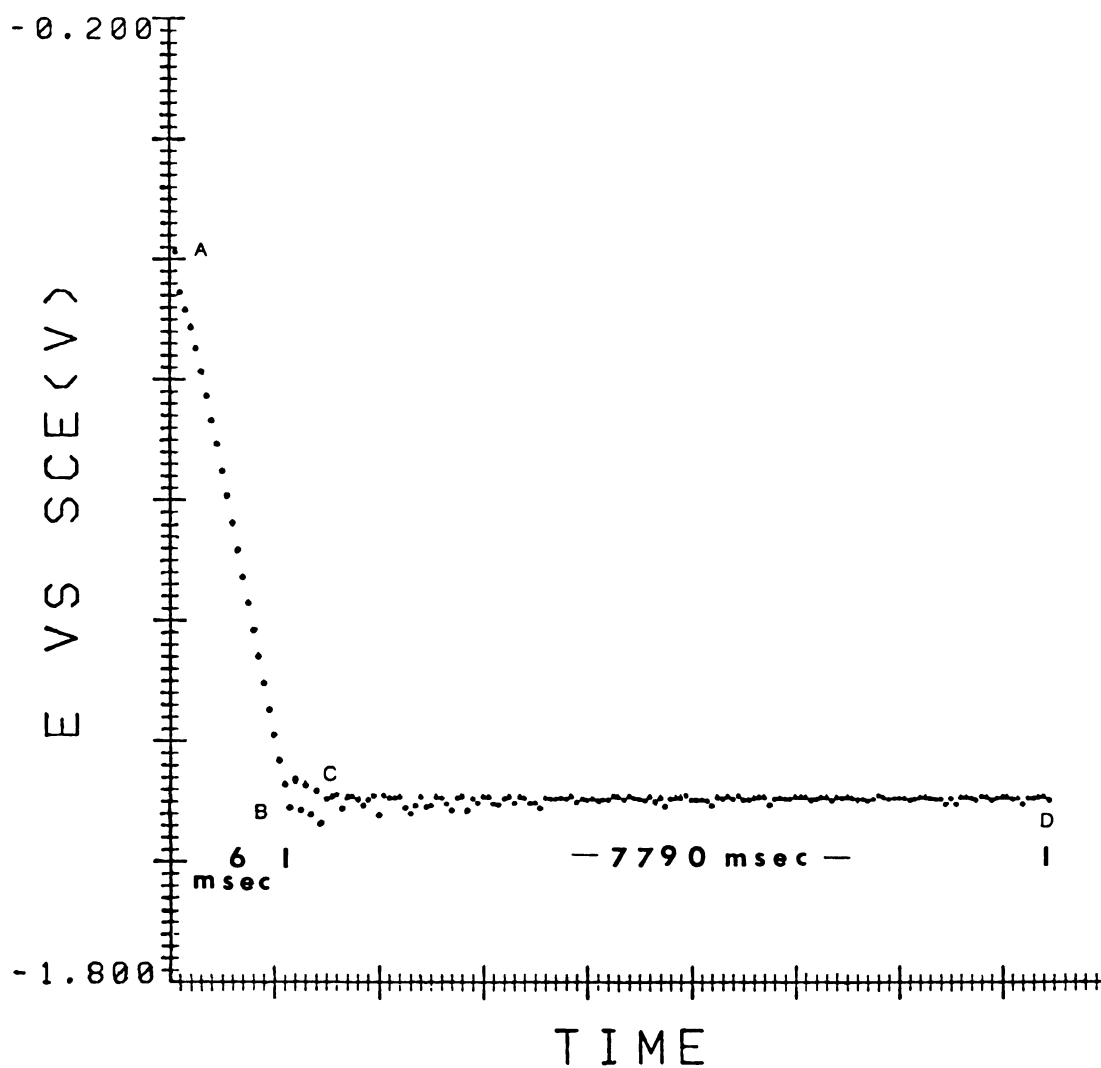


Figure 15. The electrode potential as a function of time. Controlled potential = -1500 mV. Supporting electrolyte 1×10^{-4} M KCl.

(Section B). The run parameters for the plot in Figure 14 are: VPULSE = -250 mV, VCELL = 0 mV, DVCELL = 4 mV, TEXP = 100 msec, DELAY = 200. The total number of points are 37275 and the drop time is 8998 msec. The run parameters for the plot in Figure 15 are: VPULSE = -250 mV, VCELL = 0 mV, DVCELL = 4 mV, TEXP = 100 msec, DELAY = 200. The total number of points are 29223 and the drop time is 7896 msec. The time that the system needs to establish a good control over the electrode potential is about 397 msec (Point C). After that point and until the end of the drop (7399 msec) the system controls the potential at a constant value within ± 10 mV.

Figure 16 shows the agreement between the theoretical ramp, generated by the program SCANV (Section C) and the actual ramp that the system applied to three different solutions. The run parameters for the three plots shown in Figure 16 are: VPULSE = -300 mV, VINITIAL = - mV, VFINAL = -1500 mV, DVSTEP = 50 mV, TEXP = 100 msec. The solution used contained 1×10^{-4} M Cd^{2+} in 0.1 M KCl (Plot 1), 1×10^{-4} M Cd^{2+} in 0.001 M KCl (Plot 2), and 1×10^{-4} M Cd^{2+} in 0.0001 M KCl (Plot 3). Plot 2 and Plot 3 have been shifted by 100 mV and 200 mV respectively in order to be plotted in the same figure.

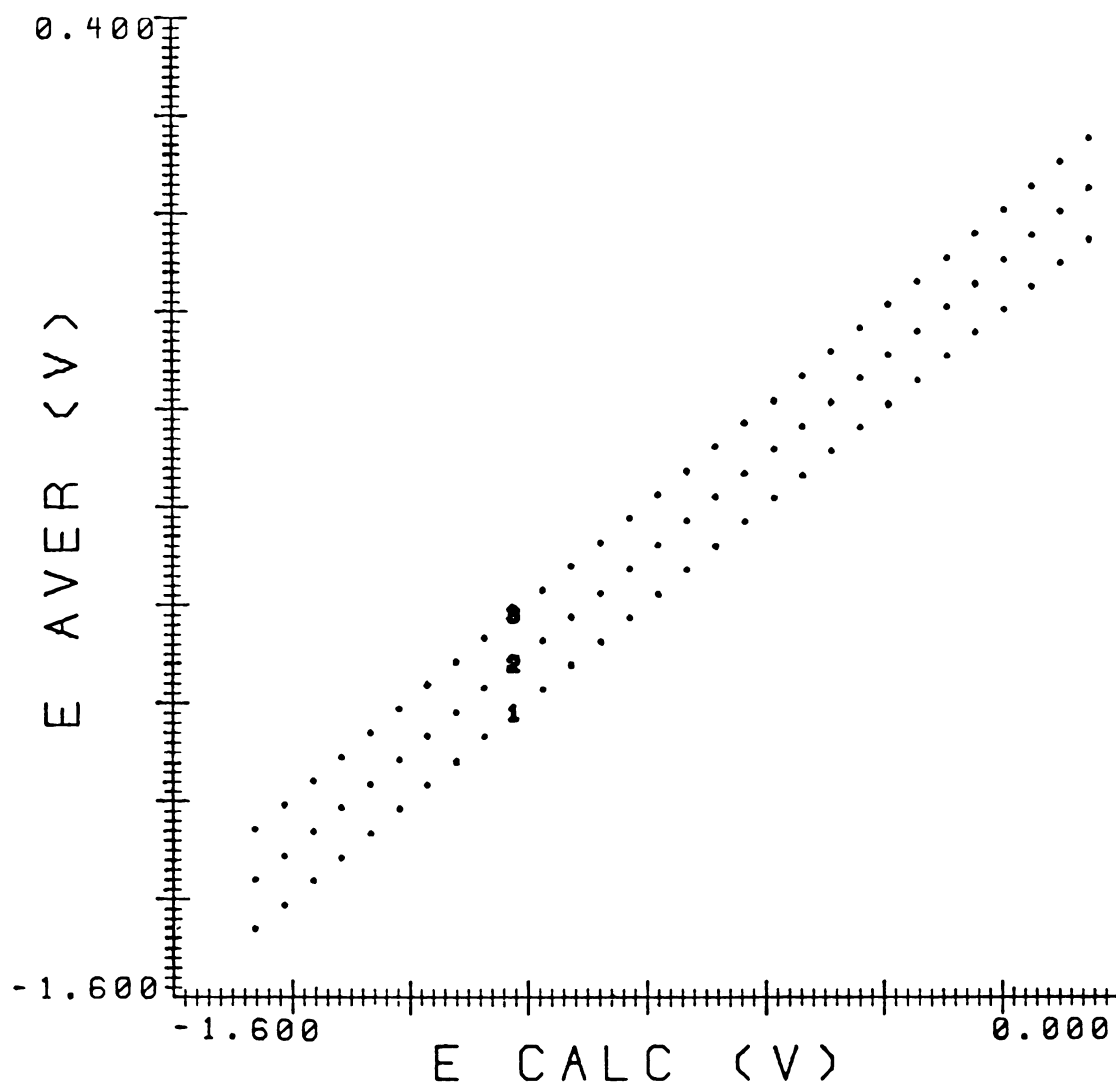


Figure 16. The actual ramp applied to the cell as a function of the theoretical ramp for three different solutions of KCl as supporting electrolyte (Plot 1 0.1 M KCl, Plot 2 0.001 M KCl, Plot 3, 0.0001 M KCl).

E. Implementation of the Coulostatic Generator in the Basic Polarization Techniques

In the previous sections the operation and the characteristics of the coulостatic generator were discussed. Also in Section B, the software drop fall detector used to synchronize the system with the beginning of the drop was discussed. The software drop fall detector does not require any extra hardware logic and so it is not critical in its adjustment. The flexibility of the system to generate different potential excitation waveforms was illustrated in Section C. The real flexibility that the system offers can be seen by its ability to perform a wide range of electrochemical experiments where the current or the potential must be measured or controlled. Since the operation of the system is under computer control, and the operating program determines the type of the experiment that the system will perform, the operator can choose almost any polarization technique to work with in order to obtain the best response of the studied chemical system.

1. Controlled Potential Experiments

One of the obvious applications of the coulостatic generator is in experiments involving control of the electrode potential while measuring the resultant current. The current needed to maintain the potential constant at

a particular value can be calculated directly from the charge content of the pulses and the number of pulses used during a specific time. In addition, information regarding the differential double layer capacitance can be obtained by measuring the potential immediately before and after the addition of a charge pulse. Once the differential double layer capacitance has been calculated in the particular potential range of interest, the system can be used to produce potential step functions. A large charging capacitor can be used to rapidly change the potential to a new value, and then smaller charge pulses can be used to maintain the potential constant. Since the large pulse is used to change the double layer capacitor to the new potential value, the number of the smaller pulses, used to maintain the potential constant, give the integral of the Faradaic current. This provides a very effective way to compensate the charging current effects.

2. Controlled Current Experiments

The coulometric generator can be used as a current source for controlled current experiments in which a constant current is passed between the working and the counter electrode, and the potential of the working electrode is measured as a function of time. By injecting charge pulses at constant time intervals to the cell, the coulometric generator acts as a current source. The

average current supplied by the coulостatic generator is controlled by the charge content and the rate at which the pulses are applied. Different current densities can be obtained under software control simply by changing these time parameters. In addition, rapid current steps or complex current waveforms can be created simply by programming changes. Again the differential double layer capacitance can be calculated from the potential measurements immediately before and after the addition of charge.

CHAPTER 3

POLAROGRAPHIC MEASUREMENTS USING THE MICROCOMPUTER CONTROLLED COULOSTATIC GENERATOR

CHAPTER 3

POLAROGRAPHIC MEASUREMENTS USING THE MICROCOMPUTER CONTROLLED COULOSTATIC GENERATOR

A. Introduction

The operation and the characteristics of the coulometric generator, and its possible implementation in the basic polarization techniques have been described in Chapter 2. In this chapter the application of the coulometric generator in polarography will be discussed.

In 1920 Jaroslav Heyrovsky used a dropping mercury electrode to observe the current-voltage curves obtained from an electrochemical cell, and he set the basis for a new electrochemical technique, named polarography. The basic principle of polarography is the application of a potential excitation signal to the cell, and the display of the resulting current as a function of the applied potential. The current-voltage curves can be used for both quantitative and qualitative analysis, and polarography has been used not only for the determination of inorganic ions but for organic substances as well. It can also be applied to solutions in some nonaqueous solvents. Polarography is probably the oldest instrumental method of analysis which is still under development, and as a classical method of analysis it has been described in many

books (35-38).

When a potential sufficient to reduce the surface concentration of the electroactive species to less than 1% of the bulk concentration is applied to the DME, the rate of the electrode reaction becomes diffusion controlled. Passage of current requires material to be transported to the electrode surface as well as away from it. Starting from Fick's second law of diffusion, a relationship can be developed to describe the diffusion limited current as a function of the concentration and the diffusion of the electroactive species. According to Fick's second law of diffusion, (38)

$$\frac{dC(x,t)}{dt} = \frac{Dd^2C(x,t)}{dx^2} \quad (1)$$

where D represents the diffusion coefficient, C the concentration of the electroactive species at distance x from the electrode surface, and t the amount of time that the concentration gradient has existed. Equation 1 can be solved to give a relationship for the concentration in terms of the parameters x and t:

$$C(x,t) = C_{\infty} \operatorname{erf} \left(\frac{x}{D^{1/2}t^{1/2}} \right) \quad (2)$$

By taking the derivative of Equation (2), the concentration gradient at the electrode surface can be found:

$$\left(\frac{dC}{dx}\right)_{x=0} = \frac{C}{\pi^{1/2} D^{1/2} t^{1/2}} \quad (3)$$

This gradient produces a flux of material crossing the electrode boundary which can be expressed in terms of the electrode current, i :

$$i = nFAD \left(\frac{dC}{dx}\right) \quad (4)$$

where n is the number of electrons involved in the reaction, F the faraday, and A the area of the electrode. When Equation (3) is substituted into this relation, an expression for the semi-infinite linear diffusion current is obtained:

$$i = \frac{nFACD^{1/2}}{\pi^{1/2} t^{1/2}} \quad (5)$$

(Cottrell Equation)

The above diffusion current equation can be extended to include the dropping mercury electrode by appropriate substitution for the area of the electrode. The area of the DME as a function of the experimental parameters is given by Equation (6):

$$A = (4\pi)^{1/3} m^{2/3} t^{2/3} d^{-2/3} \quad (6)$$

where m is the mass flow rate of mercury from the orifice of the capillary, t the life of the drop, and d the density of the mercury under the experimental conditions.

By substituting Equation (6) to Equation (5) the calculated diffusion current for the dropping mercury electrode is obtained:

$$(i_t)_{\text{calc.}} = 464 \text{ nCD}^{1/2} m^{2/3} t^{1/6} \quad (7)$$

Experimental tests indicate that the constant in Equation (7) is too small by a factor of $\sqrt{7/3}$. This correction factor is due to the fact that the growth of the mercury drop happens in the solution away from the capillary orifice. Thus the correct diffusion current expression for a dropping mercury electrode is:

$$i = 706 \text{ nCD}^{1/2} m^{2/3} t^{1/6} \quad (8)$$

which gives the current at any time up to the life time of the drop. If the drop time, t_d , is substituted, the Ilkovic equation is obtained:

$$i_d = 706 \text{ nCD}^{1/2} m^{2/3} t^{1/6} \quad (9)$$

For reversible reactions the applied potential is related to the polarographic current by the Nernst equation:

$$E = E_{1/2} + \frac{0.059}{n} \log \frac{i_d^{-1}}{i} \quad (10)$$

where i is the current at a particular applied potential. The half wave potential, $E_{1/2}$, is defined as the potential at which the current is equal to $i_d/2$ and it is also related to the standard electrode potential, E° , of the electroactive species according to:

$$E_{1/2} = E^\circ - E_{\text{ref}} - \frac{0.059}{n} \log \frac{D_{\text{ox}}^{1/2}}{D_{\text{red}}^{1/2}} \quad (11)$$

where E_{ref} is the potential of the reference electrode and D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced species respectively. Because $E_{1/2}$ is directly related to the standard reduction potential of the redox couple, it is useful for qualitative analysis of electroactive species.

B. Determination of Cd^{2+}

In order to use the coulostatic generator in the polarographic determination of Cd^{2+} in a solution, the program described in Figures 17, 18, and 19 was used. This program was used to generate and apply a ramp to the cell and to measure the resulting current as a function of the electrode potential.

The program starts with an initial dialog, similar to that described in Chapter 2, Section C to obtain the values of the run parameters. The significance and the legal values for the parameters VPULSE, VINITIAL, VFINAL, and

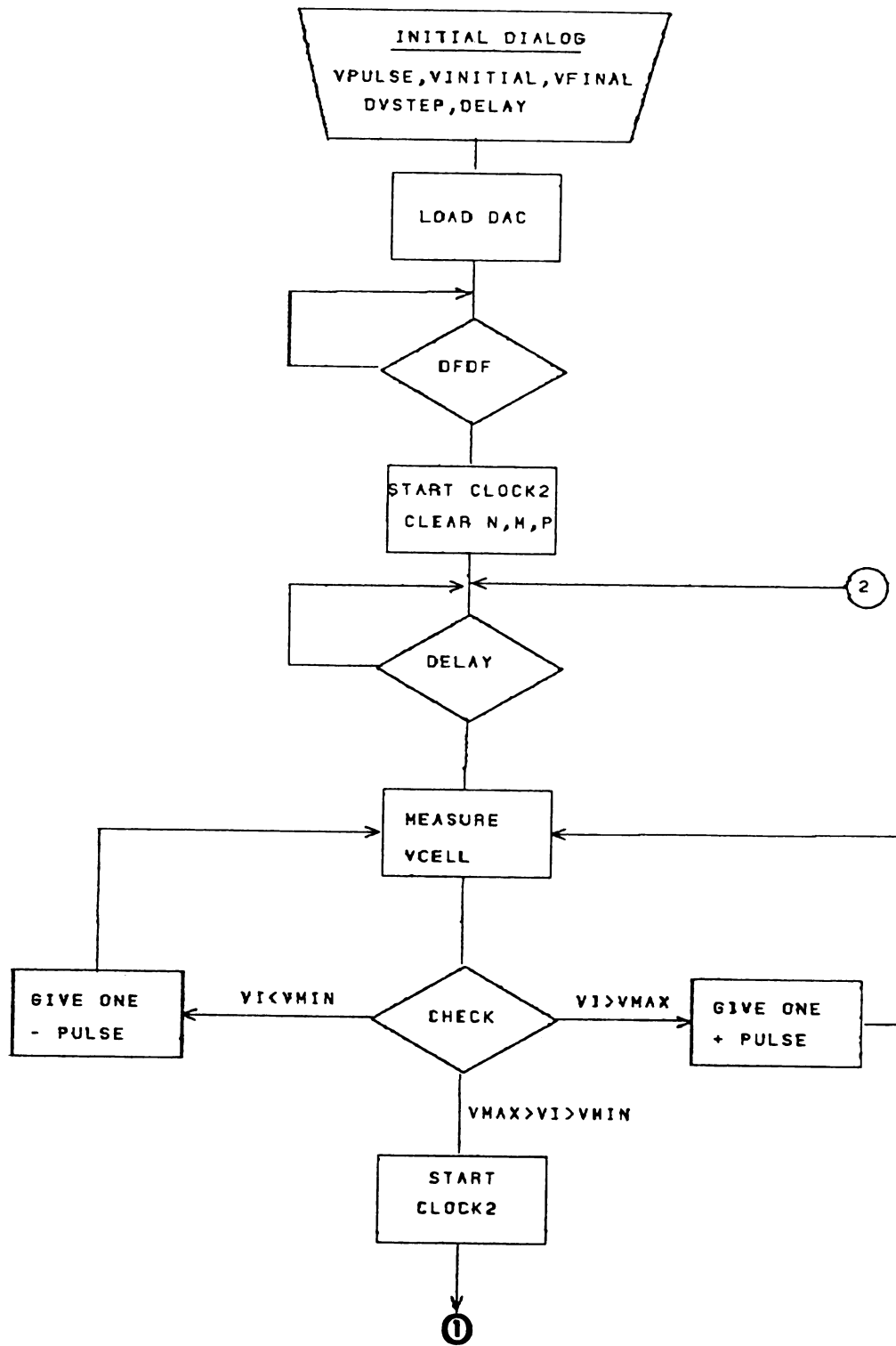


Figure 17. Flow chart of the program POLAR1. First part.

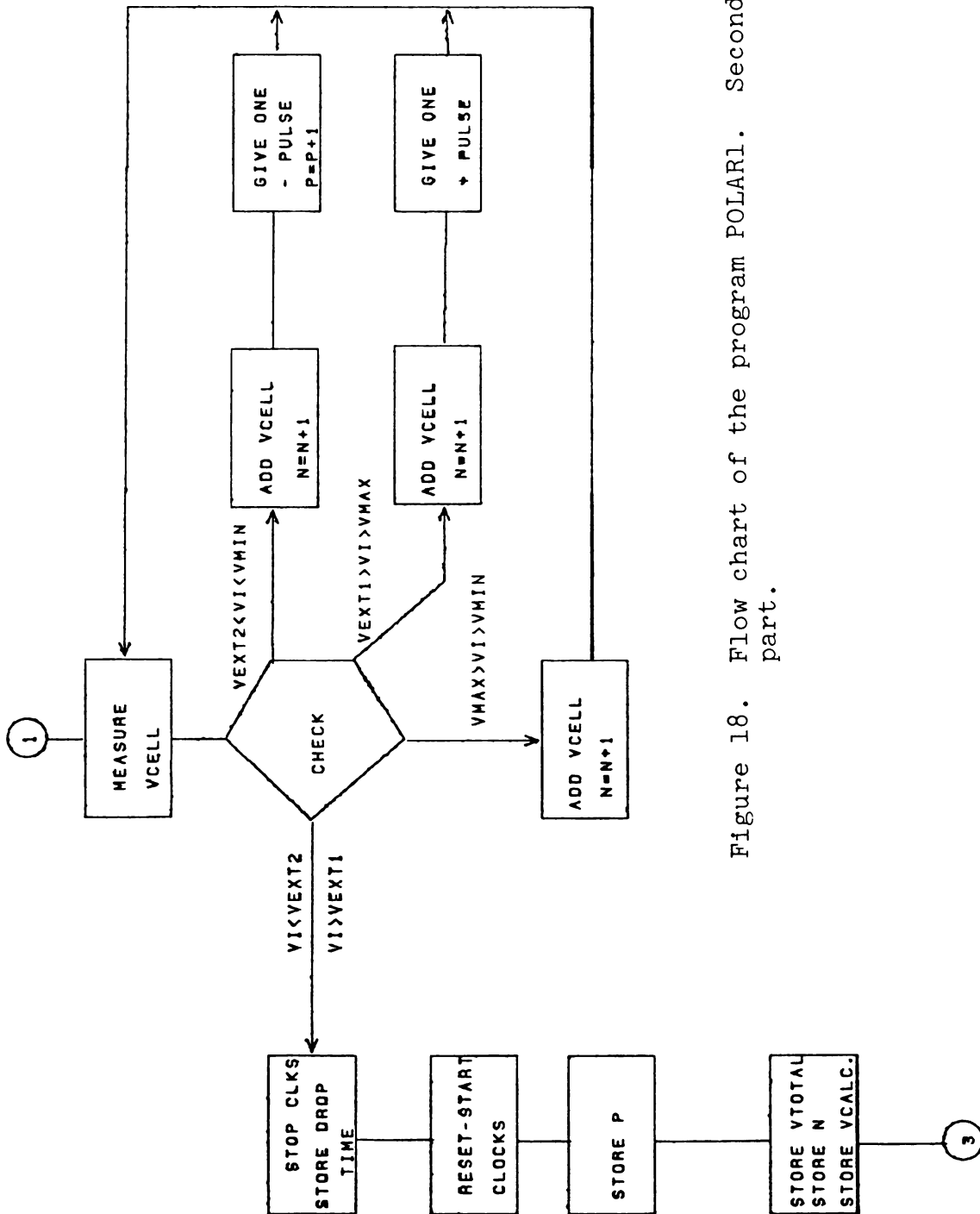


Figure 18. Flow chart of the program POLAR1. Second part.

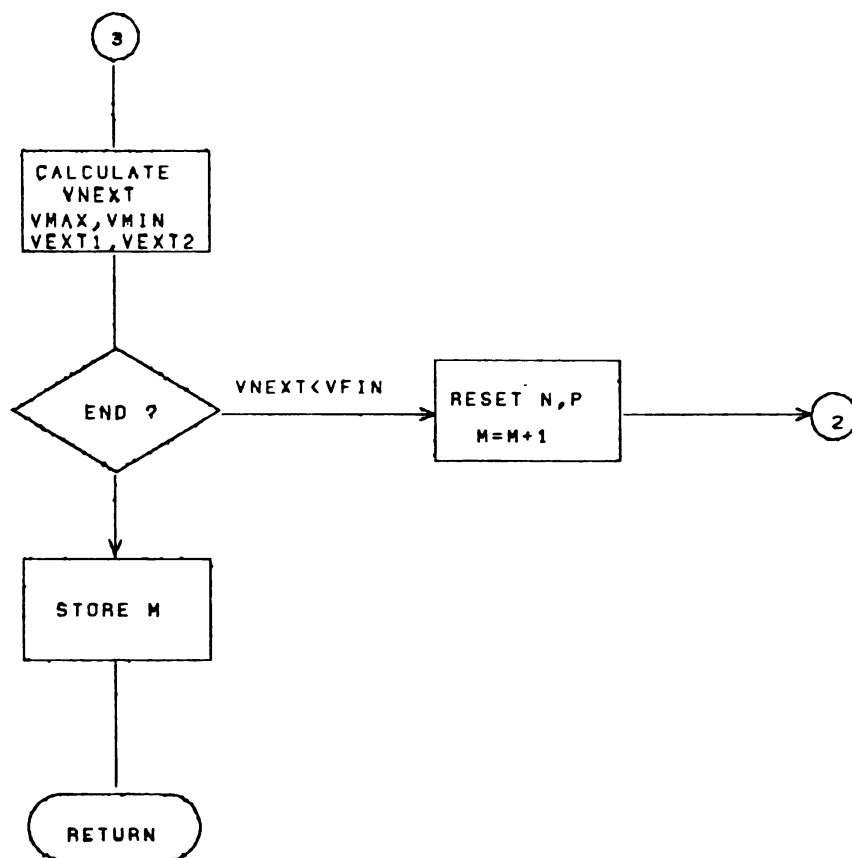


Figure 19. Flow chart of the program POLAR1. Third part.

DVSTEP are the same as in SCANV program (Chapter 2C).

The parameter DELAY has the same significance as the parameter TEXP in the SCANV program and it indicates the delay time between the beginning of the drop and the beginning of the experiment. A 16 bit software counter has been added in this program which measures the number of negative pulses that the system injects to the cell in order to keep the electrode potential constant.

After the detection of the drop fall, the computer starts CLOCK2. After DELAY has elapsed, the computer measures the electrode potential and if it is not equal to the desired value, the computer asks the pulse generator to inject positive or negative pulses in order to bring the electrode potential to the controlled value. When the electrode potential reaches the desired value, the computer starts CLOCK1 and continues to control the addition of charge pulses in order to maintain the electrode potential constant. Each measured potential value that is not beyond the two extreme values VEXT1 and VEXT2 is added to a 32-bit software buffer and the number of measurements (N) is increased by one. After every injection of a negative pulse to the cell, the tally of the number of negative pulses (P) is increased by one. When the program detects the drop fall, it stops the clocks and stores the time that has been elapsed from the moment that the electrode potential reaches the desired value until the end of the drop.

Immediately after that, the program resets and restarts the clocks. In the following steps the program stores some information (N, P, Vtotal, Vcalcul.) concerning this particular drop and calculates the potential at which the next drop must be. If $V_{NEXT} < V_{FINAL}$, the program stores V_{NEXT} , calculates the new values for V_{MAX} , V_{MIN} , V_{EXT1} , V_{EXT2} and jumps to the DELAY timing loop. If $V_{NEXT} > V_{FINAL}$, the program stores the number of drops (M) and returns to the calling program. By entering the name of the subroutine SAVE2 in the keyboard, the operator can store the acquired data on a floppy disk. The stored information is transmitted to the minicomputer for final processing and final plotting.

The current which the system provides to the cell in order to keep the electrode potential constant can be calculated from the equation

$$I = \frac{C_2 \cdot VPULSE \cdot P}{t} \quad (12)$$

where C_2 is the value of the charging capacitor, VPULSE is the charging voltage and P is the number of the negative pulses injected to the cell during time t. The quantity V_{total} and the number of points (N) can be used to calculate the average electrode potential of each drop.

The plot of the calculated current versus the average electrode potential should look like a smooth polarogram.



Figures 20, 21, and 22 show the polarograms obtained from different solutions of Cd^{2+} in 0.1 M KCl as supporting electrolyte. The run parameters for these polarograms are: VPULSE = -300 mV, VINITIAL = 0 mV, VFINAL = -1500 mV, DVSTEP = 50 mV, DELAY = 100 msec. Table 1 contains a listing of the concentrations of Cd^{2+} and the diffusion limited current corresponding to each polarogram. Figure 23 shows a plot of the measured diffusion limited current as a function of the concentration of Cd^{2+} in the solution. The working curve has a slope of 4.6×10^3 and an intercept of 2.314×10^{-2} , and as it can be seen, it does not deviate from linearity in the studied range of concentrations of Cd^{2+} (1×10^{-3} M to 5×10^{-6} M Cd^{2+}). Figure 24 shows a plot of $\log I_d$ versus $\log C$.

The accuracy of the classical polarographic method is of the order of 1 percent in the concentration range from 10^{-2} down to about 10^{-4} molar, and of the order of 5 percent between 10^{-4} and 10^{-5} molar. The lower detection limit of the classical polarographic method is in the neighborhood of 10^{-6} molar (35). One of the main factors which determines the accuracy and sets the detection limits in the conventional DC polarography is the charging current. The charging current is part of the measured current in the electrochemical cell and it is used to charge the double layer capacitor of the working electrode to the controlled potential. In order to improve the accuracy

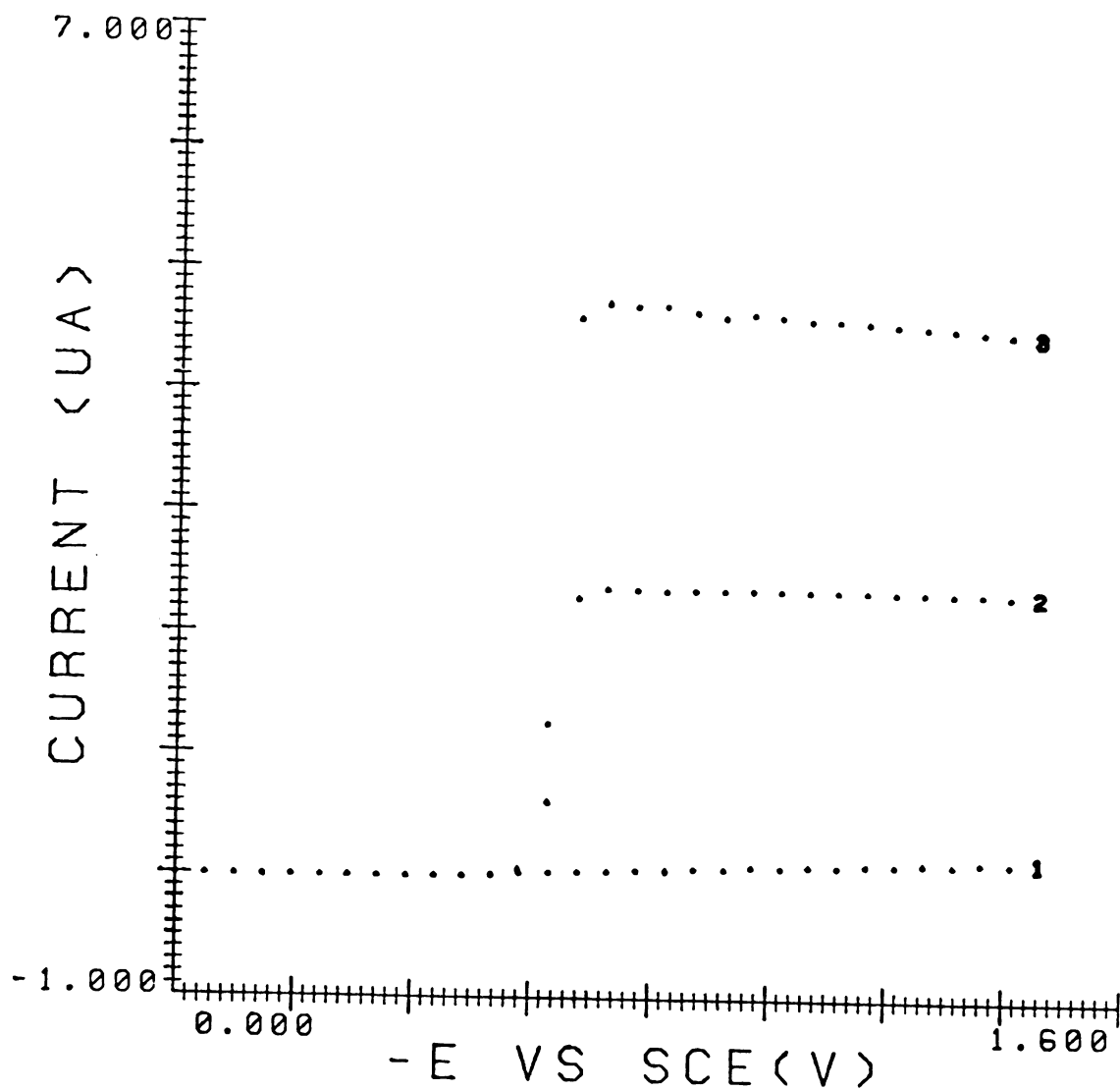


Figure 20. Polarogram of a 0.1 M KCl solution (1), 5×10^{-4} M Cd^{2+} in 0.1 M KCl solution (2), 1×10^{-3} M Cd^{2+} in 0.1 M KCl solution (3).

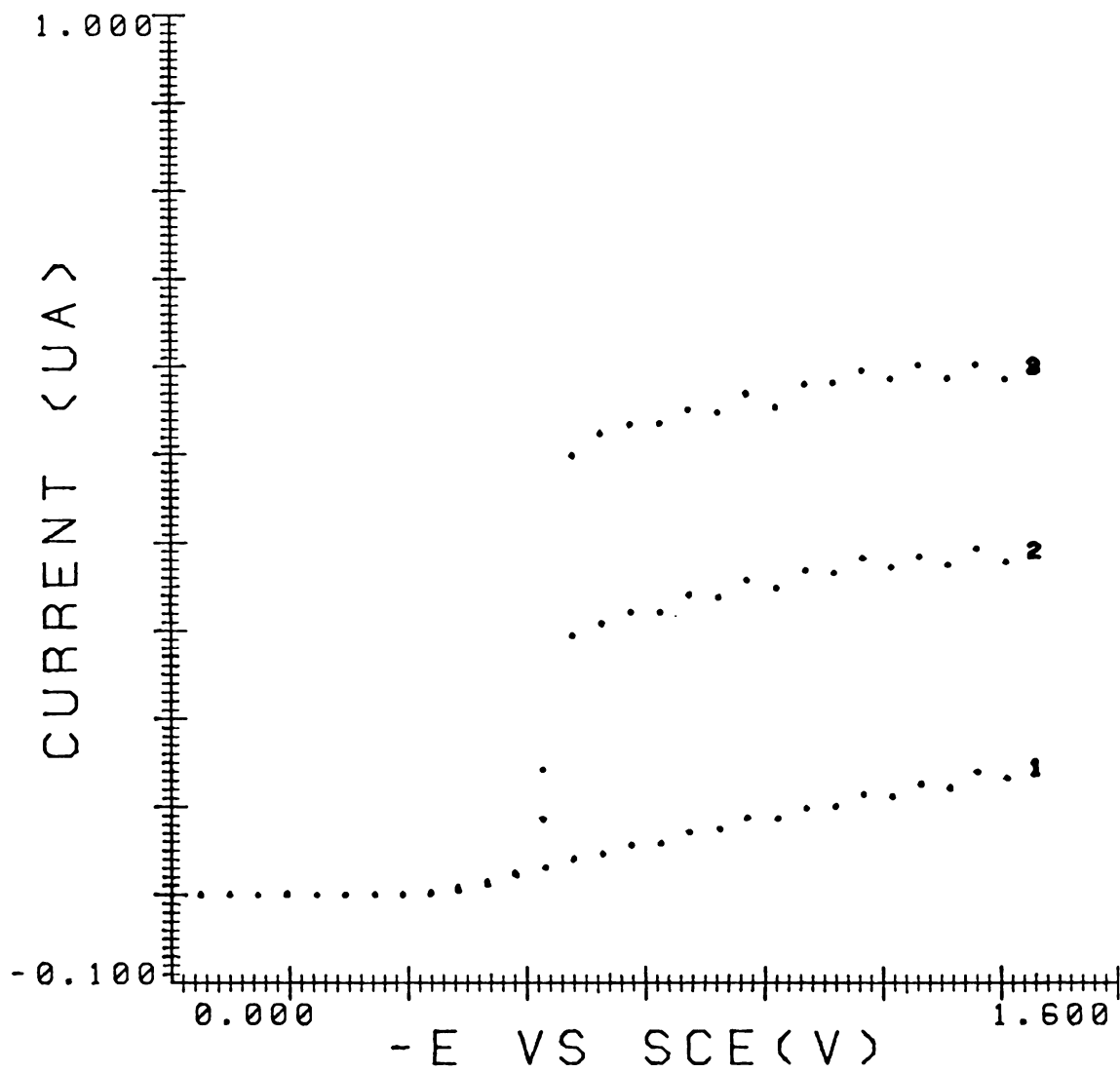


Figure 21. Polarogram of a 0.1 M KCl solution (1),
 5×10^{-5} Cd^{2+} in 0.1 M KCl solution (2),
 1×10^{-4} Cd^{2+} in 0.1 M KCl solution (3).

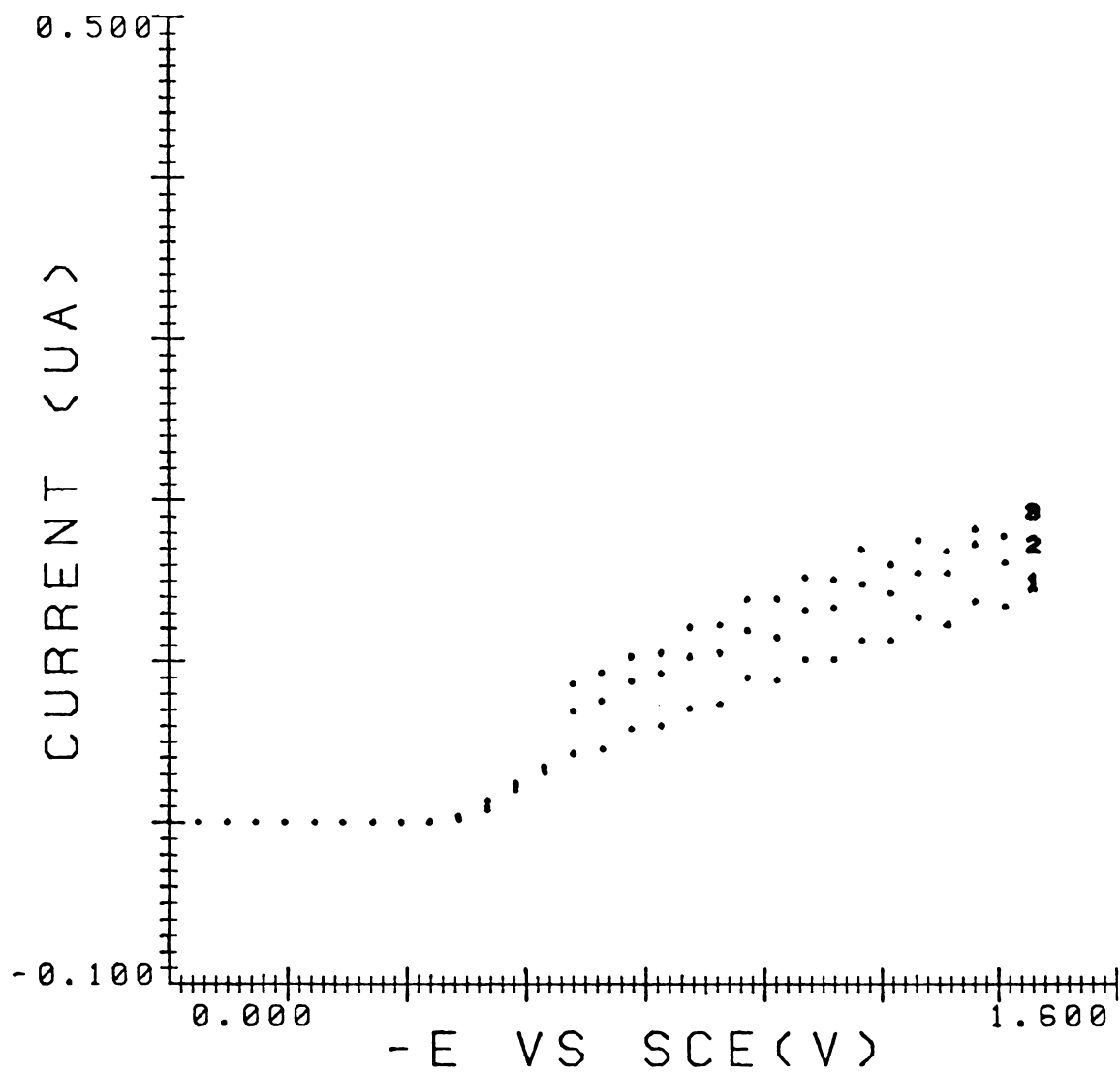


Figure 22. Polarogram of a 0.1 M KCl solution (1),
 5×10^{-6} Cd^{2+} in 0.1 M KCl solution (2),
 1×10^{-5} Cd^{2+} in 0.1 M KCl solution (3).

Table 1. Diffusion limited current at various concentration, of Cd^{2+} in 0.1 M KCl as supporting electrolyte.

Cd^{2+} Concentration	I_d	Figure
M	μA	
1×10^{-3}	4.60	20-3
5×10^{-4}	2.40	20-2
1×10^{-4}	0.47	21-3
5×10^{-5}	0.27	21-2
1×10^{-5}	0.05	22-3
5×10^{-6}	0.027	22-2

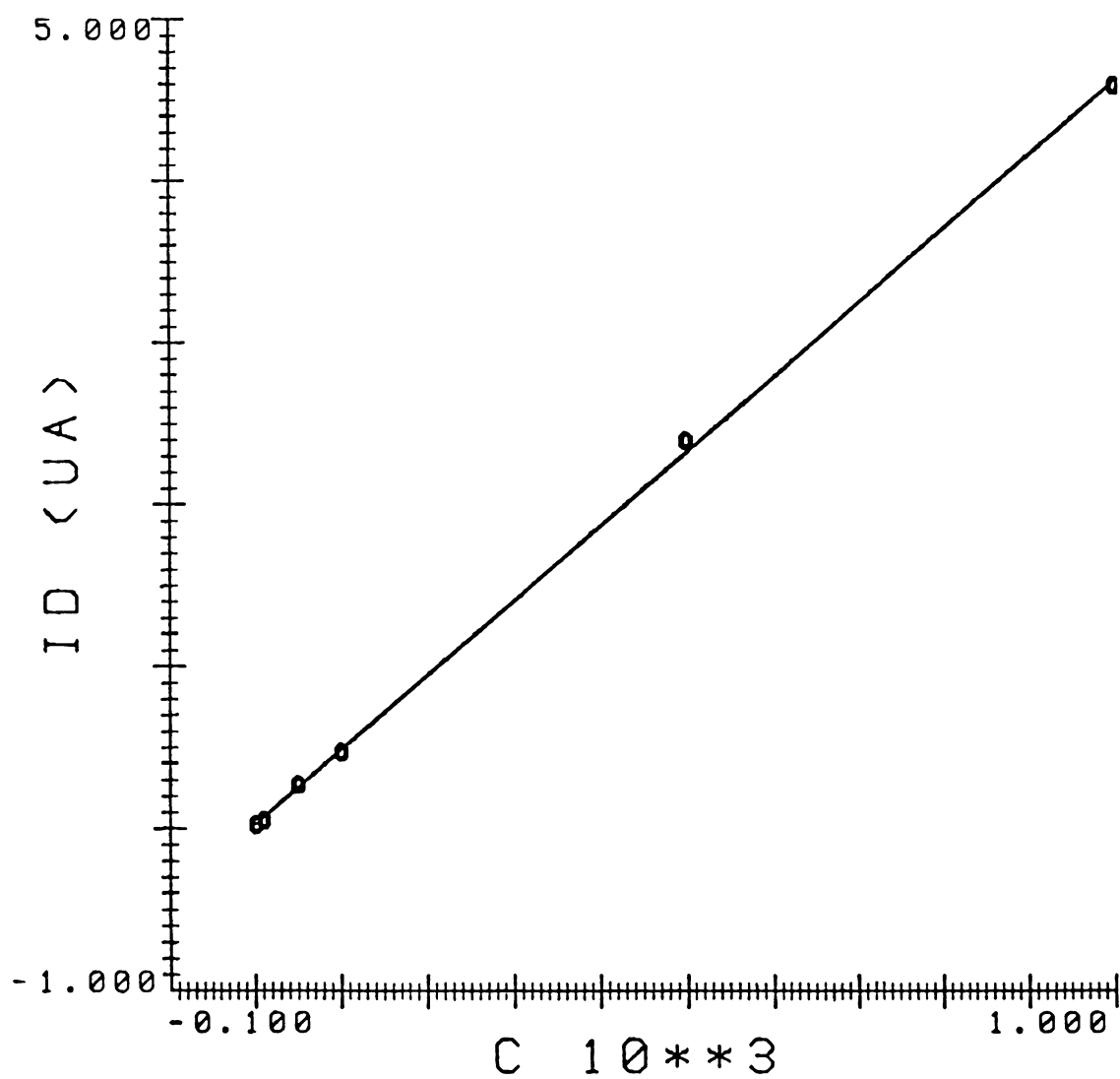


Figure 23. The working curve for Cd²⁺ determination.

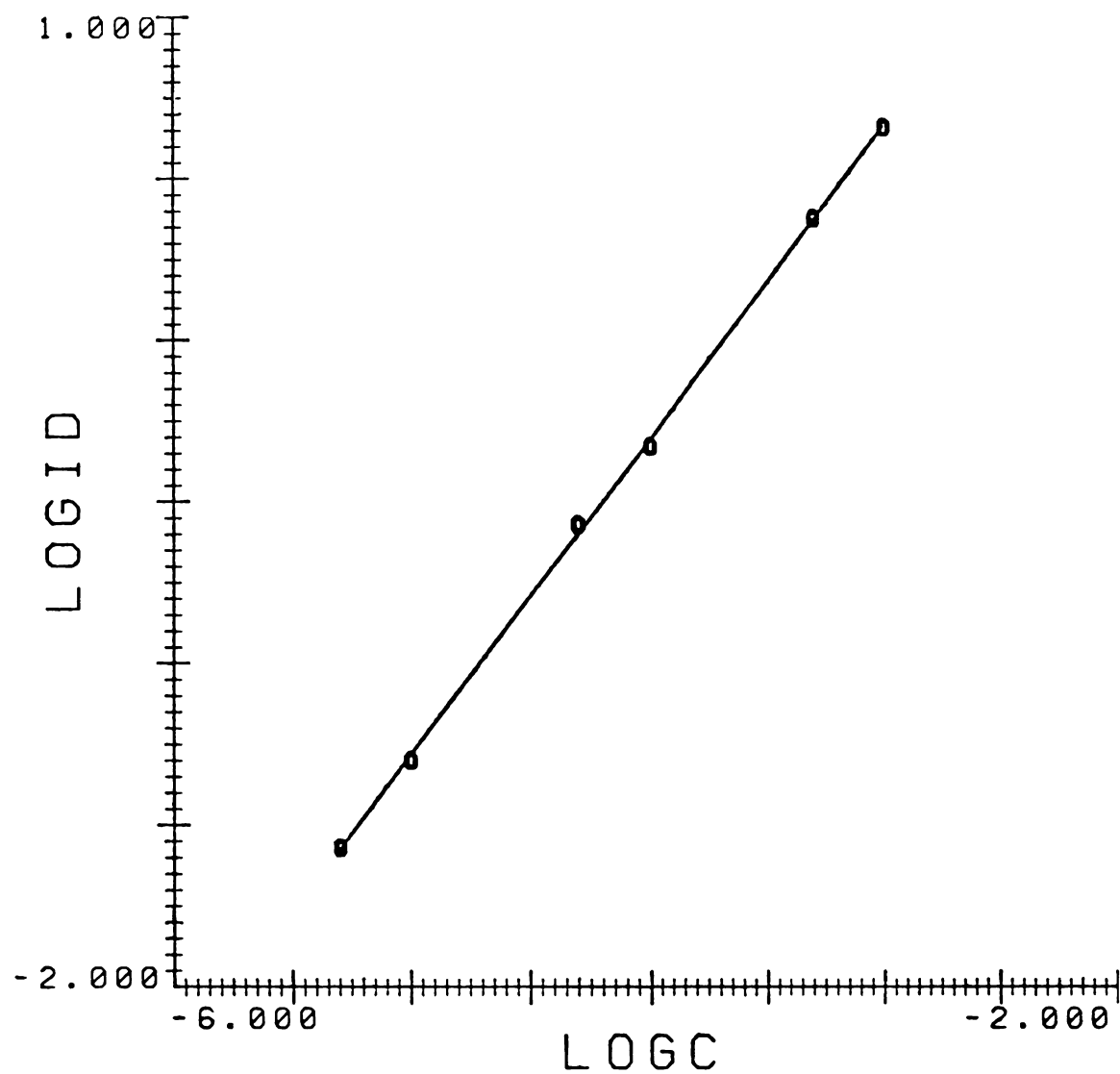


Figure 24. Plot of $\text{Log } I_d$ versus $\text{Log } C$ for Cd^{2+} determination.

and the detection limits of the polarographic method, the charging current must be reduced or eliminated from the current measurements.

The DC capacitance current is given by

$$i_c = q_{(m)} \left(\frac{dA}{dt} \right) = km^{2/3} t^{-1/3} q_{(m)} \quad (13)$$

where $q_{(m)}$ is the surface charge density and k is a constant. The ratio of the Faradaic current to the DC capacitance current is directly proportional to the drop time t at which the current measurement is made. Thus, in order to have the maximum sensitivity, it is desirable to control the electrode potential at the desired value late at the drop life.

The electrochemical system described here provides an easy way to do so. The operator has the ability to choose any time of the drop life to start controlling the electrode potential and to measure the resulting current.

Figure 25 shows the polarograms of a solution containing only the supporting electrolyte, 0.1 M KCl, obtained at two different periods of the drop life. In the first case (Plot 1) the experiment started after 100 msec from the beginning of each drop (DELAY = 100 msec) and in the second case (Plot 2) the experiment started after 5000 msec from the beginning of each drop. There still is some amount of charging current after 5000 msec from the beginning of the drop but compared to the first case there is a

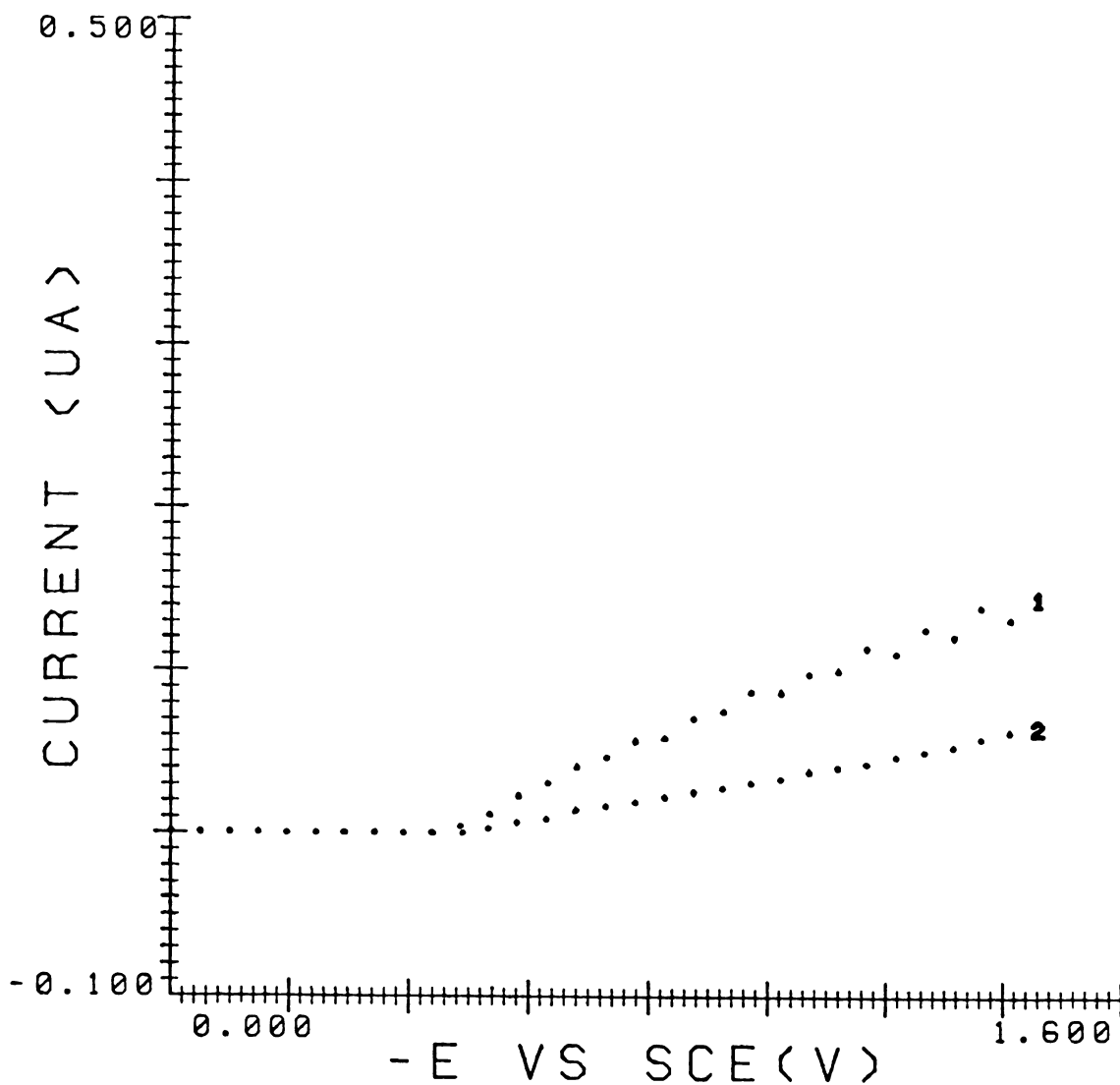


Figure 25. Polarogram of 0.1 KCl solution of two different periods of the drop life: DELAY = 100 msec (1), DELAY = 5000 msec (2). The current at the initial part of the polarograms is equal to zero because the program is written so that only the negative charge pulses are counted.

drastic improvement in the base line.

When the potential of the working electrode is suddenly stepped from one initial value to a new value, several components of the measured current must be considered (4). First there is the pulse Faradaic current which is proportional to the concentration of the electroactive species. Second there is the pulse capacitance current required to change the electrode double layer to the new potential. To optimize the sensitivity, the ratio of the Faradaic current to the sum of all other currents must be maximized.

The pulse Faradaic current is given by

$$i = nFAC\left(\frac{D}{t}\right)^{1/2} \left(\frac{P_A \delta^2 - P_A}{\delta + P_A \delta^2 + P_A + P_A^2 \delta} \right) \quad (14)$$

where

$$P_A = \exp \left(\frac{E_1 + E_2}{2} - E_{1/2} \right) \frac{nF}{RT} \quad (15)$$

and

$$\delta = \exp \left(\frac{(E_2 - E_1) \frac{nF}{RT}}{2} \right) \quad (16)$$

E_1 and E_2 are the potentials between which the potential is stepped. As the pulse potential becomes more negative than $E_{1/2}$, P_A approaches zero, so the limiting current obtained is the Cottrell current (Equation 5).



The pulse capacitance current is given by

$$i_c = (\Delta E/r) \exp(-t/rC_{dl}) \quad (17)$$

where t is the time after the step application, C_{dl} is the capacitance of the electrode double layer and r is the solution resistance. Since the pulse capacitance current decays more rapidly than the pulse faradaic current, the ratio of the two currents continues to increase as the current measurement is delayed after the step application.

The total faradaic current, after the application of a potential step to the drop is equal to

$$\int_0^t i_t = \int_0^{t_p} i_{PF} + \int_{t_p}^t i_{DCF} \quad (18)$$

The limiting pulse faradaic current (i_{PF}) is given by Equation (5) and it is a current spike decaying with time to a diffusion limiting value. The DC faradaic current (i_{DCF}) is given by Equation (9). The average current after the application of the potential step until the end of the drop is equal to

$$\begin{aligned} \frac{1}{t_d} \int_0^{t_d} i dt = \bar{I} = nFACD^{1/2} \pi^{-1/2} \frac{1}{t_1} \int_0^{t_1} t^{-1/2} dt \\ + 706nCD^{1/2} m^{2/3} \frac{1}{(T_d - T_2)} \int_{T_2}^{T_d} \\ T^{1/6} dT \end{aligned} \quad (19)$$

where t_1 is the time required for the pulse faradaic current to reach the diffusion limited value, T_2 is the drop time corresponding to t_1 and T_d is the end of the drop.

If the potential step is applied at two different periods of the drop life, the ratio of the two average currents will be equal to

$$\frac{nFA_1CD^{1/2} - 1/2 \frac{1}{t_1} \int_0^{t_1} t^{-1/2} dt}{nFA_2CD^{1/2} - 1/2 \frac{1}{t'_1} \int_0^{t'_1} t'^{-1/2} dt'} + \frac{706nCD^{1/2}m^{2/3} \frac{1}{(T_d - T_2)} \int_{T_2}^{T_d} T^{1/6} dT}{706nCD^{1/2}m^{2/3} \frac{1}{(T'_d - T'_2)} \int_{T'_2}^{T'_d} T'^{1/6} dT'} \quad (20)$$

By substituting Equation (6) into Equation (20), the ratio becomes

$$\frac{T_1^{2/3} \frac{1}{t_1} \int_0^{t_1} t^{-1/2} dt + \sqrt{\frac{7}{3}} \frac{1}{(T_d - T_2)} \int_{T_2}^{T_d} T^{1/6} dT}{T_1'^{2/3} \frac{1}{t'_1} \int_0^{t'_1} t'^{-1/2} dt' + \sqrt{\frac{7}{3}} \frac{1}{(T'_d - T'_2)} \int_{T'_2}^{T'_d} T'^{1/6} dT'} \quad (21)$$

or

$$\frac{T_1^{2/3} \times 2 \times t_1^{1/2} + \sqrt{\frac{7}{3}} \times \frac{6}{7} \times (T_d - T_2)^{1/6}}{T_1'^{2/3} \times 2 \times t_1'^{-1/2} + \sqrt{\frac{7}{3}} \times \frac{6}{7} \times (T_d - T_2')^{1/6}} \quad (22)$$

T_1 and T_1' corresponds to the drop time of which the potential step is applied. For $t_1 = 0.554$ sec, $t_1' = 0.007$ sec, $T_1 = 5$ sec, $T_2 = 5.554$ sec, $T_1' = 0.1$ sec, $T_2' = 0.107$ sec, and $T_d = 9$ sec the ratio of the two average currents is equal to 1.35. This indicates that the sensitivity increases as the pulse step is applied later in the drop life.

Figure 26 shows the polarogram of a solution of 5×10^{-6} M Cd^{2+} in 0.1 M KCl obtained with different run parameters. In the same figure the polarograms of the blank solution are shown. For plots 1 and 2 the run parameters are: VPULSE = -300 mV, VINITIAL = 0 mV, VFINAL = 01500 mV, VSTEP = 500 mV, DELAY = 100 msec. For plots 3 and 4 the run parameters are: VPULSE = -300 mV, VINITIAL = -500 mV, VFINAL = -900 mV, VSTEP = 20 mV, DELAY = 5000 msec. Plots 3 and 4 have been shifted by 0.2 units in order to be plotted in the same figure with Plots 1 and 2. The charging current has been removed from the polarographic wave of Cd^{2+} . Also the diffusion limiting current has been increased so that the accuracy and the detection limits have been improved (Plot 3 and 4).

A new working curve for the determination of Cd^{2+} was obtained using DELAY = 5000 msec. Figure 27 shows the polarograms of a 1×10^{-5} M Cd^{2+} (4), 5×10^{-6} M Cd^{2+} (3),

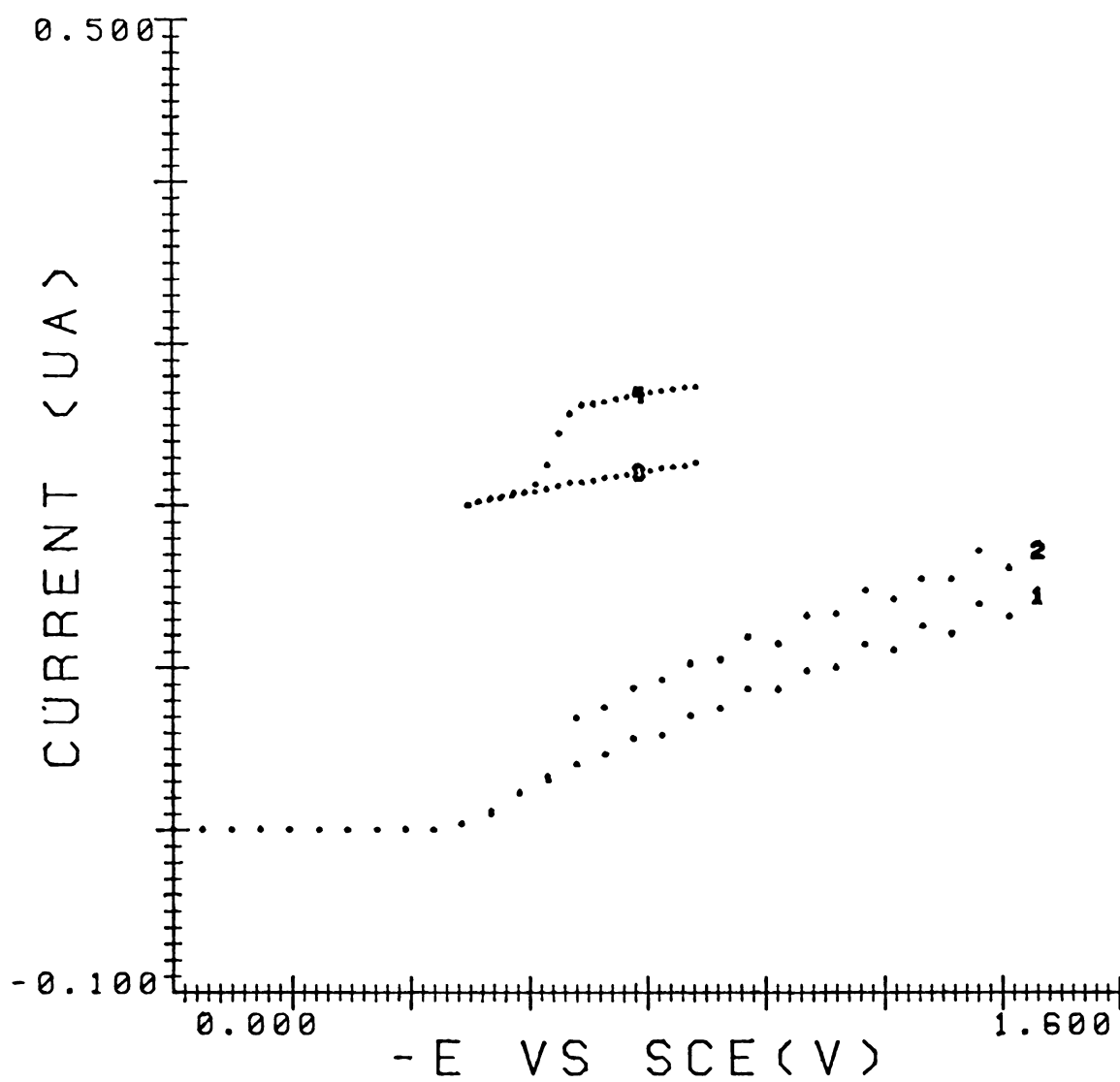


Figure 26. Polarogram of a 5×10^{-6} M Cd^{2+} in 0.1 M KCl solution at different periods of the drop life, and the corresponding polarogram of a blank solution. DELAY = 100 msec (1,2), DELAY = 5000 msec (3,4).



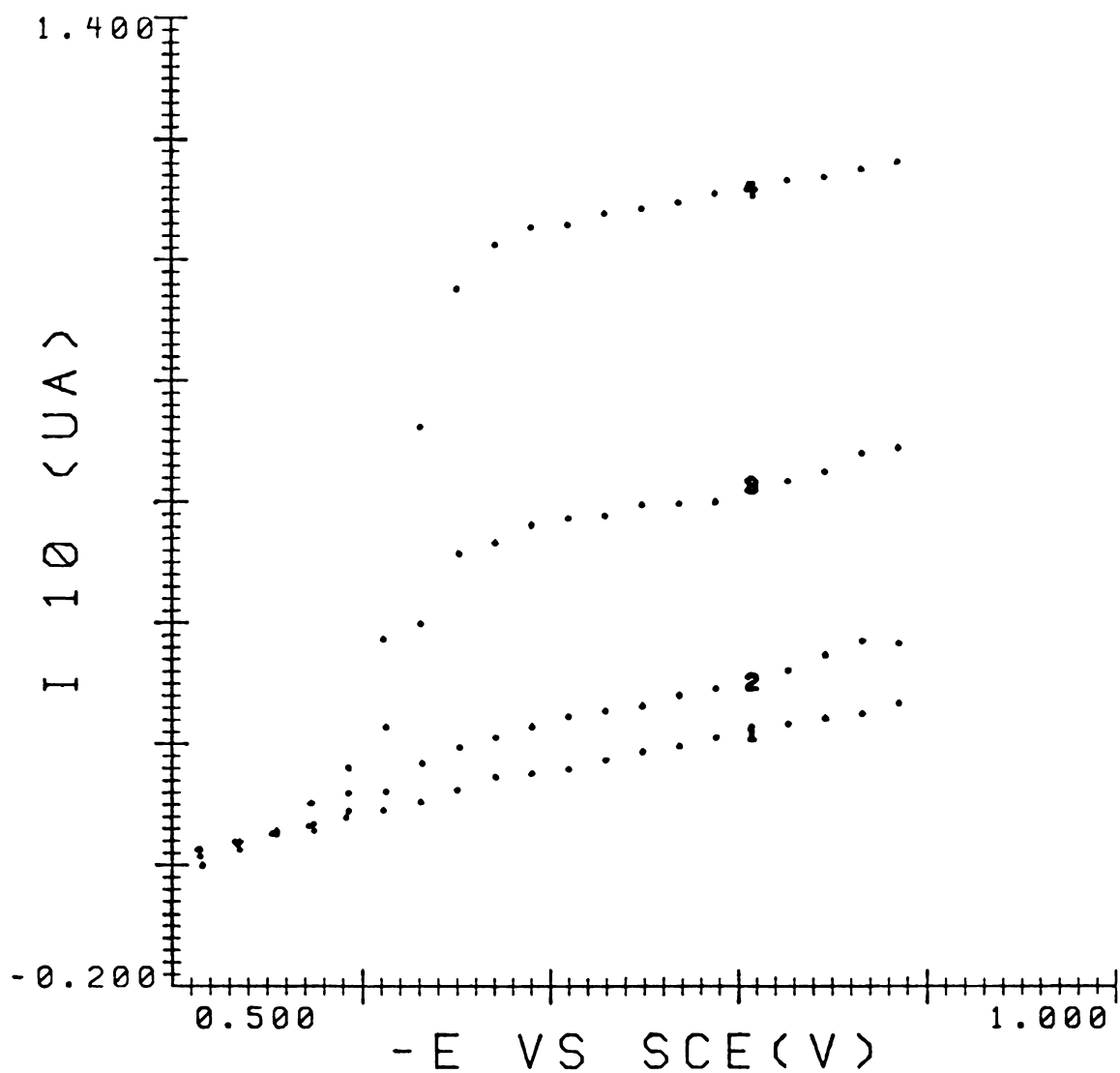
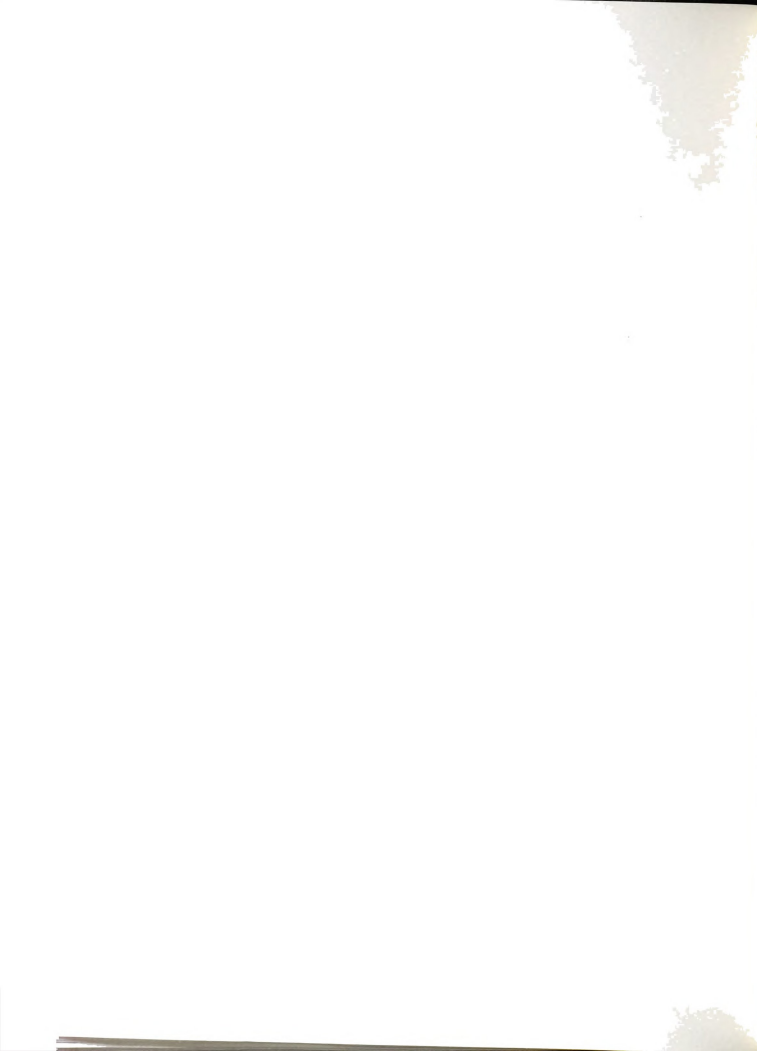


Figure 27. Polarogram of a 0.1 M KCl solution (1),
 1×10^{-6} M Cd^{2+} in 0.1 M KCl solution (2),
 5×10^{-6} M Cd^{2+} in 0.1 M KCl solution (3),
 1×10^{-5} M Cd^{2+} in 0.1 M KCl solution (4).
 DELAY = 5000 msec.

and 1×10^{-6} M Cd^{2+} (2) solution in 0.1 M KCl. The polarogram of the blank solution is also shown in the same figure (Plot 1). Figure 28 shows the polarogram of a 5×10^{-7} M Cd^{2+} (2) in 0.1 M KCl solution, and the polarogram of the blank solution (1). The run parameters for the above polarograms are: VPULSE = -300 mV, VINITIAL = -500 mV, VFINAL = -900 mV, VSTEP = 20 mV and DELAY = 5000 msec. Table 2 contains a listing of the concentrations of Cd^{2+} and the corresponding diffusion limited current. Figure 29 shows a plot of the diffusion limited current as a function of the concentration of Cd^{2+} in the solution. The working curve has a slope of 8.9×10^3 and an intercept of -8.9×10^{-4} . Figure 30 shows a plot of $\log I_d$ versus $\log C$.

C. Selectivity

According to Equation 10 the plot of the electrode potential versus $\log [(i_d - i)/i]$ should give a straight line with slope equal to $0.059/n$ at 25°C , and the potential where the log term becomes zero should be the half-wave potential. In order to verify these predictions, two polarograms of a 1×10^{-4} M Cd^{2+} in 0.1 M KCl solution were taken with different run parameters. Figure 31 shows these two polarograms. Table 3 contains a listing of the electrode potentials and the corresponding $\log [(i_d - i)/i]$ values. A plot of the log term versus the electrode



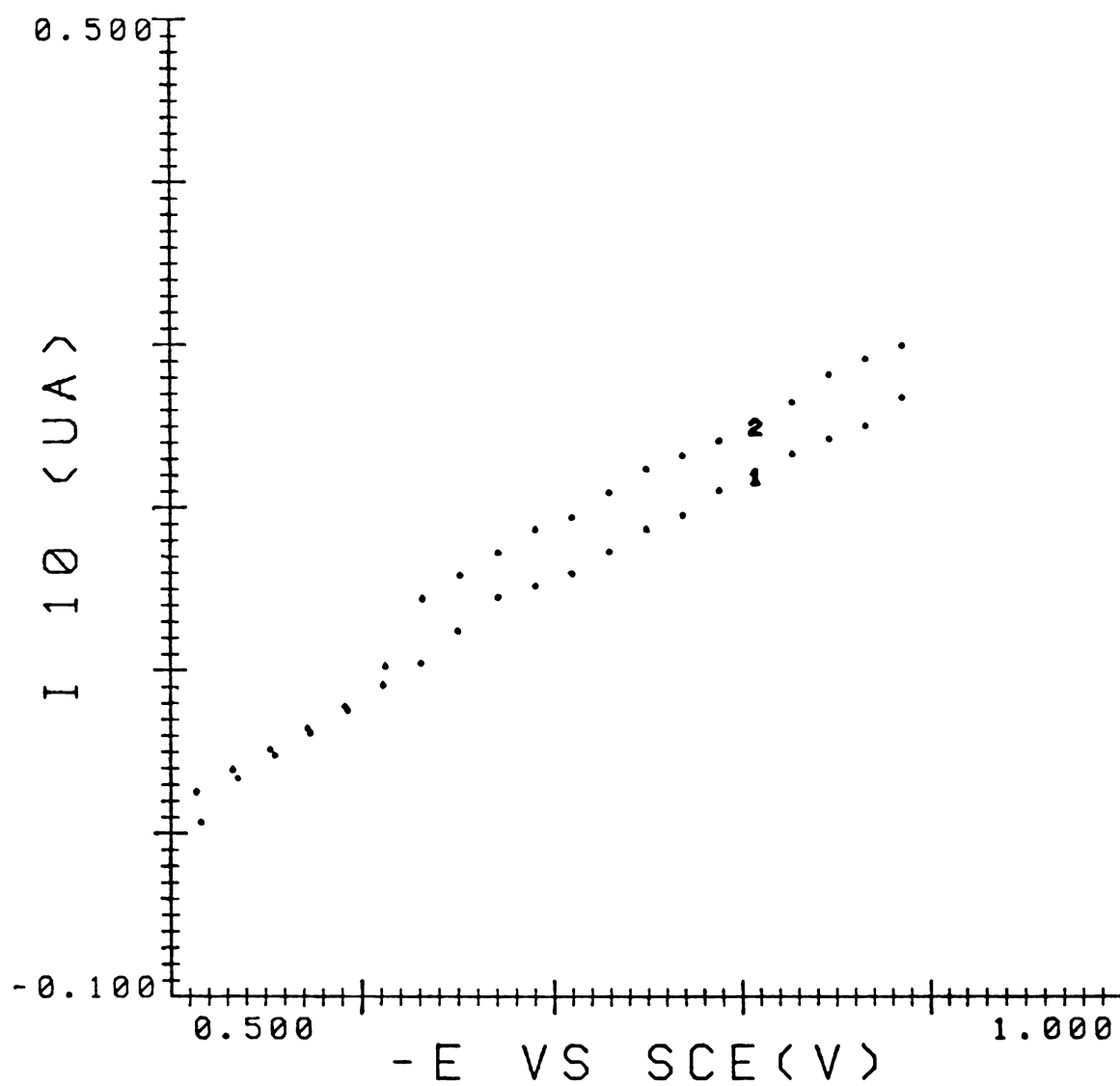


Figure 28. Polarogram of a 0.1 M KCl solution (1) and a 5×10^{-7} M Cd^{2+} in 0.1 M KCl solution (2)
DELAY = 5000 msec.



Table 2. Diffusion limited current at various concentrations of Cd^{2+} in 0.1 M KCl as supporting electrolyte. DELAY = 5000 msec.

Cd^{2+} Concentration	I_d	Figure
M	μA	
1×10^{-5}	0.0890	27-4
5×10^{-6}	0.0420	27-3
1×10^{-6}	0.0085	27-2
5×10^{-7}	0.0040	28-2



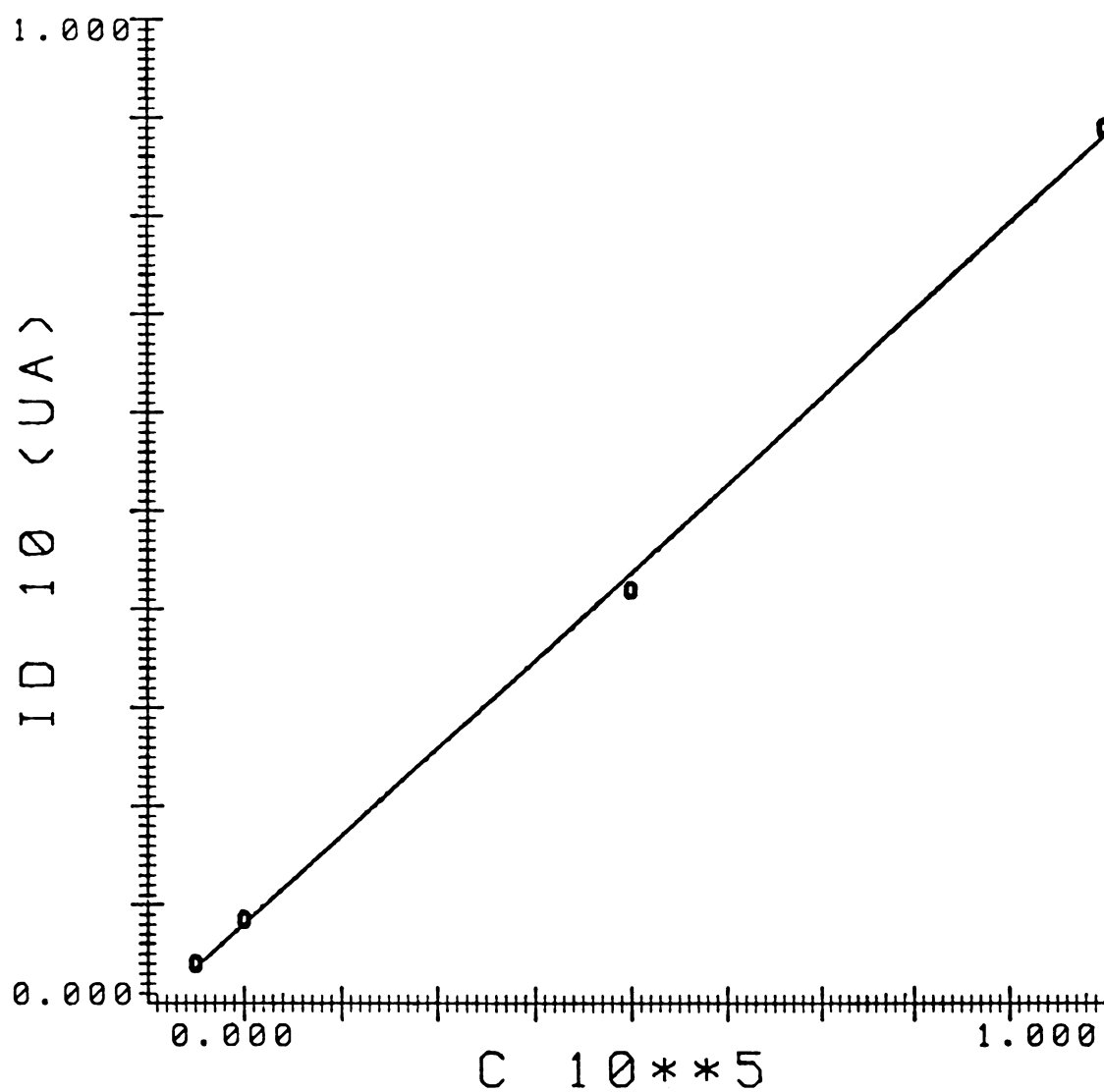


Figure 29. The working curve for Cd²⁺ determination at DELAY = 5000 msec.



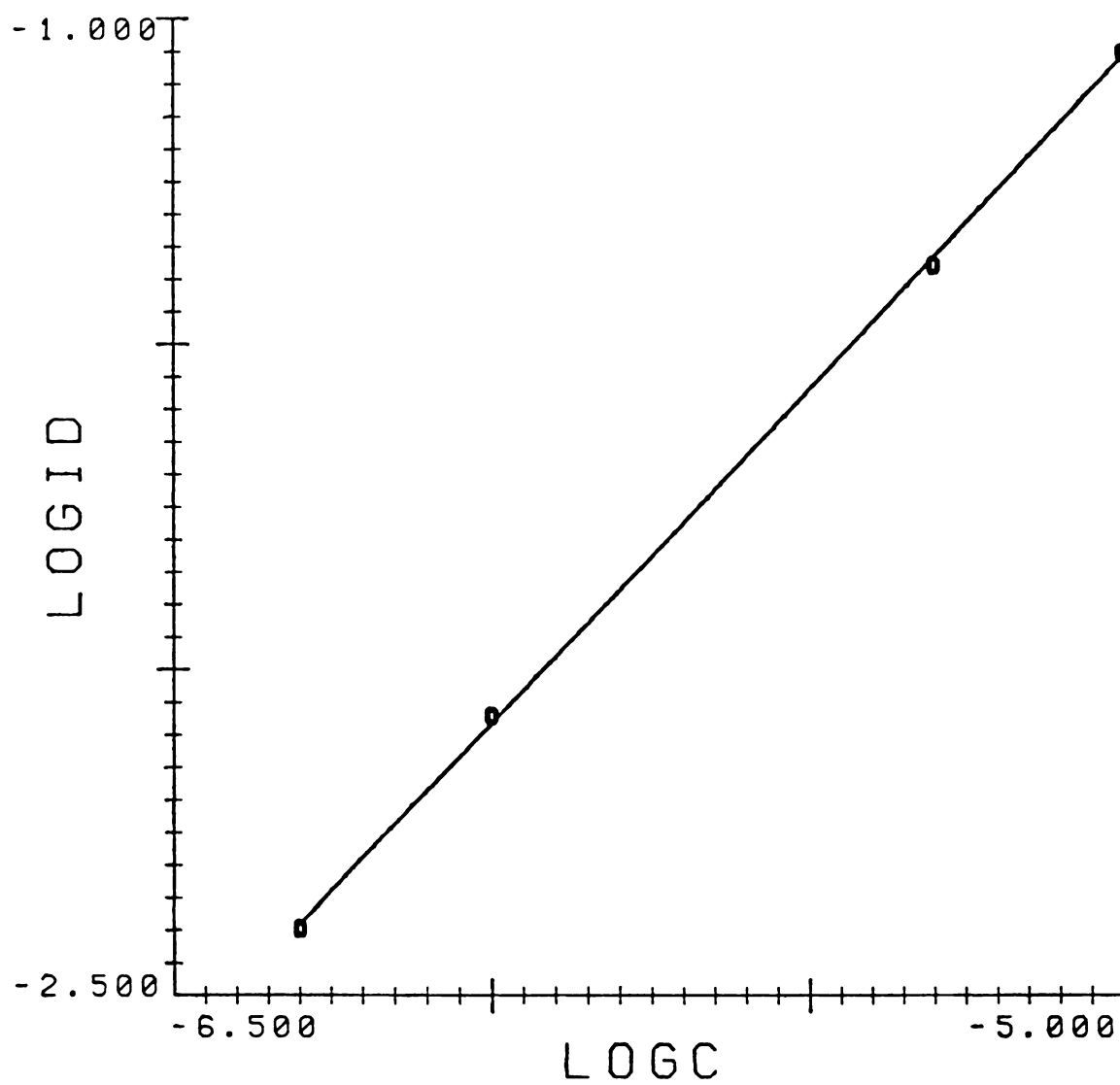


Figure 30. Plot of $\text{Log } I_d$ vs $\text{Log } C$ for Cd^{2+} determination at $\text{DELAY} = 5000$ msec.

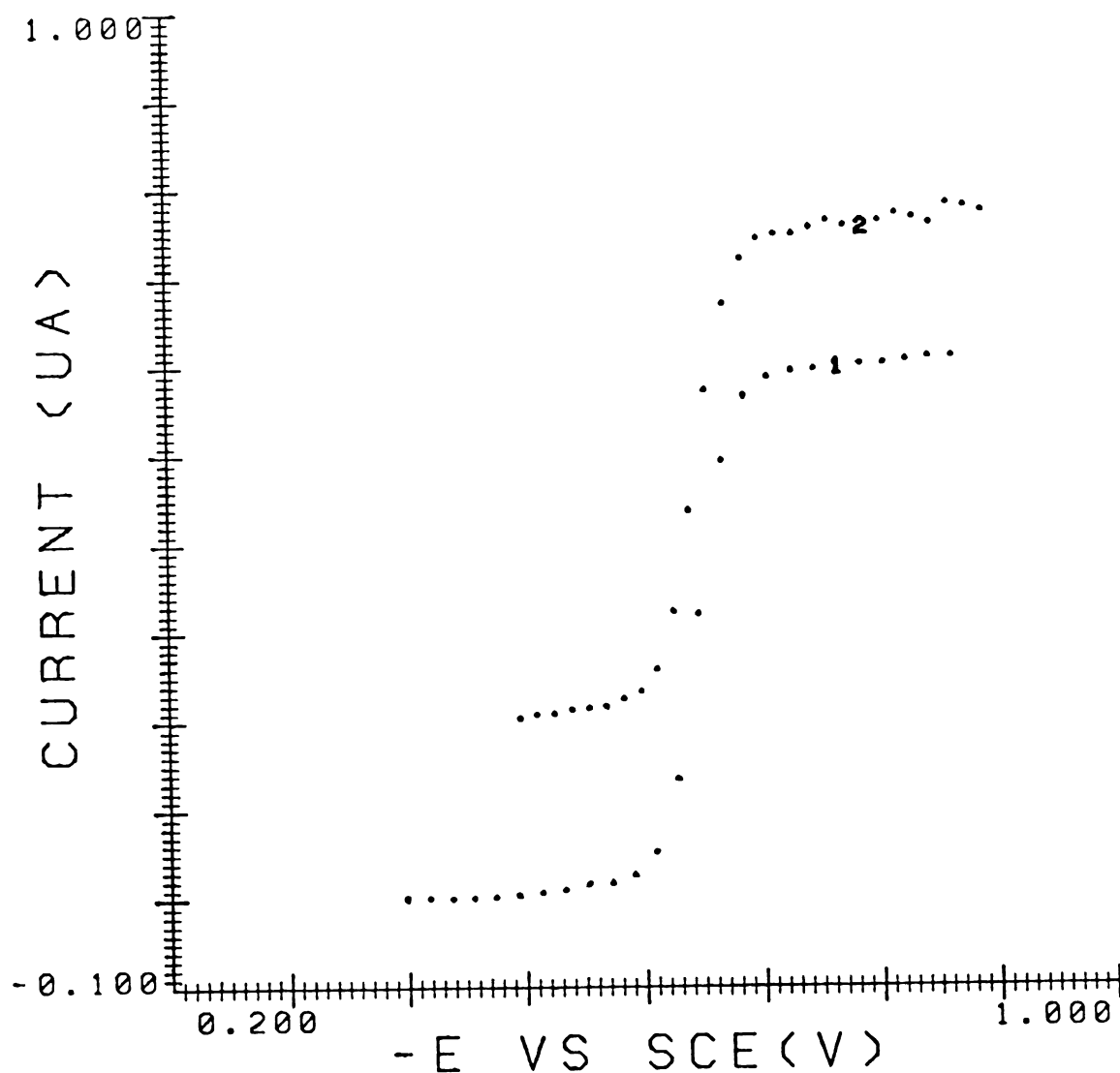


Figure 31. Polarogram of a 1×10^{-4} M Cd^{2+} in 0.1 M KCl solution obtained with different run parameters. For Plot 1 VPULSE = -300 mV, VINITIAL = -400 mV, VFINAL = -900 mV, DVSTEP = 20 mV, DELAY = 100 msec. For plot 2, VPULSE = -300 mV, VINITIAL = -300 mV, VINITIAL = -500 mV, VFINAL = -900 mV, DVSTEP = 15 mV, DELAY = 100 msec.

Table 3. $\text{Log} [(i_d - i)/i]$ as a function of the electrode potential for two different runs.

E mV	i μA	$\text{log}(i_d - i/i)$	Run
-609	0.052	0.998	1
-628	0.135	0.508	
-646	0.321	-0.110	
-667	0.494	-0.813	
-611	0.058	0.882	2
-626	0.123	0.486	
-639	0.237	0.045	
-654	0.373	-0.468	

potential for the two runs are shown in Figure 32. The reciprocal of the slope of line 1 is 0.032 V which is in good agreement with the theoretical value of 0.029 V for the reduction of Cd^{2+} ($n=2$). The reciprocal of the slope of line 2 is also 0.032 V. The half-wave potential of the reduction of Cd^{2+} is equal to -0.61 V from line 1 and -0.639 V from line 2.

Figure 33 shows the polarogram obtained from a solution of 1×10^{-4} M Cd^{2+} , 1×10^{-4} M Ni^{2+} , 1×10^{-4} M Zn^{2+} , and 0.003% sodium methyl red in 0.1 M KCl. The half-wave potentials of the reduction of Ni^{2+} and Zn^{2+} are very close together so the diffusion current is the sum of both currents of Ni^{2+} and Zn^{2+} . Under these experimental conditions it is impossible to detect one metal ion in the presence of the other. For Cd^{2+} the polarographic wave is well defined and it is possible to determine Cd^{2+} in the presence of Zn^{2+} or Ni^{2+} in the solution.

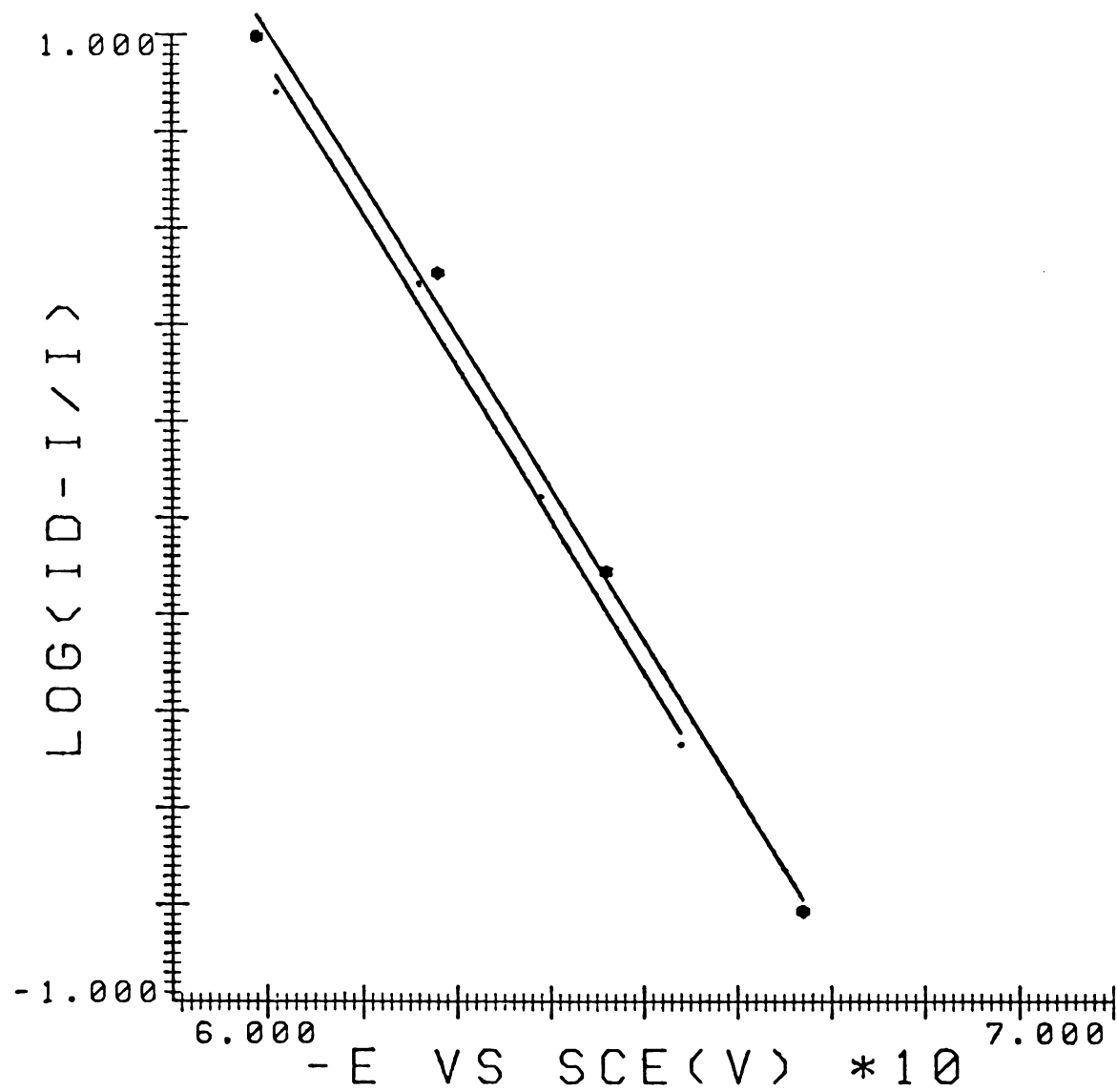


Figure 32. $\text{Log} [(i_d - i)/i]$ versus E for two different scans.



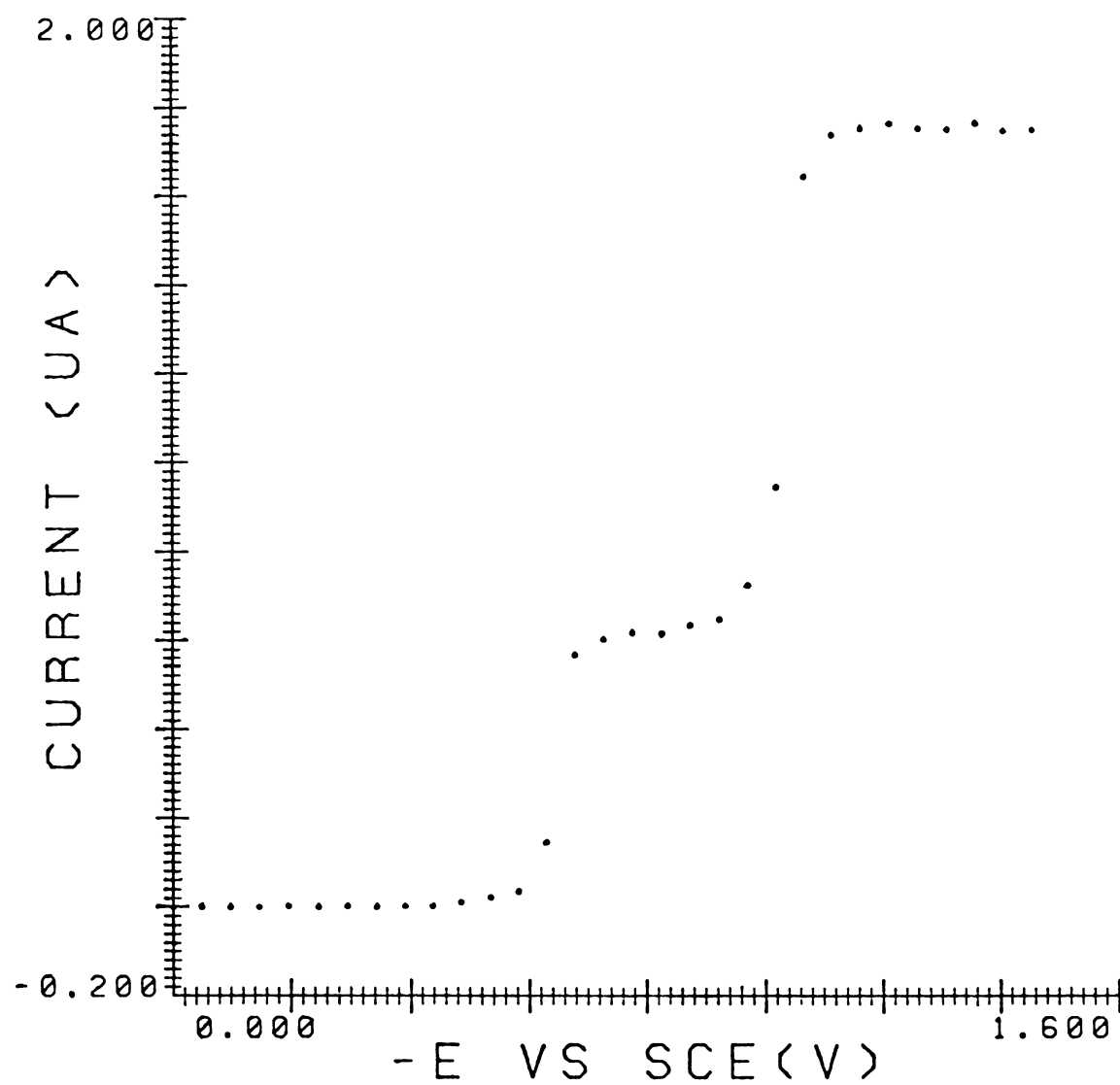


Figure 33. Polarogram of a 1×10^{-4} M Cd^{2+} , 1×10^{-4} M Zn^{2+} , 1×10^{-4} M Ni^{2+} in 0.1 M KCl solution.



CHAPTER 4

DESCRIPTION OF THE SYSTEM HARDWARE



CHAPTER 4

DESCRIPTION OF THE SYSTEM HARDWARE

The electrochemical system consists of a pulse generator, a voltage measurement system, a real-time clock, and a microcomputer system. The operation and the characteristics of the system have been discussed in Chapter 2. In this chapter and in Chapter 5, the various parts of the system will be discussed in detail. Chapter 5 includes a detailed description of the architecture and the operation of the multimicro system.

A. Pulse Generator

The pulse generator is a digitally controlled source of charge pulses. It has 3 basic units: 1) a digital-to-analog converter (DAC) to provide the necessary charging voltage, 2) a set of digitally controlled switches, a set of charging capacitors, and an output buffer amplifier to provide the necessary charge pulses to the cell, and 3) the interface to the microcomputer. The structural details of each unit will be described separately:



1. Digital-to-Analog Converter

The DAC is an Analog Devices AD7522 monolithic CMOS 10-bit converter. Figure 34 shows the analog circuit connections required for bipolar operation (39). A1, A2 and A4 are RCA CA3140 operational amplifiers. A3 is a MOTOROLA MCI741 amplifier and it is used as a buffer. Inverter A4 provides the same output voltage as amplifier A3 but opposite in sign. With a reference voltage of +2.5 V (Analog Devices AD580), the DAC provides an output voltage of ± 2.5 V. The 10-bit resolution of the converter allows control of the voltage to within ± 4.88 mV. The logic connections for interfacing the DAC to the micro-computer are also shown in Figure 34. First the least significant data byte (D0 to D7) is loaded into the input buffer on the positive edge of LBS. When the most significant data byte (D8, D1) is available on the bus, the input buffer is loaded on the positive edge of HBS. The LDAC is a 500 msec pulse and it is used to update the DAC output voltage. The DAC is built on a 6.2" x 8.2" board, which is mounted in a SR20105 BUD RACK SUB SYSTEM. The rack has eleven 58-pair PC connectors mounted on it, and a back plane which connects the PC connectors and which provides a 76-line common bus. The pin assignment of the common bus is given in Reference (33). Thirty-six free pins in each connector are used for special connections between boards. In Figure 34 the special connections between the



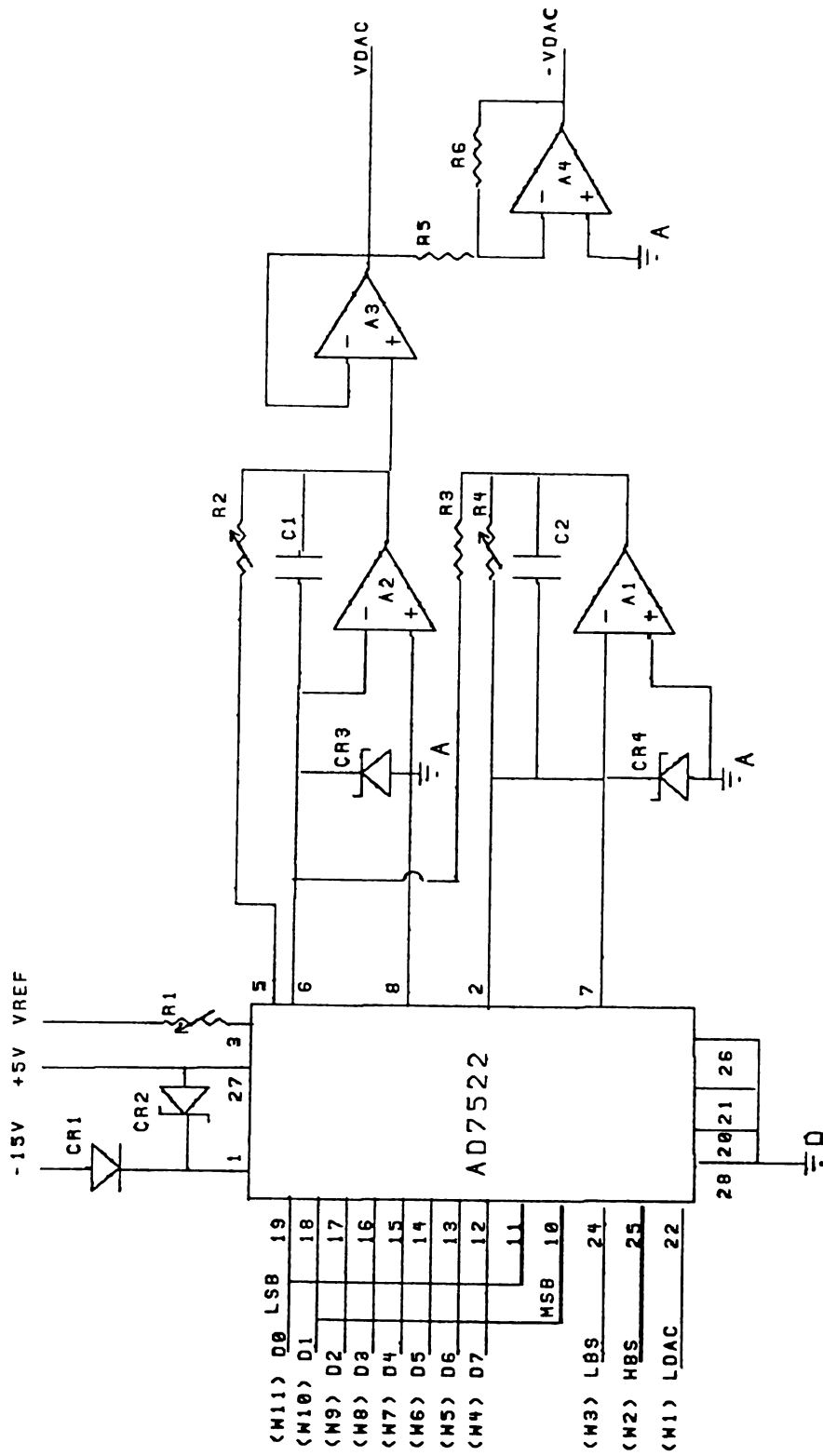


Figure 34. Digital-to-Analog Converter. Bipolar operation.



DAC and the microcomputer are shown in parenthesis. Letter w indicates a connection from the wire-wrap side of the board, and letter c indicates a connection from the component side of the board. The number which follows the letter c or w gives the pin number.

2. Switches and Charging Amplifier

In order to inject a precisely defined charge pulse to the electrochemical cell a set of switches and a set of charging capacitors are used. The switches are used to select and charge the appropriate capacitor to the pre-defined V_{DAC} voltage, and to produce the charge pulse. The charging amplifier drives the actual pulses through the cell. Figure 35 shows the details of the circuit of the switching elements and the charging amplifier. Each switching element consists of a driver (DR1) and the actual switch (SW1). The drivers are SIGNETICS SD5200 FET drivers and are used to turn on and off the switches. A zero on the cathode of the zener diode turns on the switch and a one turns the switch off. The switches are SIGNETICS SD5000 FET analog switches with on resistance of $30\ \Omega$ and off resistance of $10^{10}\ \Omega$. The charging capacitors C1 and C2 are ceramic capacitors with capacitance $0.001 \pm 10\% \mu\text{F}$ and $0.01 \pm 10\% \mu\text{F}$ respectively. The charging amplifier is a Datel AM405-2 FET input high speed monolithic amplifier with high input impedance ($10^{10}\ \Omega$)



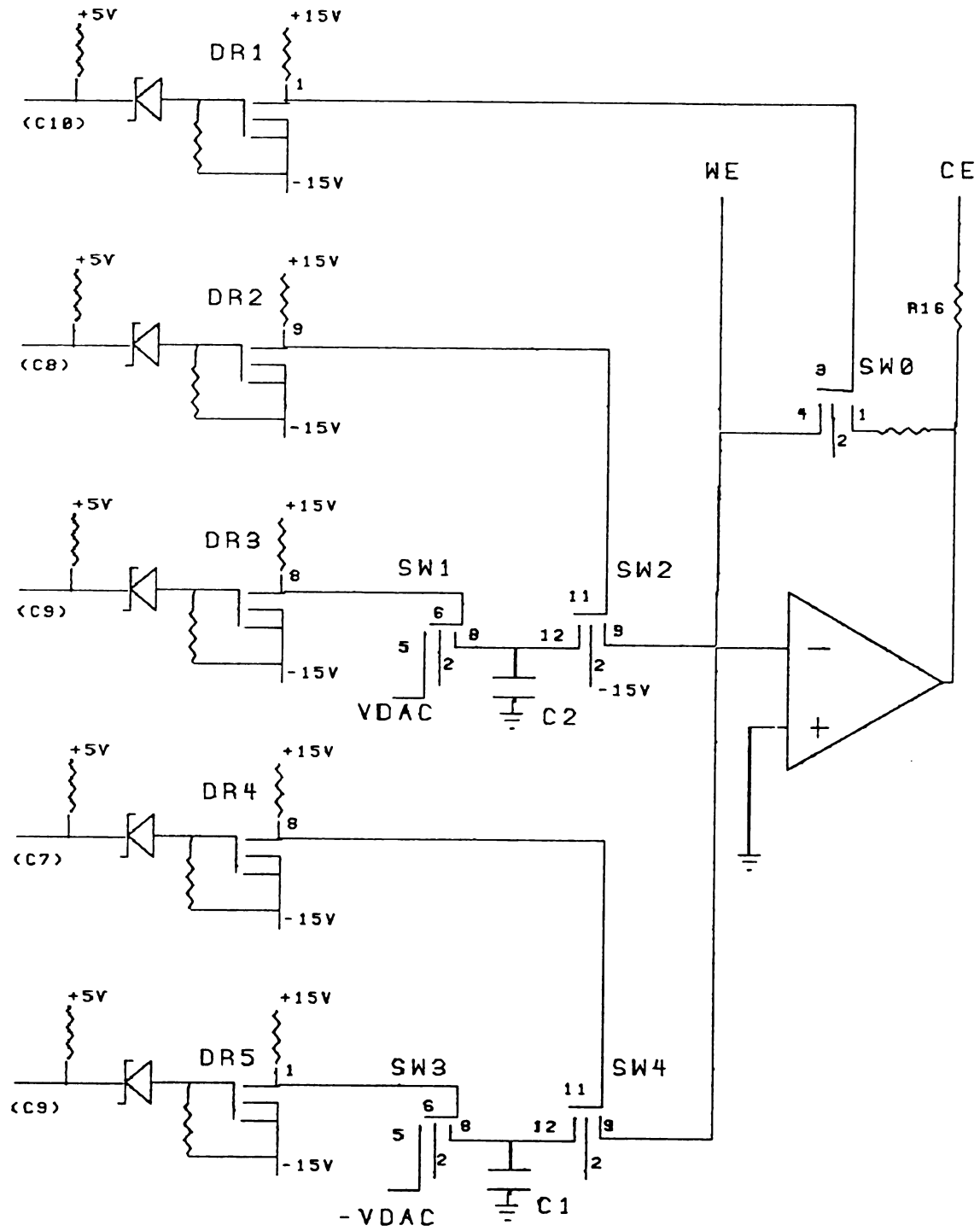


Figure 35. Switches and charging amplifier.



and slew rate of 120 V/msec. The output current capability of the amplifier is ± 10 mA with a current peak of 50 mA maximum. The amplifier is connected to the working electrode (WE) and to the counter electrode (CE) through two 30" long coaxial cables. A $270\ \Omega$ resistor (R16) is used to protect the output of the amplifier by keeping the output current within the maximum limits. Switch SW0 is used to protect the amplifier when there is no load in the feedback loop. A load must be present in the feedback loop whenever the amplifier is on, otherwise its output will limit at 15 volts.

3. The Interface Logic

The interface with the microcomputer provides the necessary digital signals to control the operation of the pulse generator. Figure 36 shows the interface logic circuit which consists of two parts. One part controls the DAC and the other part controls the switches. The interface logic is constructed on the pulse generator microcomputer board. The analog part of the pulse generator is shielded with a grounded copper board in order to protect it from the digital noise of the control unit.

In order to load the DAC with a 10 bit word, the microcomputer sends an eight bit word to the DAC and the $\overline{CS6}$ and $\overline{MEMW}$ pulses. The output of the AND gate (LBS) loads the low byte register of the DAC with the data on



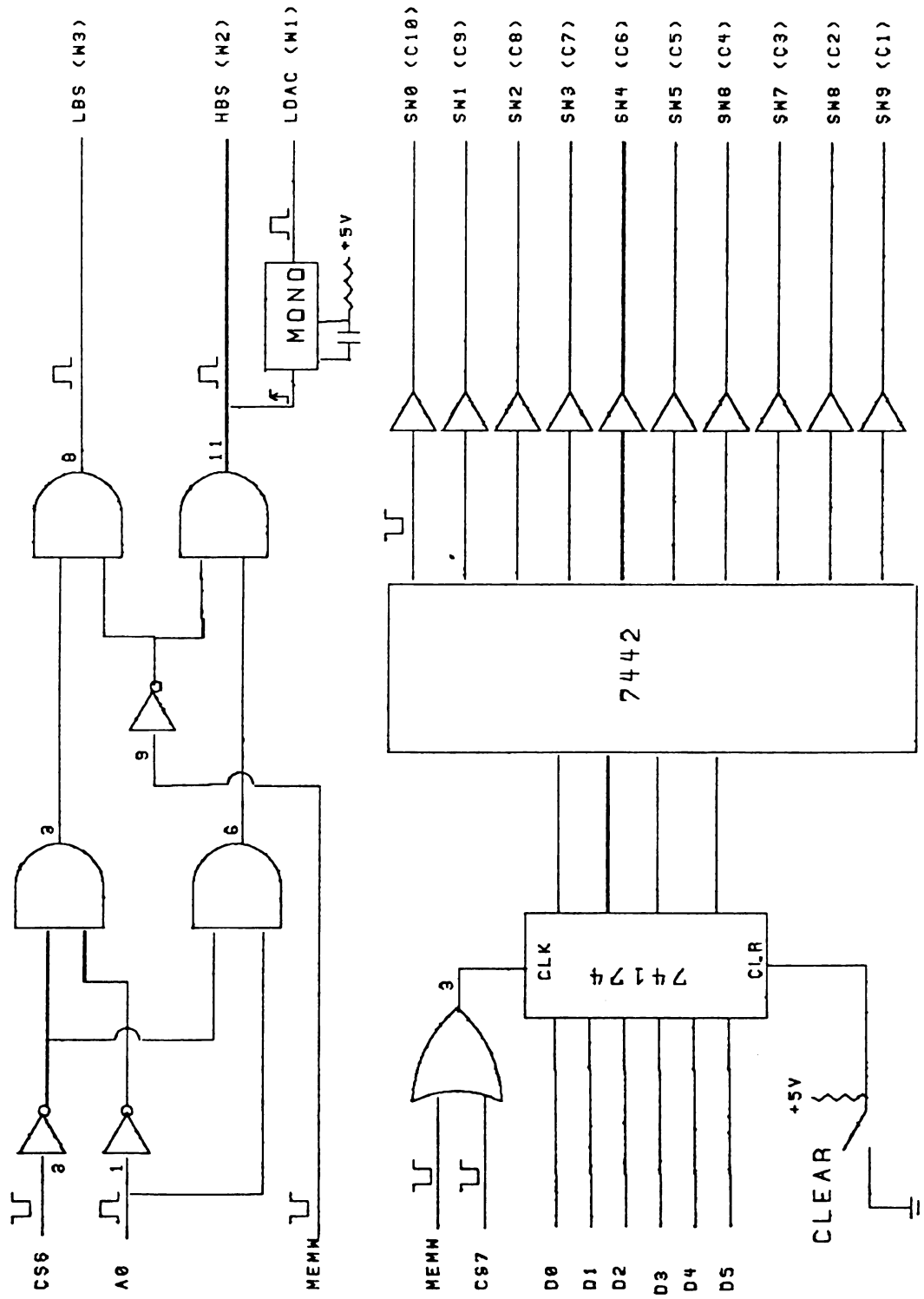


Figure 36. Charge generator interface logic.



the data bus. Next the computer sends a two bit word to the DAC and the $\overline{CS6}$, A0 and $\overline{MEMW}$ pulses. The output pulse of the AND gate (HBS) loads the high byte register of the DAC with the data on the D0 and D1 lines and triggers the monostable (MONO). The output pulse of the monostable (LDAC) updates the output voltage of the DAC. In order to select any switch, the computer latches a 4-bit word in the 74174 register. The outputs of the register are connected to a 7442 4-line-to-10-line decoder, which decodes the input signals and selects the appropriate switch driver. Two 7417 hex/open collector drivers are used to drive the output signals of the decoder to the DAC board. The CLEAR switch is used to manually reset the register.

B. Voltage Measurement System

The voltage measurement system measures the potential between the working and the reference electrodes, amplifies it, converts the analog signal to a digital number, and sends the results to the microcomputer. The system (Figure 37) consists of a buffer, an amplifier, a sample and hold to hold the voltage during the digitization, an analog-to-digital converter (A/D converter), and the interface logic which controls the operation of the voltage measurement system (Figure 38). The buffer amplifier (A1) is an RCA CA3140 operational amplifier in the



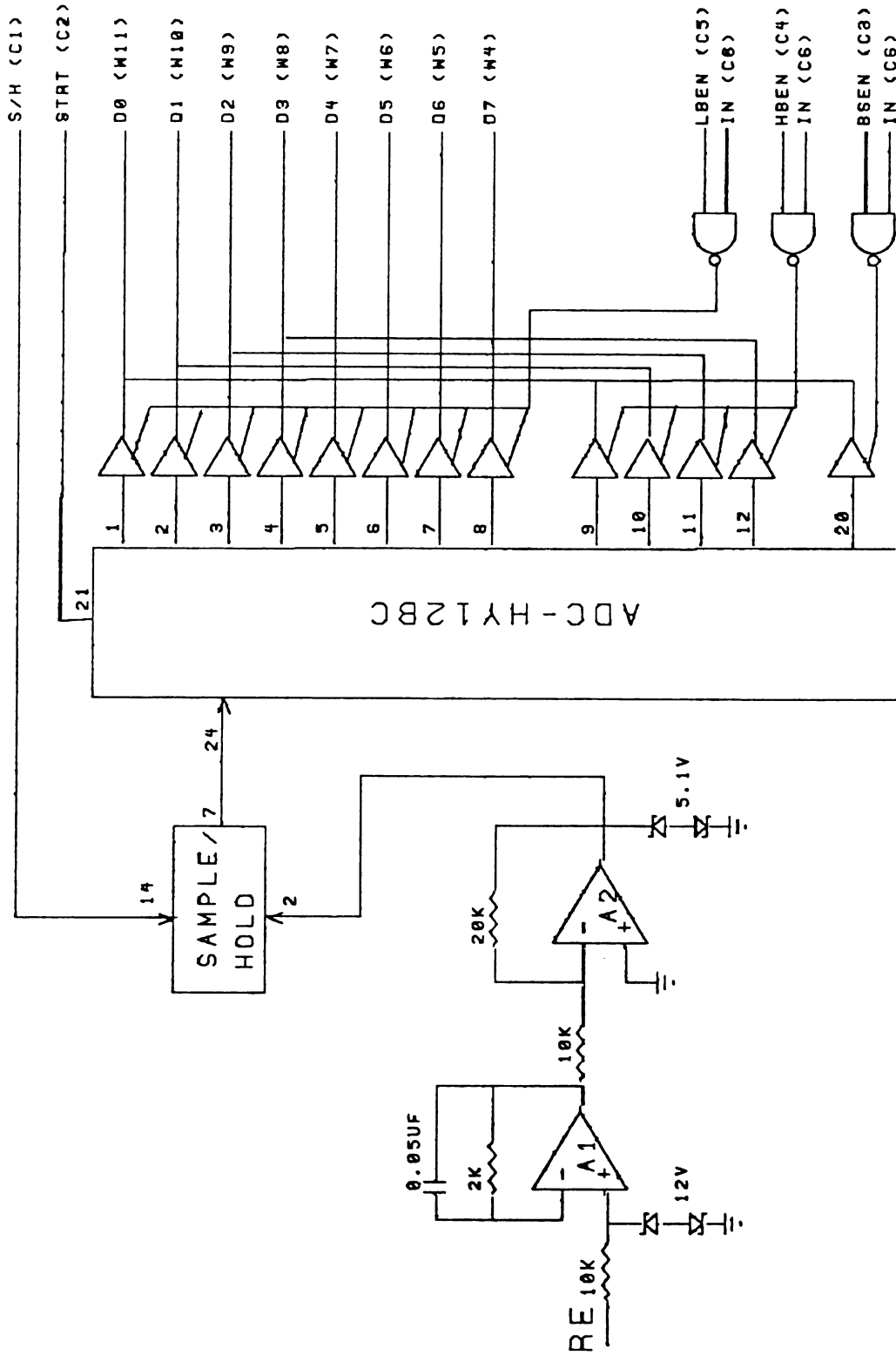


Figure 37. Analog-to-Digital converter.

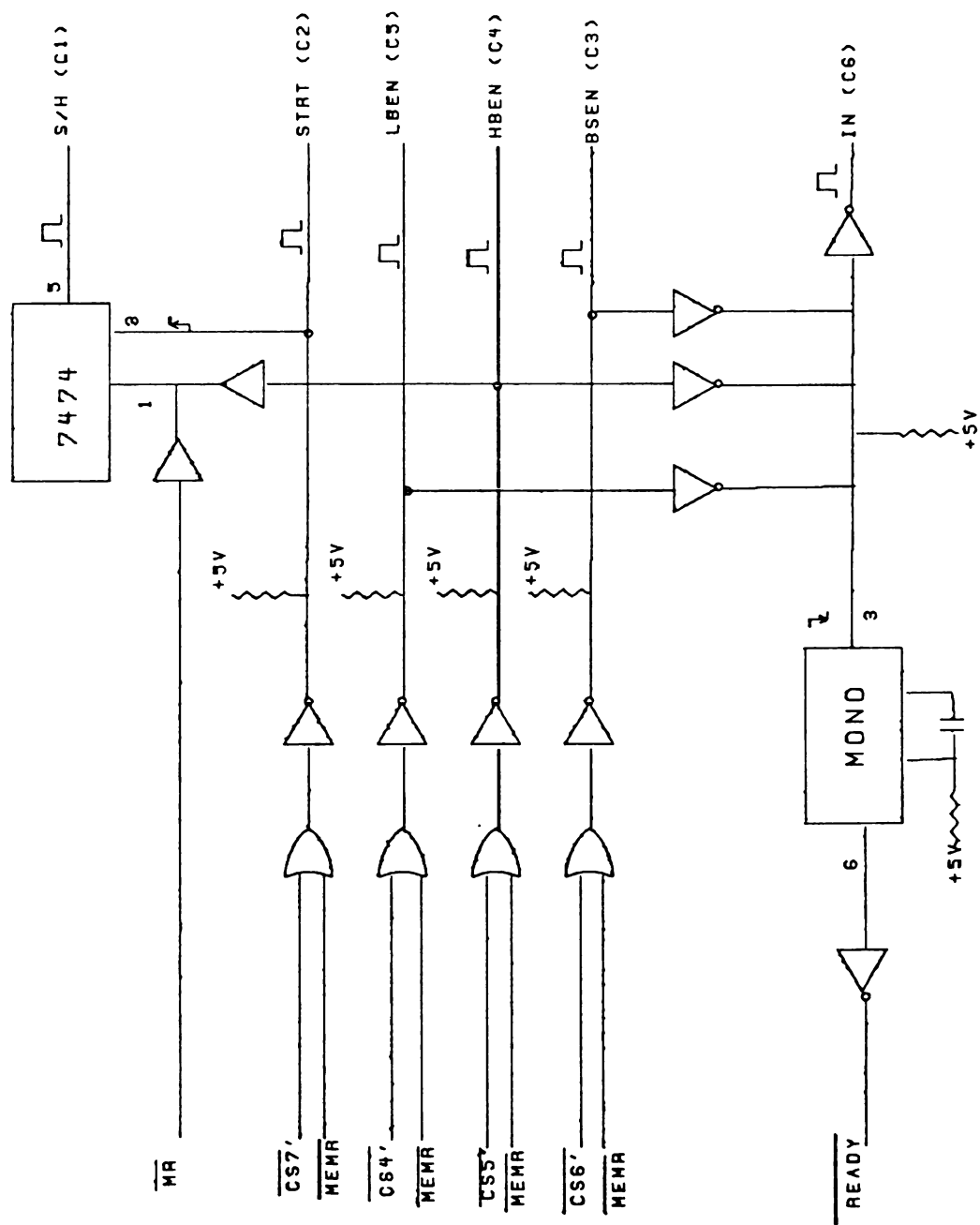


Figure 38. A/D converter interface logic.

voltage follower configuration, and is used to buffer the input signal. Two 12-volt zener diodes (1N5242) between the input and the ground protect the amplifier by keeping the input voltage between the safe limits. The resistor and the capacitor in the feedback loop prevent the oscillation of the amplifier when the amplifier is on and there is no voltage present at the positive input of the amplifier. The second amplifier (A2) is also an RCA CA3140 operational amplifier and it is used as an inverter with gain ($G=2$). The amplification is necessary if the full resolution of the A/D converter is to be utilized. The output of the inverter should be exactly equal to the potential of the working electrode with respect to the reference electrode. The sample and hold amplifier, a Harris Semiconductor Al-2425-5, tracks the voltage continuously, holding it only while the A/D converter digitizes it. Two 5.1-volt zener diodes (1N4733) between the sample and hold input and ground are used to keep the input voltage between the limits of the A/D converter.

The A/D converter is a DATEL ADC-HY12BC 12-bit successive approximation analog-to-digital converter with an input range of ± 5 V and a specified conversion time of 8 microseconds. The resolution of the A/D converter is 2.4 mV which corresponds to 1.2 mV resolution of the electrode potential. The interface of the voltage measurement system to the microcomputer is divided in two

parts. One part is built on the same board with the A/D converter and the other part is built on the microcomputer board. In Figure 37, the connections between the two boards are shown.

The operation of the system is as follows. Usually the S/H signal is low and the sample and hold is in the sampling mode. In order to read the potential of the working electrode with respect to the reference electrode, the computer sends the $\overline{CS7}$ and $\overline{MEMR}$ pulses. The output (STRT) of the inverter is a 260 msec pulse which starts the conversion sequence in the A/D converter. The rising edge of the STRT pulse clocks the 7474 flip-flop and the output of the F/F turns the sample and hold to the hold mode. During the conversion time, the STATUS output of the converter is high. The computer checks the STATUS output to see when the conversion is completed and reads the output data of the converter. The 12-bit output word is divided in two bytes, the 8-bit low byte and the 4-bit high byte. The computer reads the two bytes separately by sending the LBEN and HBEN pulses to the drivers. The HBEN pulse also clears the output of the F/F and the sample and hold is switched to the sample mode. The rising edge of the LBEN, HBEN, and BSEN signals triggers a monostable (MONO) producing a 1.0 μ sec pulse, which is connected to the READY line of the microcomputer. This pulse causes the microcomputer to enter into a WAIT state for 1.0 μ sec.

The 1.0 μ sec delay ensures that the Data Bus contains the right information during the read time. Two 8097 and one 8095 TRISTATE hex buffers are used as drivers to connect the appropriate set of signals to the Data Bus at the right time.

C. The Real-Time Clock

The real-time clock is used by the system to measure the drop time and to generate drive delays under computer control. It consists of an INTEL 8253 PROGRAMMABLE INTERVAL TIMER and a few supporting chips. The 8253 is a programmable converter/timer chip organized in three independent counters (40). Each counter consists of a single 16 bit pre-settable down counter. The counters are independent and each can have separate MODE configuration and counting operation. Counter 2 is used as a rate generator to generate a 1 KHz signal which is used as a clock input for counter 0 and counter 1. Counter 0 is used to measure the drop time and counter 1 is used to generate time delays. The interface of the real-time clock and the control logic are shown in Figure 39.

The operation of the clock is as follows. The CPU sends a control word to each counter of the 8253, to set its MODE, and its present count value. To start the operation of any counter, the CPU sets the appropriate bit in the 74174 register. A low in the Gate input of the



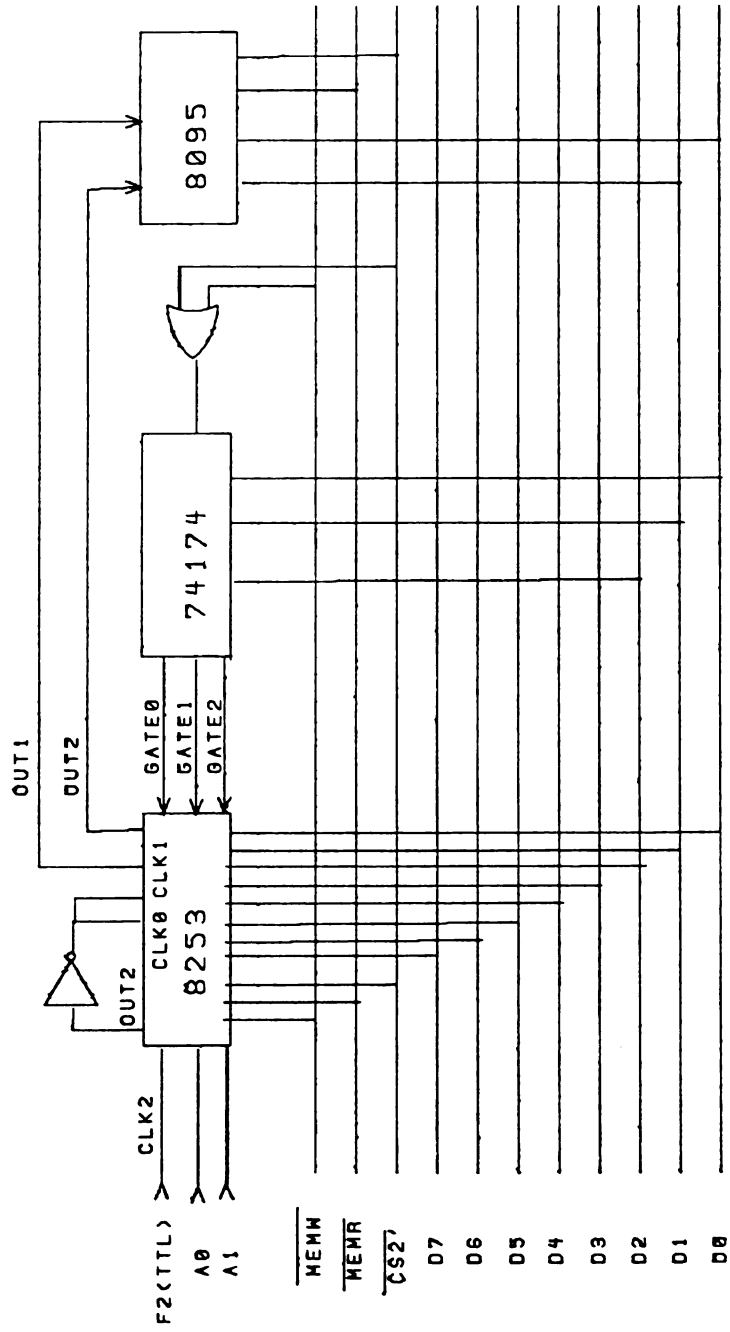


Figure 39. Real time clock.

counter inhibits its operation. A high enables the counter operation. In order to measure the drop time, the CPU sets counter 0 14 MODE 0 and loads the counter with zeroes. When the computer detects the drop fall, it sets Gate 0 and Gate 2 and starts the operation of the clock. At the next drop fall, the CPU stops the operation of Counter 0 (Gate 0 = 0) and reads the contents of this 16-bit counter. The two's complement of this number gives the drop time in milliseconds. In order to generate accurate time delays, the CPU sets computer 1 in MODE 0 and loads the counter with the appropriate counts (milliseconds). After the count is loaded into the counter, the CPU sets Gate 1 and Gate 2 and the counter starts counting. The CPU checks the output of the counter 1 (OUT1). A high in OUT1 indicates the end of the delay time.



CHAPTER 5

MULTIMICROCOMPUTER SYSTEM ARCHITECTURE

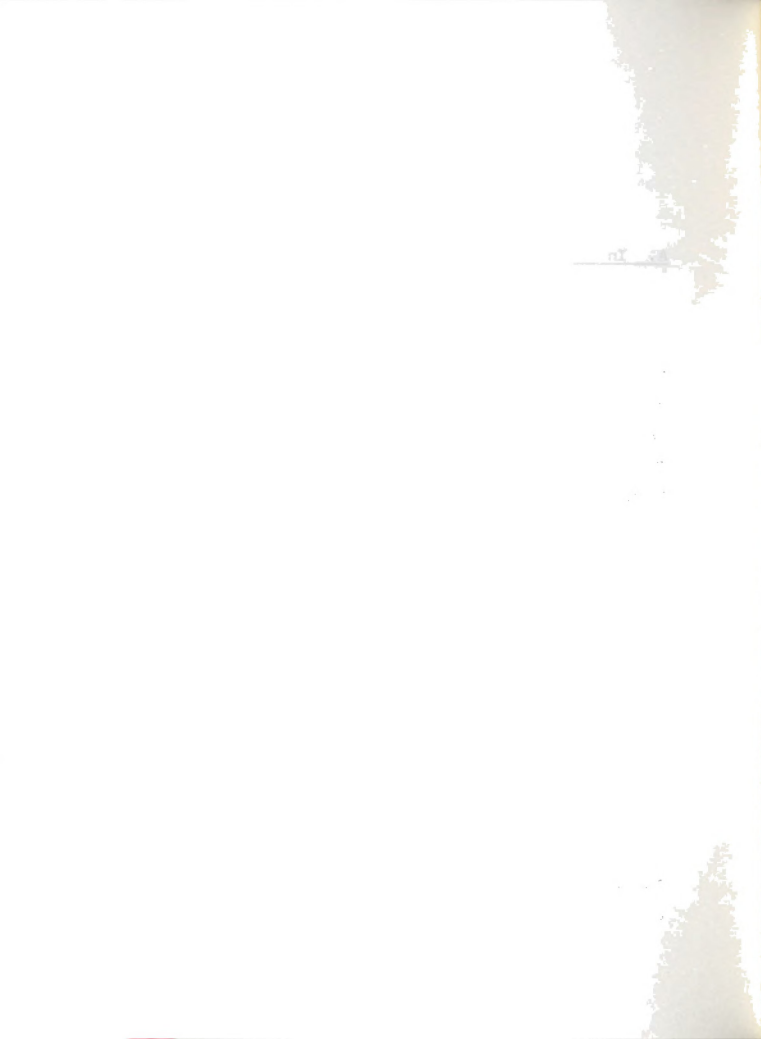


CHAPTER 5

MULTIMICROCOMPUTER SYSTEM ARCHITECTURE

A. Introduction

Digital electronics and computers have become, in recent days, standard laboratory tools for the analytical chemists. The on-line use of the computer for instrument control and operation, data acquisition and data analysis, opens new areas in analytical chemistry. Better accuracy, greater flexibility and new analytical techniques are being obtained with the automation of analytical experiments. The on-line application of the computers to the automation of analytical experiments have been studied by some workers and there are many books and reports on this subject (41,42,43,44,45,46). Electrochemistry offers the most convenient field for the on-line use of the computers since all the parameters in an electrochemical system can be set electrically rather than mechanically, and the use of digital circuitry for instrument control and operation in this field is well established. Electrochemical function generators have been described which are under computer control (47-49), and an increasing number of computer applications in the electroanalytical chemistry field have been published



(50-56). In all these applications of computers in electrochemistry, a minicomputer was directly connected to the experiment, as a dedicated computer, to control the instrument and acquire and analyze the data. The minicomputer is the ideal choice for a dedicated computer because it offers highly sophisticated software supporting systems, and it has a fast response time. The only disadvantage of the minicomputer is the price that one has to pay for it.

During 1974 a new large scale integrated circuit (LSI) appeared on the market, the microprocessor, which functions the same as the central processing unit (CPU) of larger computers. The significance and the importance of this new technological development to the analytical chemist is that a microprocessor, in conjunction with memory, control circuitry, and data input and output ports, constitutes a microcomputer (57-61). This microcomputer can be built, at low cost, as part of any analytical instrument and it can serve as a dedicated computer. The disadvantages of the microcomputer is that it is relatively slow and the available supporting software systems are not so highly sophisticated. For complex functions, the programming in the microcomputer can be difficult and long. Also, as the complexity of the function increases the response time of the microcomputer decreases.

1000

1000

1000

1000

1000

B. Multiprocessor System

In order to improve the response time of the micro-computer and to simplify programming, several micro-processors can be linked together to form an intelligent network (62,63). Such a multiprocessor system was developed in our laboratory and it was used as the control logic in the electrochemical system. A block diagram of the multiprocessor system is shown in Figure 40.

The system consists of a number of microprocessors, each one located in a different board, connected together through the main bus. The main bus includes a 16-bit address bus, an 8-bit data bus and four control lines ($\overline{\text{MEMR}}$, $\overline{\text{MEMW}}$, $\overline{\text{DBIN}}$, $\overline{\text{READY}}$). Each microprocessor, in conjunction with some supporting circuitry, constitutes a fully functional microcomputer capable of independent operation. A specific task is assigned to each micro-computer and one of them, the coordinator, coordinates the operation of all the slaves in order to obtain a unified functioning of the system. A user-defined portion of each slave's memory and task space resides in the address space of the coordinator and the local slave bus is an extension of the coordinator's bus. The coordinator has the capability to start or stop the slave processor, read or write status words to them, instruct them to execute a specific program of their software library, reprogram them, or even take complete control of the slave's

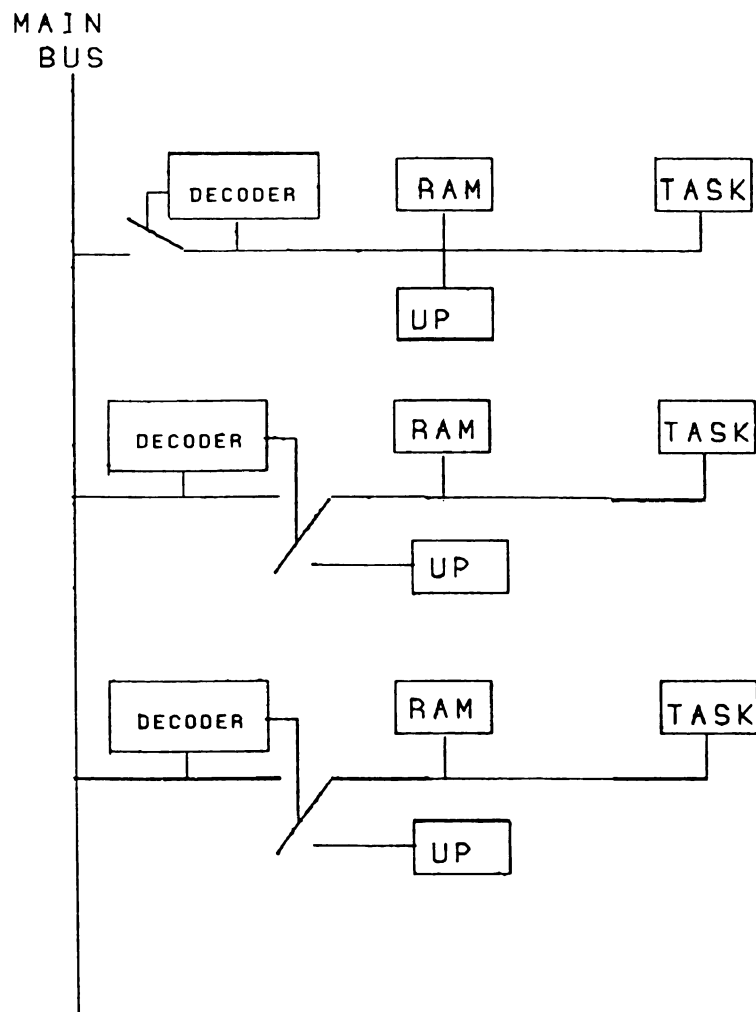


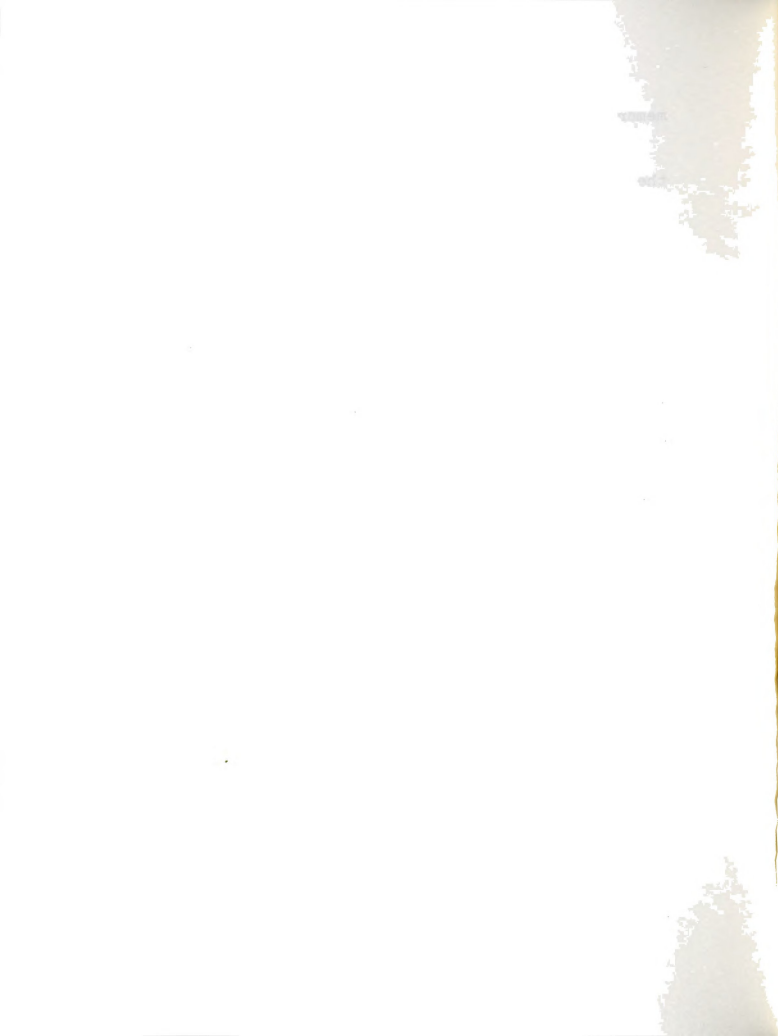
Figure 40. Block diagram of the multiprocessor system.



memory and task.

When the coordinator wishes to take over control of the memory or task space of one of the slaves, it sends the address of that particular slave's memory or task to the main bus. The address decoding circuitry of each slave microcomputer receives and decodes the address and one of them recognizes its address and informs the slave processor that the coordinator desires control of the local bus. After the slave processor finishes its current cycle, it enters in a HOLD state and the decoder switches control of the slave's bus to the coordinator. The coordinator now has full control of the slave's bus. The coordinator terminates its interaction with the slave by simply removing the slave's address from the address bus and the address decoding circuit returns control of the slave bus to the slave processor. For details on the construction of the address decoding circuit and the main bus assignment see Reference 33.

One of the main advantages of the multiprocessor system is its ability to perform simultaneously a number of different tasks with the result that the speed of the system is significantly increased. Other important advantages of the system include standardization of the design, modularity in both software and hardware, ease of expansion in software and hardware, and simplified programming.



C. Multiprocessor Control of the Electrochemical System

The control logic of the electrochemical system consists of three microcomputers, the coordinator and two slaves. Each microcomputer is responsible for specific tasks. Figure 41 shows a block diagram of the multimicrocomputer system used to control and operate the electrochemical system and the specific tasks assigned to each microcomputer. The three microcomputers and their dedicated I/O interfaces are contained in a SR20105 BUD RACK SUB SYSTEM. The rack has 12 cards slots with 12 58-pair PC connectors. A back plane was soldered to the lower 40 pair of connectors to provide a common bus across the width of the rack. The upper 18 pair of connectors were left open for special connection between boards. A typical microcard is a 6.2 x 8.2 inch double sided wire wrap board with holes in 0.1 inch centers. All of the micros have their own local memory for the storage of data and program modules. A new software system was developed (33) and was used as the operating system. The executive for this system resides in the coordinator micro.

The function and the memory map for each micro will be discussed separately:



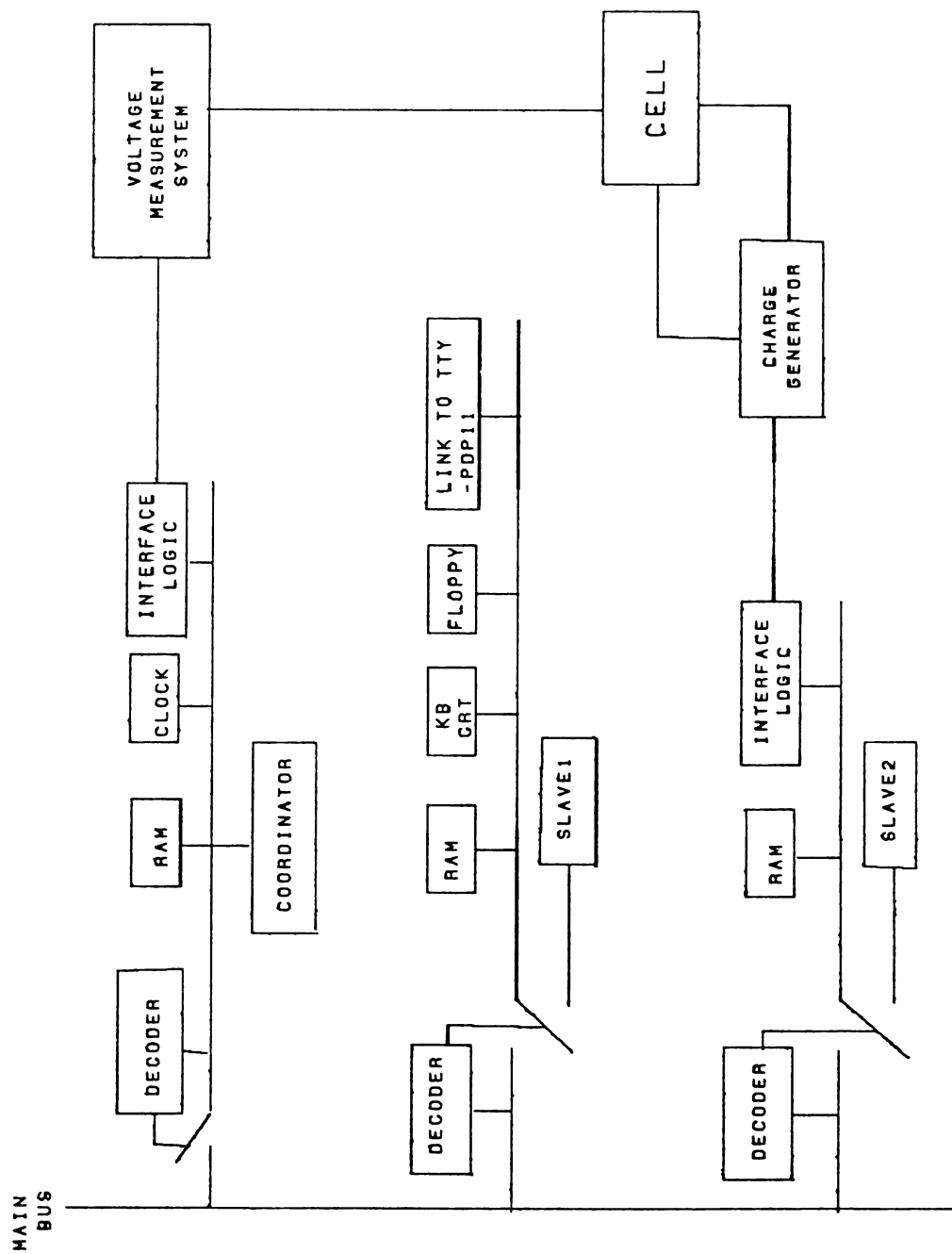


Figure 41. Multiprocessor control of the electrochemical system.



1. Coordinator Micro

The coordinator supervises the operation of the slave microcomputers and coordinates all the activities in the system. It controls also the operation of the voltage measurement system and the real-time clock. Table 4 gives the address map of the coordinator. Address 0 to address 15777 (octal) are used by 7K of Random Access Memory (RAM). OUTREGISTER1 and INBUFFER1 are used by the coordinator for intermicro communication. OUTREGISTER2 and INBUFFER2 are used by the coordinator to control the operation of the real-time clock. Addresses 16400, 16401, 16402, and 16403 are used by the real time clock (Chapter 4). Addresses 17000, 17200, 17400, and 17600 are used to control the operation of the voltage measurement system (Chapter 4). These four memory locations are Read-Only-Memory (ROM). Address 20000 to 37777 corresponds to the memory and task space of slave 1, and address 40000 to 77777 corresponds to the memory and task space of slave 2.

2. Slave 2 Micro

Slave 2 microcomputer controls the operation of the pulse generator (Chapter 4). Table 5 gives the memory map of slave 2. Address 0 to address 13777 (octal) are used by 6K of RAM. Addresses 14000 and 14001 are used

Table 4. Memory map of the coordinator.

Address (Octal)	Function	Comments
0-to-15777	7K of RAM	Memory
16000	OUTREGISTER1/IN BUFFER1	
	OUT REGISTER1	
	D0-Reset Micro1	1-Resets Micro1
	D1-Hold Micro1	0-Holds Micro1
	D2-Reset Micro2	1-Resets Micro2
	D3-Hold Micro2	0-Holds Micro2
	IN BUFFER1	
	D0-Flag Micro1	1-Micro1 is Halted
	D1-Flag Micro2	1-Micro2 is Halted
16200	OUT REGISTER2/IN BUFFER2	
	OUT REGISTER2	
	D0-Clock Gate0	1-Enables Clock register0
	D1-Clock Gate2	1-Enables Clock register2
	D1-Clock Gate1	1-Enables Clock register1
	IN BUFFER2	
	D0-Clock Out0	1-Clock register0. The terminal count is reached
	D1-Clock Out1	1-Clock register1. The terminal count is reached

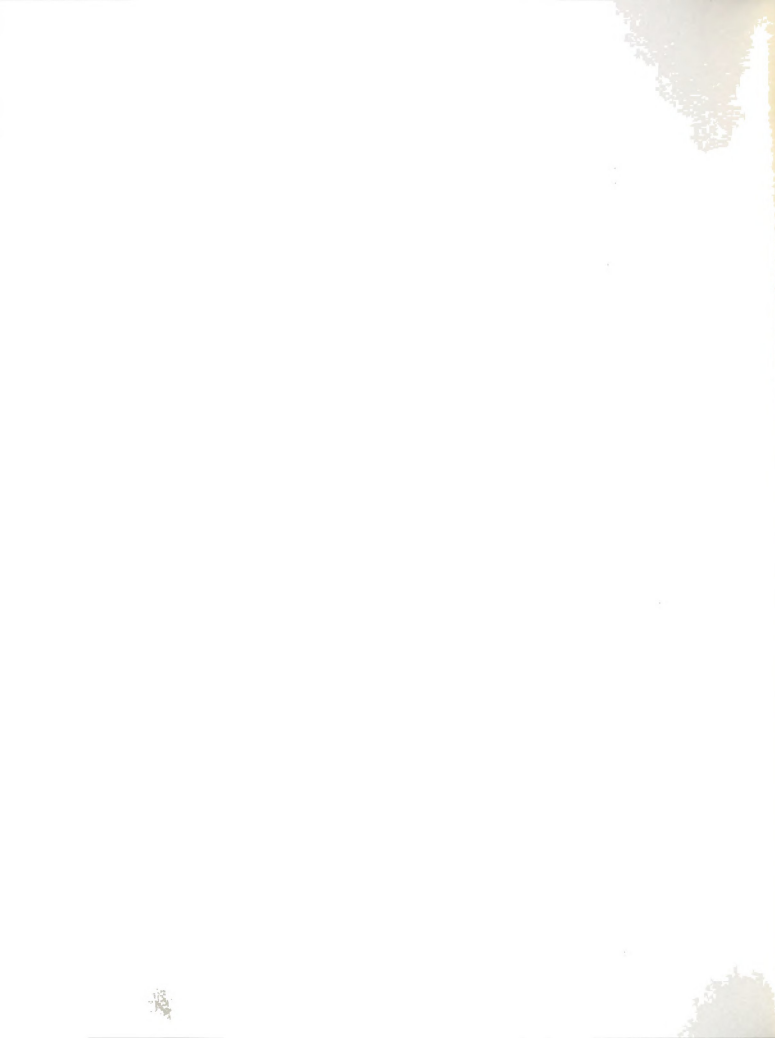


Table 4. Continued.

Address (Octal)	Function	Comments
16400	Clock register 0	
16401	Clock register 1	
16402	Clock register 2	
16403	Clock control register	
17000	Voltage Measurement system LBEN	Read low byte from A/D converter
17200	Voltage measurement system HBEN	Read high byte from A/D converter
17400	Voltage measurement system BSEN	Read busy signal from A/D converter
17600	Voltage measurement system STRT	Start Analog-to-Digital Conversion
20000-to-37777	Slave's 1 memory and task space	
40000-to-77777	Slave's 2 memory and task space	



Table 5. Memory map of Slave 2

Address (Octal)	Function	Comments
0-to-13777	6K of RAM	Memory
14000	DAC-LBS	Write low byte to digital-to-analog converter
14001	DAC-HBS, LDA	Write high byte to digital-to-analog Converter, start conversion
16000	OUT REGISTER	
	D3 D2 D1 D0	Select switch SW0
	0 0 0 0	Select switch SW1
	0 0 0 1	Select switch SW2
	0 0 1 0	Select switch SW3
	0 0 1 1	Select switch SW4
	0 1 0 0	Select switch SW5
	0 1 0 1	Select switch SW6
	0 1 1 0	Select switch SW7
	0 1 1 1	Select switch SW8
	1 0 0 0	Select switch SW9
	1 0 0 1	



to control the operation of the digital-to-analog converter and address 16000 is used to control the switches of the pulse generator. The truth table of OUTREGISTER is given in Table 5.

3. Slave 1 Micro

Slave 1 microcomputer, the communicator, is responsible for all the communications of the system with the operator. It is also communicating with the PDP-11 mini-computer and the teletype. Table 6 gives the memory map of the communicator. Chapter 6 includes a detailed description of the operation of the communicator.

Table 6. Memory map of slave 1.

Address (Octal)	Function	Comments
0-to-7774	4K of RAM	Memory
16000	OUT REGISTER/IN BUFFER	
	<u>OUT REGISTER</u>	
	D0-TTY OUT	Used to send data to the teletype
	D1-TTY REQ	1-Requests service from the TTY
	D2-PDPM REQ	1-Requests service from PDP11.
		Disables STATUS REGISTER
	<u>IN BUFFER</u>	
	D0-Flag1	1-Output register to PDP11 empty
	D1-Flag2	1-Input Register from PDP11 empty
	D2-KB Ready	0-Key board ready
16100	KB	Read key board
16200	GRAPHICS BOARD	Five locations of Graphic board
16201	GRAPHICS BOARD	
16202	GRAPHICS BOARD	
16203	GRAPHICS BOARD	
16204	GRAPHICS BOARD	

Table 6. Continued.

Address (Octal)	Function	Comments
16300	STATUS REGISTER/ INPUT-OUTPUT PDP11 REGISTER	
	<u>STATUS REGISTER</u>	
	D4-PDP11 Down	1-PDP11 is down
	D5-INTERRUPT DISABLE	1-The interrupt line has been disabled. PDP11 is busy
	D6-TTY BUSY	1-The teletype is busy
	D7-TTY FLAG	1-The teletype is ready to receive data
16400	FLOPPY	
16500	STATUS LATCH	
	D0-Motor enable	1-Disable the Floppy driver motor
	D1-Write protect0	1-Write protects disket 0
	D2-Write protect1	1-Write protects disket 1
	D3-VRAM enable	1-Enables the VRAM output
	D4-GRAPHICS enable	1-Enables the Graphics output
	D5-Reverse Graphics	1-Enables reverse Graphics
17000-to-17777	VRAM	



CHAPTER 6

COMMUNICATION IN A DISTRIBUTED INTELLIGENCE SYSTEM



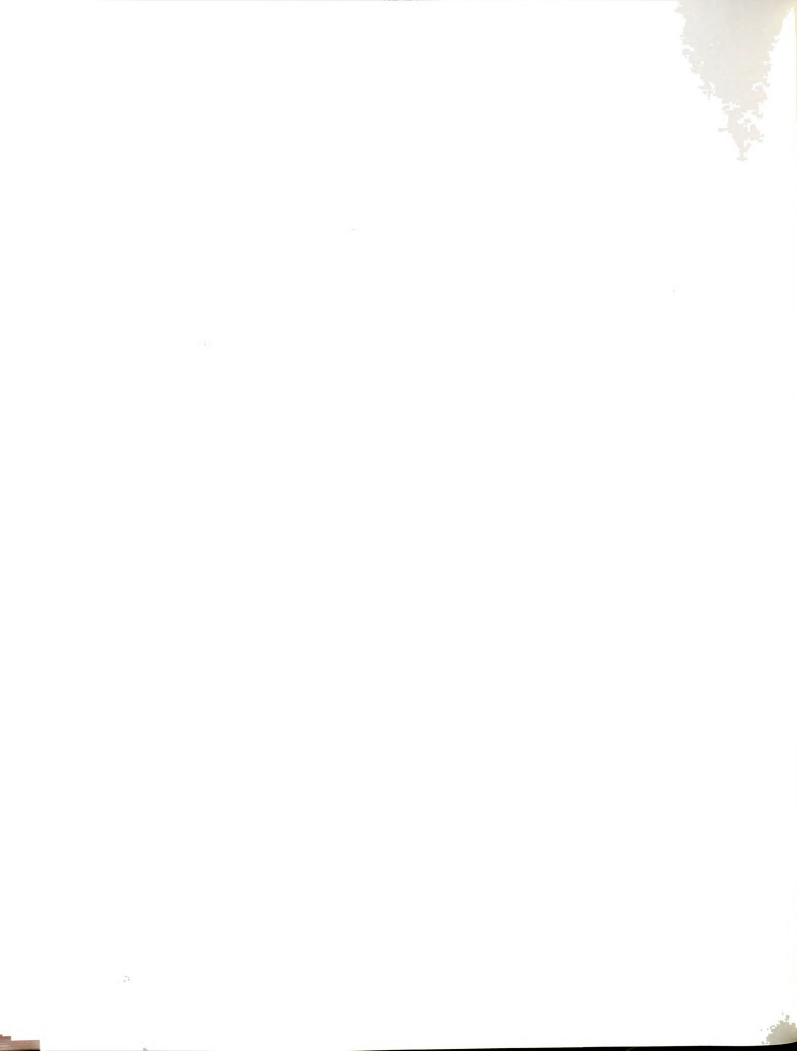
CHAPTER 6

COMMUNICATION IN A DISTRIBUTED INTELLIGENCE SYSTEM

A. Introduction

The tremendous development and the application of microelectronics in the construction and the development of new instruments in recent years has created "smart instruments", instruments that allow computer programming to replace the design of specific purpose logic. These instruments in a "stand alone" environment can perform a specific task or a series of tasks, they can acquire a large amount of data in a short time, and they can perform simple data analyses. The same instruments in a "shared resource" environment, as part of a distributed intelligence system, can acquire an extra dimension, and they can become orders of magnitude more powerful and more efficient.

A distributed intelligence system with an hierarchical structure consists of a central computer which communicates with a number of smaller computers each of which communicates with a number of computers of the next lower level. The programming level of each constructional unit of the hierarchical system follows the pyramidal arrangement with the higher members of the pyramid able to



operate in a higher programming level. The same is true for the amounts of data that each member of the system can store and manipulate, with the higher member of the system able to store and manipulate larger amounts of data. The response speed of each member of the system also follows the pyramidal arrangement with the higher members of the system able to operate in higher speeds. The result of this pyramidal arrangement of the characteristics of each member of the hierarchical system is that each member of the pyramid is able to operate in a certain level of intelligence and is able to perform a certain level of computation.

The lowest members of the pyramid, the dedicated computers, can: (Figure 42)

1. Operate the instrument;
2. Collect raw data;
3. Perform a simple data analysis (e.g., averaging, calculation of slope, calculation of transmittance);
4. Check and store the results; and
5. Change parameters and perform a new experiment.

The result of those operations is a set of data that in some cases describes satisfactorily the unknown systems, but in some other cases more mathematical treatment is required. In such cases, the higher intelligence of the

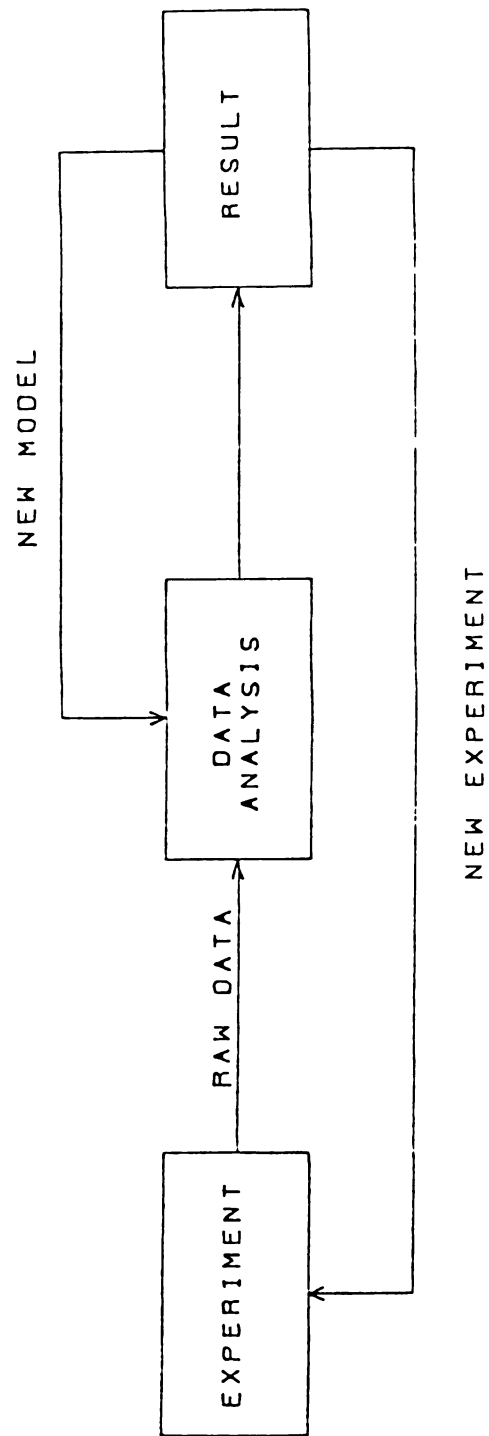


Figure 42. Operations of a dedicated computer.

next member of the pyramid is needed to: (Figure 43)

1. Perform a set analysis (e.g., smoothing, Fourier transformation);
2. Correlate the results; and
3. Ask for a new set of experiments.

In our research laboratory, in which the main effort is the development and the characterization of new automated analytical instruments and new analytical techniques, we faced the problem of the communication in a distributed intelligence system and we tried to solve this problem with a solution that will give the maximum flexibility, the maximum speed, and the lowest cost.

B. Description of the System

Until some years ago the center of the research activities and the research decision in our laboratory was a DEC PDP-11/40 minicomputer with a disk, a dual floppy disk system, a terminal, a line printer, and a DOS-BATCH operating system. The system was used for program development, for data analysis, and as a dedicated computer connected to some experiments.

In recent years, microprocessors (MPU's) were introduced in our research and a multimicrocomputer system has been developed which consists of a number of microcomputers connected together (32,33). In this system each MPU

1000

1000

1000

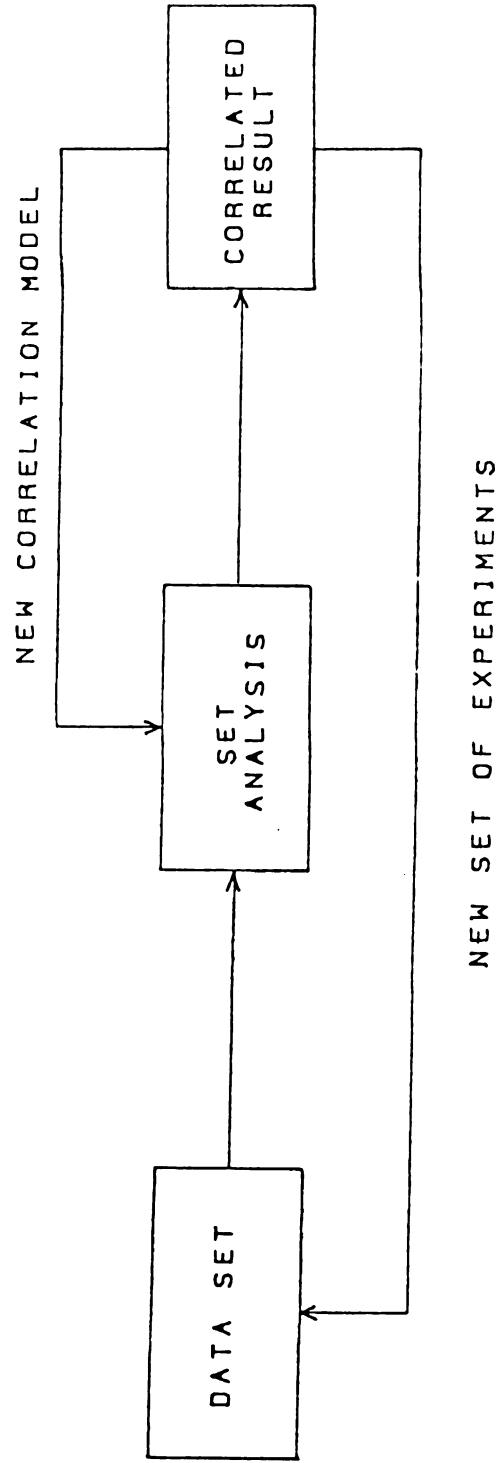


Figure 43. Operations of a "high intelligence" computer system.

is responsible for a particular portion of the system's tasks and the result of this coordinated operation is a powerful microcomputer system, a completely independent "working" unit which can perform the following functions:

1. Instrument control and operation;
2. Data acquisition;
3. Data storage;
4. Simple data analysis;
5. Data display;
6. Instrument-Operator communication; and
7. Program development.

With the application of this system in our research effort, decentralization occurred. Some of the centers of research activities and research decisions were removed from the minicomputer and the minicomputer's operation became more efficient. However, during the development and the characterization steps of an automated instrument, or a new analytical technique, the higher intelligence of the minicomputer with the more sophisticated software library is needed. This is also true for program development, and for more extensive data processing. Also the presence of expensive peripherals interfaced to the minicomputer, peripherals that can be used on a "shared" basis by a number of instruments, makes the link to the minicomputer essential.



A block diagram of the hierarchical system is shown in Figure 44. Each of the multimicrocomputer systems has a keyboard, a CRT for Alphanumeric text and simple graphics, and a local mass storage device for programs and data storage. These local peripherals are interfaced to the communicator MPU which is responsible for all the communications: operator-instrument, operator-minicomputer, instrument-minicomputer. A number of slave MPU's are connected to the experiment and the coordinator MPU coordinates the operation of the system.

The "external I/O link" is a common connection point for all the multimicrocomputer systems and it is an extension of the minicomputer bus. A teletype is connected to the external I/O link and it can be used by any microcomputer system for hardcopy of programs, data and parameters. The external I/O link is a BUD rack with twelve PC connectors mounted on it. A backplane connects the PC connectors together and forms the External I/O Bus. This bus can become an extension of the minicomputer's bus, by connecting one end of the "bridge" to any PC connector and the other end to the minicomputer's Unibus TM. A number of peripherals can be interfaced to the minicomputer through the external I/O bus, using only one general purpose interface board.

The micro I/O port interfaced to the external I/O bus is the common connection point for all the multimicro-



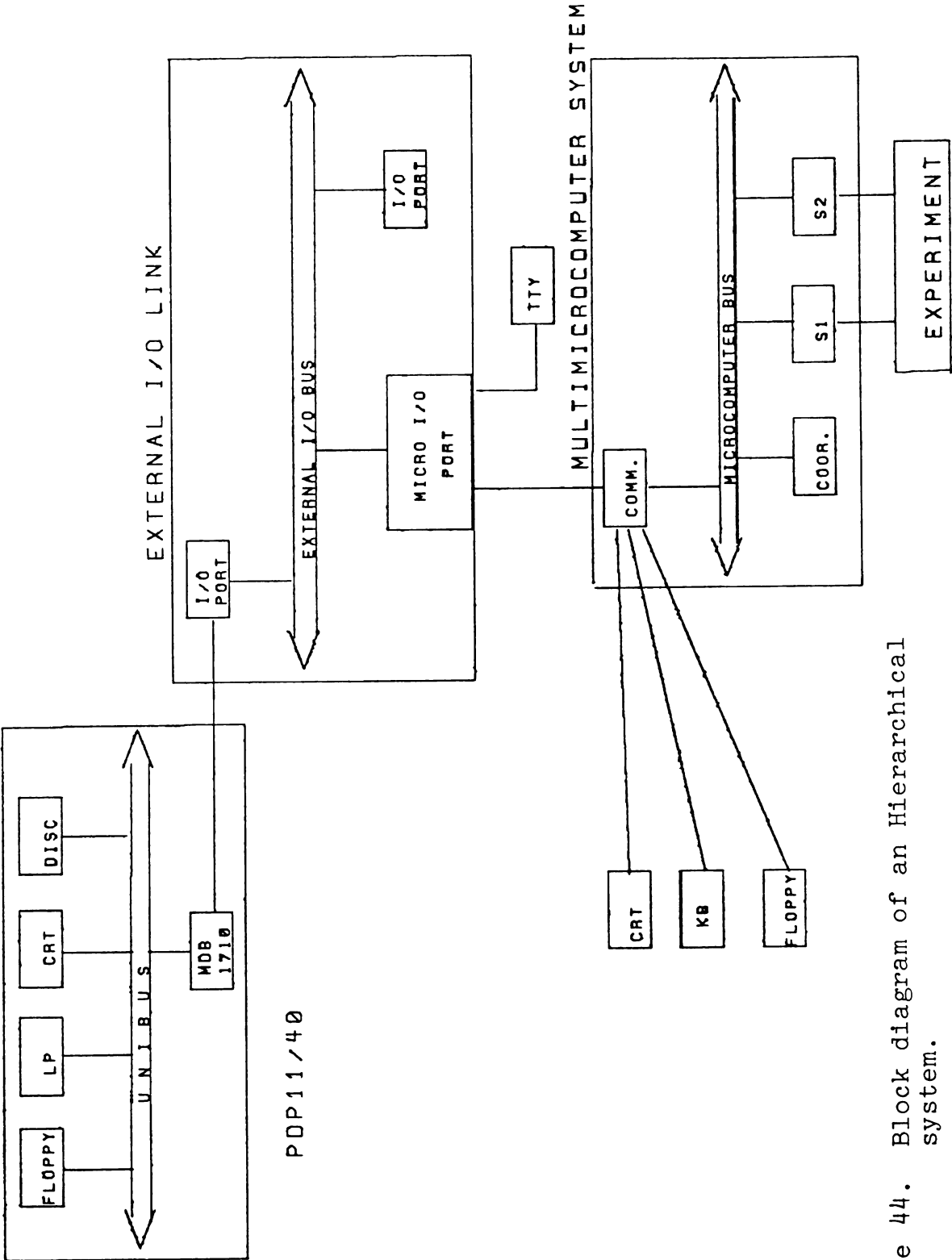


Figure 44. Block diagram of an Hierarchical system.

computer systems connected to the minicomputer. Its function is to:

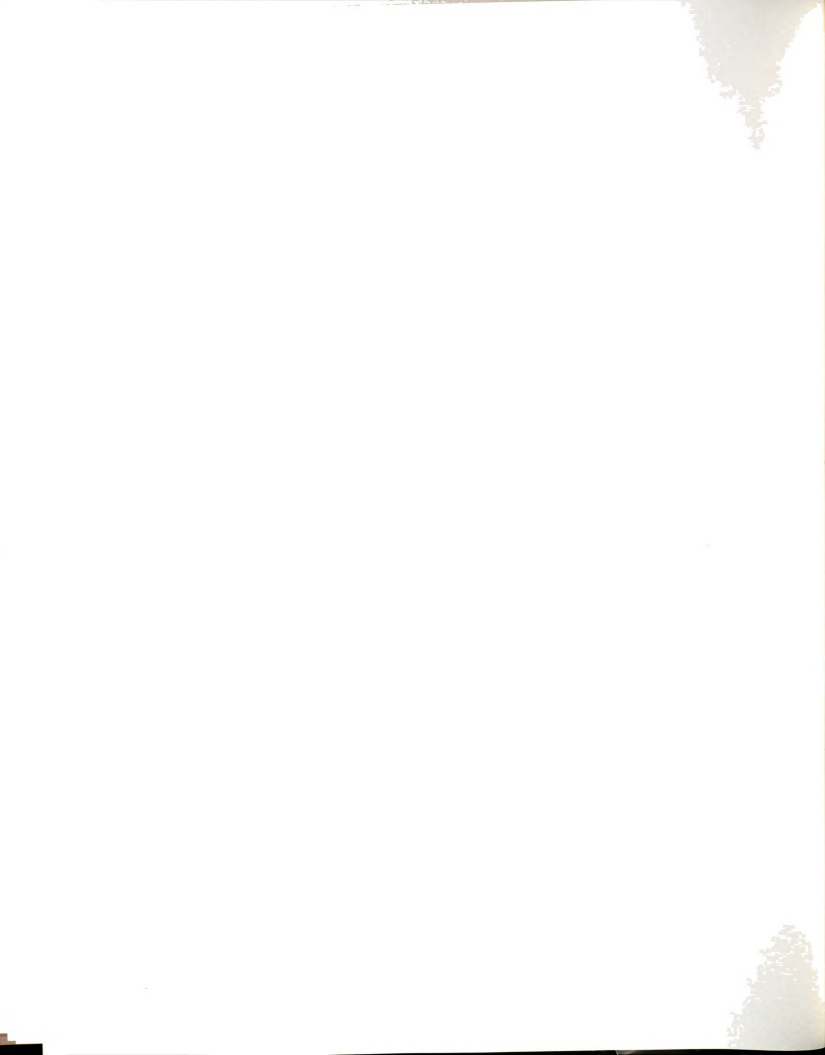
1. Give information to any micro system regarding the operation and the conditions of the minicomputer;
2. Control and coordinate the service requests and the data transfer from any micro system to the minicomputer, or from the minicomputer to any micro system; and
3. Control and coordinate the service requests and the data flow from any micro system to the teletype.

The operation of the system can be divided in three functional units, and each unit will be described separately.

C. The Minicomputer Side of the Link

Figure 45 shows a block diagram of the minicomputer side of the link. The MDB-1710 General Purpose Interface Module was used to interface the external I/O Bus to the minicomputer. The MDB-1710 consists of a single quad module containing two parts:

- (a) The fixed logic which includes receivers, drivers, device address selection and decoder logic, and dual interrupt vector logic.
- (b) The User's interface logic with circuit board facilities and wire wrap posts to accommodate up



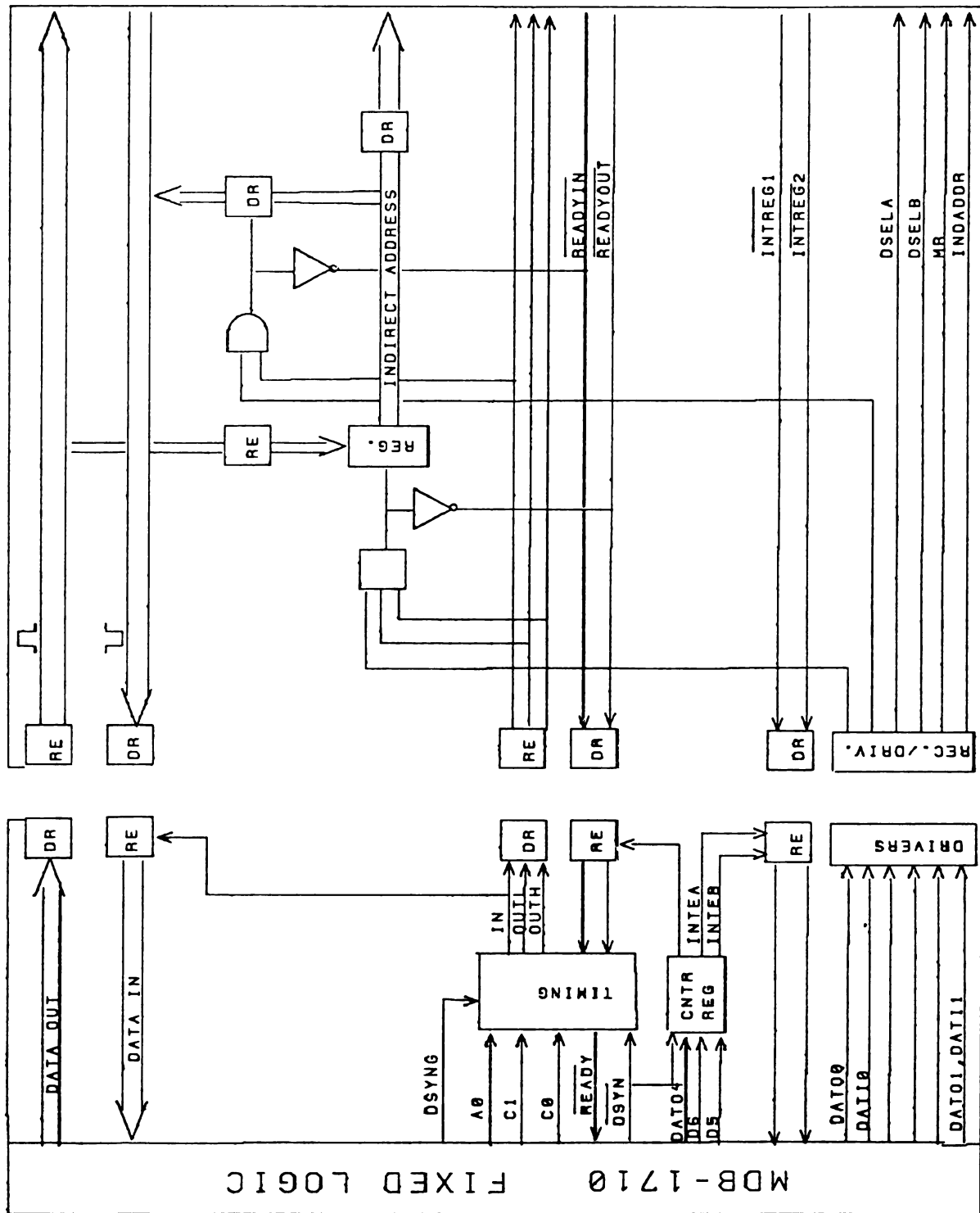
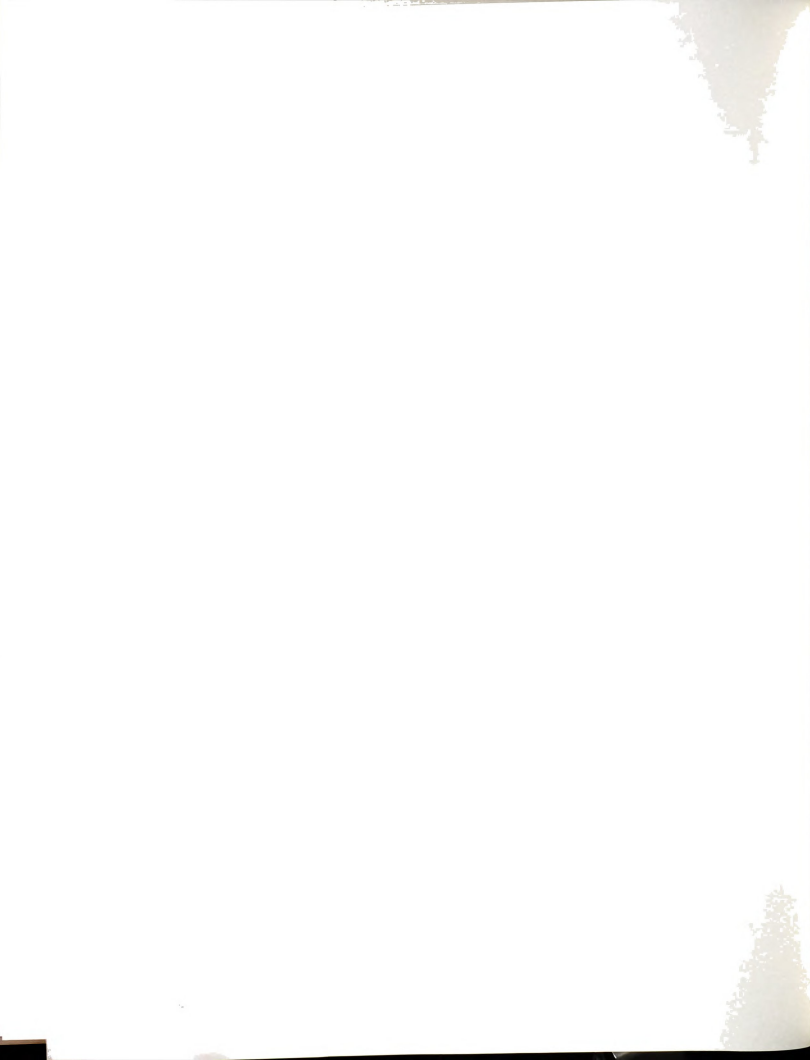


Figure 45. Block diagram of the MDB-1710 and the external I/O port.

to 40 integrated circuit devices. These facilities were used to build the logic which interfaces the fixed logic of the module with the external I/O Bus.

The basic element of the operation of the interface is the indirect addressing capability of the systems, and the interfacing logic which provides all the necessary signals for it. The AO, Cl, CO, DSYNG, and $\overline{DSYN}$ signals were used to create three new signals useful for gating input data onto the UnibusTM (IN), or loading external registers during an output operation (OUTL, OUTH). In response to these signals issued by the central processing unit (CPU), the slave sends a $\overline{READY\ IN}$ or $\overline{READY\ OUT}$ signal to inform the CPU that the operation is completed. In order to obtain this interlocked communication, the MDB-1710 was changed. The connection between the output (8) of the gate 4C and the input (5) of the inverter 15A was cut. The signal READY, which is the combined $\overline{READY\ IN}$ and $\overline{READY\ OUT}$ signals, was connected to the input (5) of the inverter 15A. The interlocked communication of the CPU with any remote slave connected to the external I/O Bus, makes the communication independent of the physical length of the link and the response time of the slave.

To select any peripheral interfaced to the external I/O bus, the CPU loads the INDIRECT ADDRESS REGISTER with



a 16 bit word, using one address of the MDB 1710 module (DAT00) and the OUTL and OUTH signals. The INDIRECT ADDRESS REGISTER consisting of two SN74198 8-bit registers latches this word and sends it to the ADDRESS lines of the external I/O Bus. All the peripherals receive the address and decode them and only one of them decides that it is the slave for this operation. Next the CPU uses a second address of the MDB 1710 module (DAT01 or DAT11) to indicate to all the peripherals that this is an indirect address operation (IND ADDR) and sends the control signals to define the direction of the transfer (IN, or OUTL, OUTH). The selected peripheral receives the IND ADDR and the control signals and uses them for gating data onto the DATA IN bus or getting data from the DATA OUT bus and sends the READY signal to inform the CPU that the transfer is completed.

The Bus Drivers shown in this figure permit the CPU to read and check the address that appears on the ADDRESS Bus. For this operation the DAT10 address of the MDB1910 module and the IN signal was used.

The CNTR REGISTER shown in this figure is used to enable the INTERRUPT REQUEST1, INTERRUPT REQUEST2 and READY IN, READY OUT signals. The DAT04 address of the MDB 1710 module and the DSYN signals are used to load CNTR REG. with a two bit word. The CNTR REG permits the CPU to enable any interrupt request or both requests or to turn

off completely the link to the external I/O Bus.

Five addresses of the MDB 1710 module are used for the link to the External I/O Bus and there are eleven more addresses that can be used for direct interface to the CPU.

D. The Micro I/O Port

Figure 46 shows a block diagram of the Micro I/O Port. In this diagram the link to one microcomputer system is shown. The main function of the Micro I/O Port is to connect seven different microcomputer systems to the minicomputer and to the local teletype. The STATUS REGISTER is an eight bit register which provides information to all microcomputer systems regarding the operation and the status of the minicomputer and the link itself.

Bit D7 (TTYFLG) is a flag to inform the microcomputer system that the teletype request ($\overline{\text{TTYREG}}$) issued by this microcomputer system was granted.

Bit D6 (TTYBUSY) is set when the teletype is busy with any microcomputer system. Any TTYFLG can set the TTYBUSY flag.

Bit D5 (IND DIS) is set when the minicomputer is serving any microcomputer system and indicates to all microcomputer systems that the interrupt request line has been disabled and that no interrupt request will be granted.

Bit D4 (11DOWN) is set when the minicomputer is down.



Figure 46. Block diagram of the Micro I/O port.



Bits D3, D2, D1 and D0 can be set by the minicomputer and they provide informations to all microcomputer systems regarding the operation and the status of the minicomputer. All the information that is contained in the STATUS REGISTER are available to all microcomputer systems through the STATUS BUS and STATUS BUFFERS.

The INTERRUPT LOGIC section receives and controls the service requests from the microcomputer systems and creates the necessary signals to interrupt the operation of the minicomputer.

The DECODER decodes the indirect address signals and provides eight signals to enable the link to any microcomputer system.

TIMING LOGIC provides the timing signals for the communications. IND ADDR and OUTL and IN signals, from the External I/O Bus, are used to create two new signals, $\overline{\text{READ}}$ and $\overline{\text{WRITE}}$, which are used for gating data onto the External I/O Bus ($\overline{\text{READ}}$), or loading the OUTPUT REGISTER with data from the DATA OUT Bus ($\overline{\text{WRITE}}$).

During a transfer of data from the microcomputer system to the minicomputer the following steps are involved: The microcomputer changes the level on the $\overline{\text{PDP11REQ}}$ line to zero and disables the STATUS BUFFER and the OR-gate 4. The microcomputer puts an eight bit word on the DATA Bus and sends the $\overline{\text{MW}}$ pulse. The falling edge of the $\overline{\text{MW}}$

pulse triggers the Monostable2 and the rising edge of $\overline{MW}$ clocks the Flip/Flop2. The falling edge of the output pulse of Monostable2 loads the INPUT REGISTER with the data from the DATA Bus. The output of F/F2, through an open collector driver, puts a " ϕ " on the $\overline{INTERRUPT REQUEST}$ line and triggers the INTERRUPT LOGIC which issues an interrupt request to the minicomputer. The INTERRUPT LOGIC also disables the $\overline{INTERRUPT REQUEST}$ line and sets bit D5 in the STATUS REGISTER. The output of F/F2 is also used to set a bit in the INTERRUPT REGISTER, which is part of the INTERRUPT LOGIC, and it is used as a flag to indicate to mini and microcomputer that the input register is full. When the minicomputer acknowledges the interrupt request, it sends the DSELB signal and clears the $\overline{INTEG2}$ signal. Next the minicomputer sends the indirect address of the INTERRUPT REGISTER, the decoder enables this register, and the minicomputer reads the register to see which micro system asked for service and jumps to its service routine.

In order to read the INPUT REGISTER the minicomputer sends the indirect address of the microsystem, which asked for service, the decoder decodes the address and enables the OR gate 2. The minicomputer sends the $\overline{READ}$ pulse, and enables the selected INPUT REGISTER and the INPUT BUFFER,

and clears F/F2. For the next micro to mini transfer the minicomputer sends the indirect address of the FLAG BUFFER and checks FLAG1 of the selected micro system to see when a new word is available in the INPUT REGISTER and repeats the read operation.

During a transfer of data from the minicomputer to any micro system the following steps are involved: The minicomputer sends the indirect address of the micro system, the decoder decodes the address and enables the OR gate 3 and disables the Interrupt Request signal. The minicomputer puts the data on the DATA OUT Bus and sends the $\overline{\text{WRITE}}$ pulse. The output pulse of OR gate 3 fires the Monostable 1 and clocks F/F1. The falling edge of the output pulse of the Monostable 1 loads the OUTPUT REGISTER, with the data. The output of F/F1 is used as a flag to indicate to mini and microcomputer that the OUTPUT REGISTER is full. In order to read the OUTPUT REGISTER the microcomputer puts a zero on the $\overline{\text{PDP11REQ}}$ line to disable the STATUS BUFFER and to enable the OR gate 1, and sends the $\overline{\text{MR}}$ pulse. The output pulse of OR gate 1 clears the F/F1 and enables the OUTPUT REGISTER and the OUTPUT BUFFER. To terminate the communication with any micro system, the minicomputer enables the $\overline{\text{INTERRUPT REQUEST}}$ line.

TTY logic is a separate and independent part of the Micro I/O Port. TTY logic receives the teletype service



requests from any micro system and controls the flow of data to the teletype. In order to access the teletype the microcomputer puts a one on the PDP11REQ line to enable OR gate 4, and puts a zero on the bidirectional FLG1/TTYREQ line. The TTY logic receives the request and if the teletype is free, it opens the link to the teletype and sets two bits (TTY BUSY, and TTY FLG) in the STATUS REGISTER. The microcomputer can now send data to the teletype using the TTYOUT line. To terminate the link to the teletype, the microcomputer removes the teletype request by changing the level on the FLG1/TTYREQ line to one. The TTYLOGIC clears the TTYBUSY and TTYFLG bits in the STATUS REGISTER and disables the TTYOUT line.

E. The Communicator

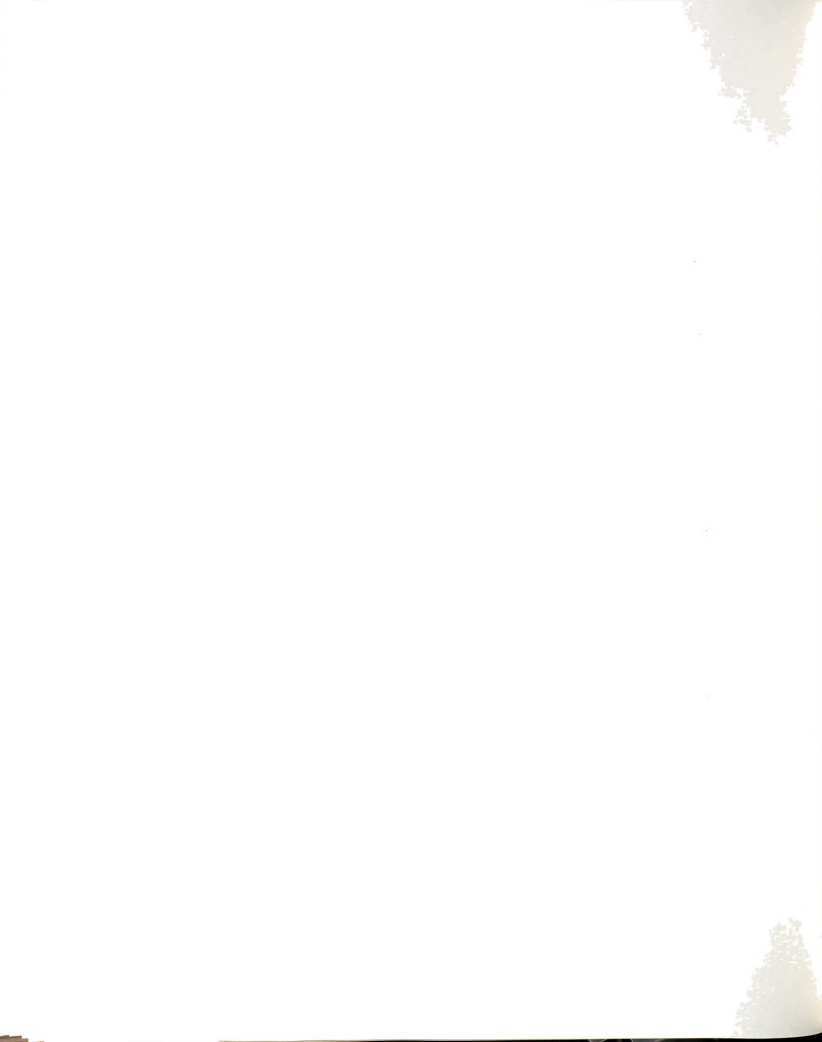
The communicator is a microcomputer with 5K of RAM built around an Intel 8080A microprocessor. It is part of the multimicrocomputer system and its main task is to communicate with all the peripherals interfaced to the multimicrocomputer system and with the operator. Figure 47 shows a block diagram of the interface of the peripherals to the communicator's bus.

The Floppy Controller is a PERSCI 1070 Intelligent Diskette Controller which can support up to four single diskette drives or up to two dual diskette drives.

The FLOPPY DRIVE is a PERCI 277 Dual Diskette Drive.



Figure 47. Block diagram of the interface of the peripherals to the micro-computer's bus.



The Diskette Controller and the Dual Diskette Drive provide a low cost random access data storage system with an on-line capacity of more than one million bytes.

The VRAM-GRAPHICS peripheral consists of a MATROX MTX-1632SL Video RAM and a MATROX MTX-256**2 Graphic System. The VRAM is used to display alphanumeric data and its output can drive a CRT monitor to provide a 16 x 32 field of 512 ASCII characters. The Graphic System generates a matrix of 256 lines with 256 dots in each line, and allows a microcomputer controlled plot of different graphic figures formed by a 256 x 256 dot raster on the screen.

The CRT is a Ball TV-9" Data Display Monitor.

The microcomputer controls the data display on the monitor, and the operation of the Diskette Drive through the CONTROL LOGIC which consists of a six bit CONTROL REGISTER and Drivers. The bit assignment and the function of each bit in the CONTROL REGISTER are as follows:

BIT D0 : Spindle motor enable. A zero on this bit turns off the spindle motor of the diskette drive.

Bit D1 : Write protect ϕ . A zero on this bit write protects the diskette ϕ and the write circuitry of the diskette drive is prevented from writing on this diskette.

Bit D2 : Write protect 1. A zero on this bit write

protects the diskette 1.

Bit D3 : VRAM. The TTL Video output of the VRAM is gated with this bit so the microcomputer can turn on or off the alphanumeric output of the VRAM. A zero on this bit disables the alphanumeric output to the monitor.

Bit D4 : GRAPHICS. The TTL Video output of the Graphic System is gated with this bit. A zero on this bit disables the graphic output to the monitor.

Bit D5 : REVERSE GRAPHICS. The inverted TTL Video output signal of the graphic system is gated with this bit. A one on this bit enables the reverse graphics.

The KB is an ELECTRONICS WAREHOUSE EW-100 63 Key ASCII Encoded keyboard with parallel data output. INPUT REGISTER latches the data from the KB and sets a flag to inform the microcomputer that data are available on this register.

The communication between the microcomputer system and the minicomputer is obtained through the Communicator and the block diagram in Figure 6 shows the logic of the link. Usually $\overline{\text{PDP11REG}}$ is high and the STATUS BUFFER on the Micro I/O Port is enabled. In order to read the STATUS REGISTER the microcomputer sends the address of the INPUT BUFFER1 and $\overline{\text{MEMR}}$. The output pulse of OR gate 2 enables the OUTPUT BUFFER on the Micro I/O Port and triggers

Monostable2. The output pulse of the monostable pulls the Ready line low for 1.5 μ sec causing the CPU to enter the WAIT state for 1.5 μ sec. To read a data word from the minicomputer, the microcomputer changes the level on the $\overline{\text{PDPI1REQ}}$ line to zero to disable the STATUS BUFFER and repeats the read operation. $\overline{\text{FLG2}}$ is used as a flag to inform the microcomputer that data are available on the Micro I/O Port.

During a transfer of data from the microcomputer to the minicomputer, the following steps are involved: The microcomputer changes the level on the $\overline{\text{PDPI1REQ}}$ line to zero to disable the STATUS BUFFER and sends the address of the DRIVERS, $\overline{\text{MEMW}}$, and the data word. The output pulse of OR gate 1 enables the DRIVERS and loads the INPUT REGISTER on the Micro I/O Port. During the write operation, the ready line goes low for 1.5 μ sec causing the CPU to enter in the WAIT state for 1.5 μ sec. $\overline{\text{FLG1}}$ is used as a flag by the microcomputer for coordinating the transfer of information to the minicomputer.

In order to use the teletype, the microcomputer changes the level on the $\overline{\text{PDPI1REQ}}$ line to one to disable the link to the minicomputer and to enable the teletype logic on the Micro I/O Port, and asks for teletype service by changing the level on the $\overline{\text{TTYREQ}}$ line to zero. When the link to the teletype has been established, the microcomputer sends the data as a series of pulses using the $\overline{\text{TTYOUT}}$

line. The serial output to the teletype is created by a program which transforms the parallel data word to a serial data word with a rate of 110 bits/sec.

F. Operation

In the present mode of operation, the system can support four different types of communications:

1. Mini to microcomputer ASCII (UA)
2. Mini to microcomputer NORMAL (UN)
3. Micro to minicomputer ASCII (MA)
4. Micro to minicomputer NORMAL (MN)

The ASCII mode of communication is actually a transfer of Formatted ASCII files from one floppy disk to the other. Source programs can be created in the minicomputer using its powerful software operating system and transferred to the minicomputer using the ASCII mode of communication.

The NORMAL mode of communication is actually a transfer of unformatted ASCII files from one floppy disk to the other. Data files can be transferred, using the NORMAL mode of communication, as images from the microcomputer to the minicomputer for extensive data analysis.

The interrupt capability of the system is not used in the present mode of operation and the flags $\overline{\text{FLG1}}$ and $\overline{\text{FLG2}}$ are used to coordinate the communication between the minicomputer and the microcomputer systems. The procedure



and the protocol of the communication between the minicomputer and the microcomputer is the following:

The operator loads the communication programs of both ends of the link and by typing a two-letter command on the local keyboard he instructs the microcomputer to ask for service.

The microcomputer sends an ACK to the minicomputer.

The minicomputer reads and checks the character to see if it is an ACK. If the character is not an ACK the minicomputer ignores the request and returns to the wait loop. If the character is an ACK the minicomputer reads the FLAG REGISTER to see which microsystem asked for service, it sends the address of this micro system to the Micro I/O Port to enable the link to this micro system and sends an ACK-EOT.

The microcomputer sends the two letter command and an EOT.

The minicomputer replies with a BEL-EOT if the command is valid or with a NAK-ERROR MESSAGE-EOT if the command is not valid.

The microcomputer sends the file specification (up to 24 characters)-EOT.

The minicomputer replies with

- (a) ENQ-EOT if the transfer is from the microsystem to the minicomputer;

1000
1000
1000
1000

- (b) SOH if the transfer is from the minicomputer to the microsystem; or
- (c) NAK-ERROR MESSAGE-EOT if there is a file error.

The actual data transfer is as follows:

Sender : Sends a 8-bit byte count (N). Zero byte count indicates the end of the transfer.
Sends N bytes of data
Sends Checksum

Receiver : Reads checksum and sends ACK-EOT if checksum is the same or NACK-EOT if checksum is different.

The procedure is repeated until the sender sends a zero byte count to terminate the transfer.

After the communication with the microsystem is terminated the minicomputer clears the Micro I/O Port and returns to the wait loop ready to accept any other service request.



APPENDICES

APPENDIX A

CONVERSE LIBRARY FOR THE MICROCOMPUTER SYSTEM

The name and the function of the programs used to operate the electrochemical system are included here. The listings of the basic subroutines are also included here. These subroutines constitute the programs SCANV and POLAR1 which are discussed in the text.

Table 7. Converse Library for Operation of the Electro-Chemical System.

<u>Coordinator Library</u>	
Name	Function
DIV	16-bit binary by 8-bit binary unsigned division
BINDEC	16-bit binary to 5-digit BCD
DECOUT	Outputs a decimal number to the CRT
ADCN	Reads the A/D Converter. Registers H and L contains the 12-bit data word
CNTR0	Sets Clock0
CNTR2	Sets Clock2. Clock2 is used as a 1 KHz signal generator
TEXP	Sets Clock11
WRITE1	Outputs the drop time and the number of points per drop to the CRT
SAVE1	Saves on floppy the data obtained with program CELLT5
CHECK1	Checks VCELL to see if negative or positive pulse is needed or if it is the end of the drop. CHECK1 is used with CELLT5

Table 7. Continued.

Name	Function
DFD	Detects the end of the drop. DFD is used with CELLT5
DAT1	Gets one VCELL value, stores it in memory, plots it on screen
VCELL5	Keeps the electrode potential constant at a controlled value
CELLT5	Program described in Chapter 2, Section B
CHECK2	The same function as CHECK1. It is used with programs SCANV and POLAR1
DTIM	Sets Clock1
DFDF	The same function as DFD. It is used with programs SCANV and POLAR1
SAVE2	The same function as SAVE1. It is used with programs SCANV and POLAR1
DROP1	Keeps the potential of one drop constant at a controlled value. Stores data in memory
SCANV	Program described in Chapter 2, Section C.
CURRT	Keeps the potential of one drop constant at a controlled value. Measures number of pulses and drop time. Stores data in memory.
POLAR1	Program described in Chapter 3
<u>Slavel Library</u>	
SWFILE	Opens a file in the floppy disc
SCFILE	Closes an opened file in the floppy disc
STRSF	Writes data to a floppy disc file
DECBIN	5-digit BCD to 16-bit binary
AXISX	Draws axes and tickmarks on the CRT
POINT1	Plots one point on the CRT
PARAM2	Initial dialog for CELLT5 program
PAR3	Initial dialog for SCANV and POLAR1

Table 7. Continued.

<u>Slave2 Library</u>	
Name	Function
SW2	Gives a positive pulse. Controls SW1 and SW3
SW1	Gives a negative pulse. Controls SW1 and SW2
VPD	Loads DAC
SETPG1	Sets the run parameters for CELLT5 program
SETPG2	Sets the run parameters for SCANV and POLAR1 programs
VNEXT	Calculates the value of the electrode potential of each drop.


```

<< DIV                                ; 16-BIT BY 8-BIT UNSIGNED DIVISION
PUSH PSW                                ; SAVE STATUS AND REGISTERS
PUSH H
PUSH D
PUSH B
OFF                                     ; GET DIVISOR
MOV B, A
POP2                                     ; GET DIVIDEND
MVI C, 21                               ; BIT COUNTER
: 10 MOV D, A
MOV A, L
RAL                                     ; ROTATE LOW BYTE
MOV L, A
MOV A, H
RAL                                     ; ROTATE HIGH BYTE
MOV H, A
DCR C                                   ; DECREMENT COUNTER
JZ .30
MOV A, D
RAL
JNC .20
SUB B
STC
CMC
JMP .10
: 20 SUB B
JNC .10
ADD B
JMP .10
: 30 MOV A, H                                ; COMPLEMENT HIGH BYTE OF QUOTIENT
CMA
MOV H, A
MOV A, L
CMA                                     ; COMPLEMENT LOW BYTE
MOV L, A
PUSH2                                   ; QUOTIENT ON STACK
MOV A, D
ON                                     ; REMAINDER ON STACK
POP B
POP D
POP H
POP PSW
>>
<< ADCN
PUSH B
PUSH D
: 20 LDA 17600                                ; HOLD, STRT
: 10 LDA 17400                                ; BSEN
ANI 1
JZ .10                                     ; READY?
LDA 17200                                ; GET H BYTE
ORI 360
ANI 17                                     ; MASK
MOV H, A                                ; SAVE H BYTE
LDA 17000                                ; GET L BYTE
MOV L, A                                ; SAVE L BYTE
POP D
POP B
>>
; MEASURE THE TIME
; BETWEEN DROPS
<< CNTR0
MVI A, 60                                ; CONTROL WORD FOR
STA 16403                                ; COUNTER 0
XRA A
STA 16400                                ; SEND L BYTE
STA 16400                                ; SEND H BYTE
>>
; OUTPUT FREQ. = 1KHZ
<< CNTR2
MVI A, 264                                ; CONTROL WORD FOR
STA 16403                                ; COUNTER 2
MVI A, 377                                ; SEND L BYTE
STA 16402
MVI A, 10                                ; SEND H BYTE
STA 16402
>>
<< CHECK2
PUSH D
PUSH H
LDA 40046                                ; GET V H BYTE
CMA

```

```

MOV H, A
LDA 40045      ; L BYTE
CMA
MOV L, A
LXI D, 1
DAD D
XCHG          ; REG. D, E=-V
LHLD 40043    ; GET VEXTREM
DAD D         ; (H, L)=VEXTREM-V
JNC .1        ; ERROR VEXTREM< V
LHLD 40041    ; GET VMAX
DAD D         ; (H, L)=VMAX-V
JNC .6        ; OK VMAX>=V
LHLD 40033    ; (H, L)=VEXTREM2-V
DAD D
JC .5         ; DROP !
LHLD 40035    ; GET VMIN
DAD D         ; (H, L)=VMIN-V
JC .3         ; VMIN>=V      MORE PULSES
:2 MVI A, 0    ; OK
JMP .4
:3 MVI A, 1    ; MORE PULSES
JMP .4
:5 MVI A, 3
JMP .4
:6 MVI A, 4
JMP .4
:1 MVI A, 2
:4 POP H
POP D
>>
<< DTIM
MVI A, 160
STA 16403
LDA 40030      ; LOW BYTE
STA 16401
LDA 40031      ; HIGH BYTE
STA 16401
>>
<< DFDF
SETUP 2 VPG
CALL .10
:3 SETUP 2 SW1
ADCN
SHLD 40045
CHECK2
CPI 0          ; OK
JZ .1
CPI 2          ; POSITIVE PULSE
JZ .2
CPI 4          ; POSITIVE PULSE
JZ .2
CALL .10      ; NEGATIVE PULSE
JMP .3
:1 ADCN
SHLD 40045
CHECK2
CPI 0
JZ .1
CPI 2
JZ .5
CPI 3          ; EXIT
JZ .5
CPI 4          ; EXIT
JZ .4
CALL .10
JMP .1
:5 RET
:2 SETUP 2 SW2
CALL .10
SETUP 2 SW1
JMP .3
:4 SETUP 2 SW2
CALL .10
SETUP 2 SW1
JMP .1
:10 RUN 2
:11 FLAG 2
JZ .11
MVI A, 0
STA 46
>>
<< SAVE2

```



```

PUSH B
PUSH D
PUSH H
SETUP 1 SWFILE ; SEND TEXT TO FLOPPY
CALL .10
CALL .20 ; GET COMM. STACK
LDAX D ; GET STATUS
ANA A ; OK TO WRITE ?
JZ .1
CALL .21 ; RESET COMM. STACK
STC ; FLAG
POP H
POP D
POP B
RET
: 1 CALL .21
CALL .20
LDA 40061 ; GET # OF POINTS L BYTE
MOV L, A ; STORE IT
DCX D ; SEND IT TO COMM.
STAX D
LDA 40062 ; H BYTE
MOV H, A
DCX D
STAX D
CALL .30 ; SEND # OF POINTS TO FLOPPY
CALL .40 ; GET PG STACK
: 2 PUSH2
: 3 LXI H, 6
DCX B
LDAX B ; L BYTE
DCX D ; SEND IT TO COMM.
STAX D
DCX B ; H BYTE
LDAX B
DCX D
STAX D
CALL .30 ; SEND IT TO FLOPPY
DCR L
JNZ .3
POP2
DCX H ; LAST POINT ?
MOV A, H
ORA L
JNZ .2
SETUP 1 SCFILE ; CLOSE THE FILE
CALL .10
POP H
POP D
POP B
RET
: 10 RUN 1
: 11 FLAG 1
JZ .11
RET
: 20 PUSH H
LHLD 20014
MOV A, H
ORI 40
MOV H, A
XCHG
POP H
RET
: 21 INX D
: 22 PUSH H
MOV L, E
MOV A, D
ANI 37
MOV H, A
SHLD 20014
POP H
RET
: 30 CALL .22
SETUP 1 STRSF
CALL .10
CALL .20
RET
: 40 PUSH H
LHLD 40014
MOV A, H
ORI 100
MOV B, A
MOV C, L

```



```

                POP H
>>
<< DROP1
                PUSH B
                LXI H,1          ; M=1
                SHLD 40055
: 1             ADCN            ; GET VCELL
                SHLD 40045
                SHLD 40051
                SHLD 40057
                CHECK2
                CPI 0
                JZ .2            ; OK
                CPI .2
                JZ .50
                CPI 4
                JZ .50
                CALL .20         ; PULSE
                JMP .1
: 2             CALL .30         ; SAVE FIRST GOOD VALUE
: 3             ADCN            ; GET VCELL
                SHLD 40045
                CHECK2
                CPI 1            ; PULSE
                JZ .4
                CPI 4
                JZ .51
                CPI 2            ; EXIT
                JZ .5
                CPI 3            ; EXIT
                JZ .5
                SHLD 40057
                CALL .40         ; ADD
                JMP .3
: 4             CALL .20         ; GIVE PULSE
                SHLD 40057
                CALL .40         ; ADD
                JMP .3
: 50            SETUP 2 SW2
                CALL .20
                SETUP 2 SW1
                JMP .1
: 51            SETUP 2 SW2
                CALL .20
                SETUP 2 SW1
                SHLD 40057
                CALL .40
                JMP .3
: 5             MVI A,0          ; STOP COUNTERS
                STA 16200
                DTIM             ; RESET COUNTER 1
                MVI A,7          ; START COUNTERS
                STA 16200
                CALL .30         ; SAVE LAST GOOD VALUE
                LHL 40051
                SHLD 40057
                CALL .30
                LHL 40053        ; SAVE M
                SHLD 40057
                CALL .30
                LHL 40055        ; SAVE M
                SHLD 40057
                CALL .30
                LHL 40037        ; SAVE VCAL.
                SHLD 40057
                CALL .30
                POP B
                RET
: 30            LHL 40014
                MOV A,H
                ORI 100
                MOV H,A
                XCHG
                LHL 40057
                MOV A,L
                DCX D
                STAX D
                MOV A,H
                DCX D
                STAX D
                MOV L,E
                MOV A,D
                ANI 37

```



```

MOV H, A
SHLD 40014
RET
: 40 LXI B, 4
LXI D, 40051
LXI H, 40045
XRA A
: 41 LDAX D
ADC M
STAX D
DCR C
JZ .42
INX D
INX H
JMP .41
: 42 LHLD 40055 ; M=M+1
INX H
SHLD 40055
RET
: 20 RUN 2
: 21 FLAG 2
JZ .21
MVI A, 0
STA 46
>>
<< SCANV
PUSH D
PUSH B
PUSH H
SETUP 1 PAR3
CALL .10
CALL .20 ; GET COMM. STACK
MVI L, 17
LXI B, 40020 ; STORE PARAM. AT PG
: 30 LDAX D
STAX B
INX D
INX B
DCR L
JNZ .30
CALL .21 ; CLR COMM. STACK
SETUP 2 SETPG2
CALL .40
MVI A, 0 ; STOP COUNTERS
STA 16200 ; SET COUNTERS
CNTR0
CNTR2
DTIM
MVI A, 1 ; OPEN SW C
STA 56000
DFDF ; DROP!!!!!!!!!!!!
MVI A, 7 ; STERT COUNTERS
STA 16200
LXI B, 1 ; N=1
: 1 LDA 16200 ; TIME ?
ANI 2
JZ .1
DROP1
WHAT
SETUP 2 VNEXT
CALL .40
LDA 40032 ; END ?
CPI 0
JZ .2
INX B ; N=N+1
SETUP 2 SW1
JMP .1
: 2 MVI A, 0
STA 16200
MOV A, C ; SAVE # OF POINTS
STA 40061 ; L BYTE
MOV A, B
STA 40062 ; H BYTE
LXI H, 13500 ; RESET PG STACK
SHLD 40014
POP H
POP B
POP D
RET
: 10 RUN 1
: 11 FLAG 1
JZ .11
RET

```



```
:20      LHLD 20014
          MOV  A,H
          ORI  40
          MOV  H,A
          XCHG
          RET
:21      MOV  L,E
          MOV  A,D
          ANI  37
          MOV  H,A
          SHLD 20014
          RET
:40      RUN  2
:41      FLAG 2
          JZ   41
          MVI  A,0
          STA  46
>>
```



```

<< CURRT
      PUSH B
      LXI H,0
      SHLD 100
      LXI H,1      ; M=1
      SHLD 102
: 1   ADCN          ; GET VCELL
      SHLD 40045
      SHLD 40051
      CHECK2
      CPI 2
      JZ 1          ; AGAIN
      CPI 0
      JZ 3          ; OK
      CALL 20       ; PULSE
      JMP 1
: 3   MVI A,7        ; START COUNTER 0
      STA 16200
      ADCN          ; GET VCELL
      SHLD 40045
      CHECK2
      CPI 1          ; PULSE
      JZ 4
      CPI 2          ; EXIT
      JZ 5
      CPI 3          ; EXIT
      JZ 5
      CALL 40        ; ADD
      JMP 3
: 4   CALL 20        ; GIVE PULSE
      LHL 100
      INX H
      SHLD 100
      CALL 40        ; ADD
      JMP 3
: 5   MVI A,0        ; STOP COUNTERS
      STA 16200
      LDA 16400      ; GET DROP TIME
      CMA
      MOV L,A
      LDA 16400
      CMA
      MOV H,A
      SHLD 101      ; STORE IT
      CNTR0
      DTIM          ; RESET COUNTER 1
      MVI A,6        ; START COUNTERS
      STA 16200
      LHL 100        ; SAVE # OF PULSES
      PUSH2
      CALL 30
      LHL 101        ; SAVE DROP TIME
      PUSH2
      CALL 30
      LHL 40051
      PUSH2
      CALL 30        ; SAVE L TOTAL
      LHL 40053
      PUSH2
      CALL 30        ; SAVE H TOTAL
      LHL 102        ; SAVE H
      PUSH2
      CALL 30
      LHL 40037      ; SAVE VC
      PUSH2
      CALL 30
      POP B
: 30  RET
      LHL 40014
      MOV A,H
      ORI 100
      MOV H,A
      XCHG
      POP2
      MOV A,L
      DCX D
      STAX D
      MOV A,H
      DCX D
      STAX D
      MOV L,E
      MOV A,D
      ANI 37

```



```

MOV H, A
SHLD 40014
RET
: 40 LXI B, 4
LXI D, 40051
LXI H, 40045
: 41 XRA A
LDAX D
ADC M
STAX D
DCR C
JZ . 42
INX D
INX H
JMP . 41
: 42 LHLD . 102 ; M=M+1
INX H
SHLD . 102
RET
: 20 RUN 2
: 21 FLAG 2
JZ . 21
MVI A, 0
STA 46
RET
: 100 0, 0
: 101 0, 0
: 102 0, 0
>>

```



```

<< POLAR1
    PUSH D
    PUSH B
    PUSH H
    SETUP 1 PAR3
    CALL .10
    CALL .20      ; GET COMM. STACK
    MVI L, 17
    LXI B, 40020  ; STORE PARAM. AT PG
: 30    LDAX D
        STAX B
        INX D
        INX B
        DCR L
        JNZ .30
        CALL .21      ; CLR COMM. STACK
        SETUP 2 SETPG2
        CALL .40
        MVI A, C      ; STOP COUNTERS
        STA 16200
        CNTR0         ; SET COUNTERS
        CNTR2
        DTIM
        MVI A, 1      ; OPEN SW C
        STA 56000
        DFDF          ; DROP!!!!!!!!!!!!
        MVI A, 6      ; STERT COUNTERS
        STA 16200
        LXI B, 1      ; N=1
: 1     LDA 16200      ; TIME ?
        ANI 2
        JZ .1
        CURRT
        WHAT
        MVI A, 0
        STA 56000
        SETUP 2 VNEXT
        CALL .40
        LDA 40032      ; END ?
        CPI 0
        JZ .2
        INX B          ; N=N+1
        SETUP 2 SW1
        MVI A, 1
        STA 56000
        JMP .1
: 2     MVI A, 0
        STA 16200
        MOV A, C        ; SAVE # OF POINTS
        STA 40061      ; L BYTE
        MOV A, B
        STA 40062      ; H BYTE
        LXI H, 13500
        SHLD 40014      ; RESET PG STACK
        POP H
        POP B
        POP D
        RET
: 10    RUN 1
: 11    FLAG 1
        JZ .11
        RET
: 20    LHLD 20014
        MOV A, H
        ORI 40
        MOV H, A
        XCHG
        RET
: 21    MOV L, E
        MOV A, D
        ANI 37
        MOV H, A
        SHLD 20014
        RET
: 40'   RUN 2
: 41    FLAG 2
        JZ .41
        MVI A, 0
        STA 46
>>

```



```

<< SWFILE
    PUSH PSW
    PUSH B
    PUSH D
: 5    MVI A, 52
    CRT
    LINE
    JC .25
    FCMD
    CPI 3
    JNZ .5
    LXI B, .50
    MVI D, 34
: 10   LDAX B
    INX B
    CRT
    DCR D
    JNZ .10
: 15   LINE
    JC .30
    OFF
    MOV B, A
: 20   OFF
    CPI 15
    JNZ .22
    CALL 1123
    MVI A, 12
: 22   CALL 1123
    DCR B
    JNZ .20
    MVI A, 15
    CALL 1123
    MVI A, 12
    CALL 1123
    JMP .15
: 25   MVI A, 1
    JMP .35
: 30   MVI A, 3
    CALL 1123
    LXI B, .55
    MVI D, 7
: 40   LDAX B
    INX B
    CRT
    DCR D
    JNZ .40
    XRA A
: 35   ON
    POP D
    POP B
    POP PSW
    RET
: 50   43, 111, 116, 120, 125, 124, 40, 124, 105, 130, 124, 40, 55, 40,
    34, 103, 40, 124, 105, 122, 115, 111, 116, 101, 124, 105, 123, 15
: 55   120, 117, 111, 116, 124, 123, 72
>>
<< SCFILE
    CALL 1171
    CALL 1106
    CPI 6
    JNZ .10
    CALL 1106
    RET
: 10   CALL 1106
    CPI 4
    JNZ .20
    RET
: 20   CRT
    JMP .10
>>
<< STRSF
    OFF
    CALL 1123
    OFF
    CALL 1123
>>
<< DECBIN
    PUSH H
    PUSH B
    PUSH D
    PUSH PSW
    OFF
    ; *****SLAVE 1*****
    ; OUTPUT "*"
    ; GET COMMAND
    ; IF IT IS A CRL/C EXIT
    ; CALL FLOPPY
    ; IS IT OK TO WRITE?
    ; GET ADDR. OF MESSAGE1
    ; GET CHARACTER
    ; POINT TO NEXT CHAR.
    ; DECREMENT BYTE COUNT
    ; GET MESSAGE
    ; GET #OF CHARACTERS
    ; GET CHAR.
    ; CR?
    ; SEND IT TO FLOPPY
    ; LF
    ; NEXT CHAR.
    ; END?
    ; SEND CR
    ; SEND LF
    ; GET ANOTHER COMMAND STRING
    ; SEND AN ETX
    ; DECIMAL TO BINARY CONVERSION
    ; # CHARACTERS

```



```

MOV      B,A
LXI      H,0
MVI      D,0
: 10     OFF
MOV      E,A
CPI      12
JNC      .30
DAD      D
JC       .30
DCR      B
JZ       .20
MVI      C,11
MOV      E,L
MOV      D,H
: 15     DAD      D
JC       .40
DCR      C
JNZ      .15
JMP      .10
: 20     PUSH2
POP      PSW
POP      D
POP      B
POP      H
STC
CMC
RET
: 30     DCR      B
: 40     MOV      A,B
ON
POP      PSW
POP      D
POP      B
POP      H
STC
>>

```

; INITIALIZE THE BUFFER
 ; GET A DIGIT
 ; IS IT BCD?
 ; JUMP IF ERROR
 ; ADD THE DIGIT TO THE BUFFER
 ; TOO LARGE IF CARRY
 ; LAST DIGIT?
 ; JUMP IF DONE
 ; IF NOT THEN BUFFER X 10
 ; ADD 10 TIMES FOR MULTIPLY
 ; TOO LARGE IF CARRY
 ; ADDED 10 TIMES?
 ; BACK TO GET A DIGIT!!
 ; PUT THE RESULT ON THE STACK
 ; CLEAR THE CARRY (NO ERROR)
 ; # CHARACTERS LEFT
 ; SET THE CARRY (ERROR FLAG)

<< AXISX

```

PUSH B
PUSH D
PUSH H
XRA A
STA 16203
MVI A,37
STA 16500
MVI D,377
MVI E,377
MVI H,121
MVI B,377
MVI C,40
MVI L,241
MOV A,D
STA 16201
MOV A,E
STA 16202
: 10     MOV A,H
STA 16200
DCR D
DCR C
CZ .11
DCR B
JNZ .10
MVI D,0
MVI E,377
MVI H,241
MVI L,21
MVI B,377
MVI C,40
MOV A,D
STA 16201
MOV A,E
STA 16202
: 12     MOV A,H
STA 16200
DCR E
DCR C
CZ .11
DCR B
JNZ .12
POP H
POP D
POP B
RET

```

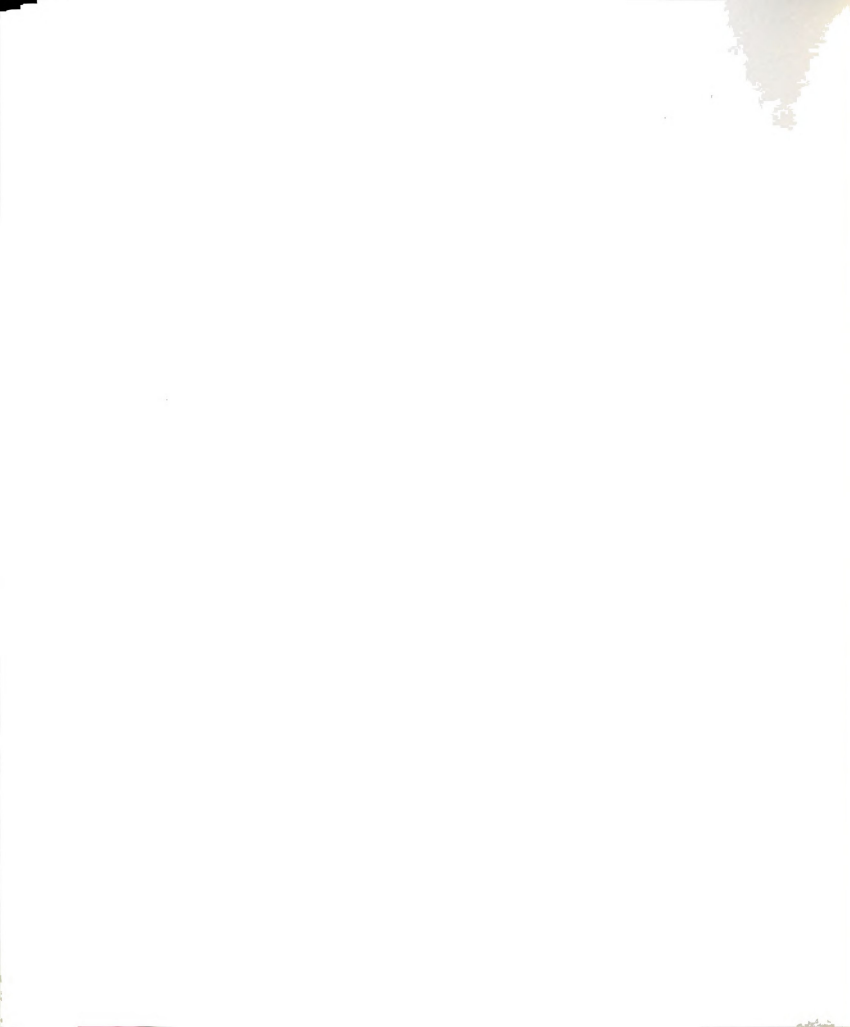
; CLR GRAPHICS


```

:11      MOV A,L
          STA 16200
          STA 16200
          MOV A,D
          STA 16201
          MOV A,E
          STA 16202
          MVI C,40
          >>
<< POINT1
          PUSH B
          PUSH D
          PUSH H
          OFF
          STA 16201
          POP2
          MVI B,17
          MOV E,L
          MOV D,H
:12      DAD D
          DCR B
          JNZ .12
          MOV A,H
          STA 16202
          MVI A,1
          STA 16200
          POP H
          POP D
          POP B
          RET
          >>
<< PAR3
          PUSH B
          PUSH D
          PUSH H
:13      CALL 334
          LXI B,.100
          MVI D,13
          CALL .10
          LXI B,.101
          LDAX B
          MOV D,A
          INX B
          CALL .10
          MVI A,15
          CRT
          LXI B,.110
          MVI D,15
          CALL .10
          LXI B,.111
          LDAX B
          MOV D,A
          INX B
          CALL .10
          MVI A,15
          CRT
          LXI B,.120
          MVI D,13
          CALL .10
          LXI B,.121
          LDAX B
          MOV D,A
          INX B
          CALL .10
          MVI A,15
          CRT
          LXI B,.130
          MVI D,12
          CALL .10
          LXI B,.131
          LDAX B
          MOV D,A
          INX B
          CALL .10
          MVI A,15
          CRT
          LXI B,.140
          MVI D,12
          CALL .10
          LXI B,.141
          LDAX B
          MOV D,A
          INX B

```

; GET X
; CLR SCREEN
; WRITE FIRST VAR.
; WRITE VALUE OF
; FIRST VAR.
; WRITE SECOND VAR.
; WRITE VALUE OF
; SECOND VAR.
; WRITE THIRD VAR.
; WRITE VALUE OF
; THIRD VAR.
; WRITE FOURTH VAR.
; AND ITS VALUE
; WRITE FIFTH VAR.
; AND ITS VALUE



```

:12 CALL .10
LINE
JC .30 ; GET VAR. AND NEW VAL.
OFF ; IF C/C CONTINUE
MOV B, A ; GET # OF CHAR.
LXI D, .177; SAVE # OF CHAR. ; SET COUNTER
STAX D
:11 OFF ; READ MESSAGE AND
INX D ; STORE IT
STAX D
DCR B
JNZ .11
LXI H, .100 ; POINT TO FIRST VAR.
LXI D, .101 ; AND ITS VALUE
CALL .20
JZ .13
LXI H, .110 ; POINT TO SECOND VAR.
LXI D, .111 ; AND ITS VALUE
CALL .20
JZ .13
LXI H, .120 ; POINT TO THIRD VAR.
LXI D, .121 ; AND ITS VALUE
CALL .20
JZ .13
LXI H, .130 ; POINT TO FOURTH VAR.
LXI D, .131 ; AND ITS VALUE
CALL .20
JZ .13
LXI H, .140 ; POINT TO FIFTH VAR.
LXI D, .141 ; AND ITS VALUE
CALL .20
JZ .13
MVI A, 15 ; SEND CR
CRT
MVI A, 77 ; SEND "?"
CRT
:30 JMP .12
LXI H, .141 ; DTIM
CALL .40
LXI H, .131 ; DV
CALL .40
LXI H, .121 ; VFIN
CALL .40 ; DECBIN
LXI H, .111 ; VINIT
CALL .40 ; DECBIN
LXI H, .101 ; VPULSE
CALL .40 ; DECBIN
POP H
POP D
POP B
RET
:10 LDAX B
INX B
CRT
DCR D
JNZ .10
RET
:20 PUSH D ; SAVE POINTER
LXI B, .177 ; POINT TO NEW VAR.
LDAX B ; GET # OF CHAR.
MOV E, A ; SAVE IT
MVI D, 3 ; CHECK FOR 3 LETTERS
INX B ; POINT TO NEXT CHAR.
:21 LDAX B ; GET CHAR.
CMP M
JNZ .25
INX B ; NEXT CHAR.
INX H
DCR E
DCR D
JNZ .21
:22 LDAX B ; IF OK CHECK FOR =
DCR E
CPI 75
JZ .23
INX B
JMP .22
:23 XCHG ; SAVE # OF CHAR. TO L
POP D ; GET POINTER
MOV A, L ; GET # OF DIGITS
STAX D
:24 INX B
INX D ; GET NEXT DIGIT

```




```

<< DIV                                ; 16-BIT BY 8-BIT UNSIGNED DIVISION
PUSH PSW                                ; SAVE STATUS AND REGISTERS
PUSH H
PUSH D
PUSH B
OFF                                     ; GET DIVISOR
MOV B, A
POP2                                    ; GET DIVIDEND
MVI C, 21                               ; BIT COUNTER
: 10 XRA A
MOV D, A
MOV A, L
RAL                                     ; ROTATE LOW BYTE
MOV L, A
MOV A, H
RAL                                     ; ROTATE HIGH BYTE
MOV H, A
DCR C                                   ; DECREMENT COUNTER
JZ .30
MOV A, D
RAL
JNC .20
SUB B
STC
CMC
JMP .10
: 20 SUB B
JNC .10
ADD B
JMP .10
: 30 MOV A, H                                ; COMPLEMENT HIGH BYTE OF QUOTIENT
CMA
MOV H, A
MOV A, L
CMA                                     ; COMPLEMENT LOW BYTE
MOV L, A
PUSH2                                  ; QUOTIENT ON STACK
MOV A, D
ON                                     ; REMAINDER ON STACK
POP B
POP D
POP H
POP PSW
>>
<< SW2
MVI A, 7
STA 16000
MVI A, 3
STA 16000
NOP
NOP
NOP
NOP
NOP
NOP
MVI A, 1
STA 16000
>>
<< SW1
MVI A, 1
STA 16000
MVI A, 7
STA 16000
MVI A, 2
STA 16000
NOP
NOP
NOP
NOP
NOP
MVI A, 1
STA 16000
>>
<< VPG
LDA 20
STA 14000
LDA 21
STA 14001
>>
<< SETPG2
PUSH B
PUSH D
PUSH H

```




```

LXI B,20          ; GET VPULSE
CALL .10          ; CAL. VPULSE=2.5-X/RES. OF PG
OFF
POP2
SHLD 20
LXI B,23          ; CAL VINIT=2.5-VINT/RES OF ADC
CALL .20
OFF
POP2
SHLD 22
SHLD 37
LXI B,26          ; CAL. VFIN
CALL .20
OFF
POP2
SHLD 24
LHLD 32           ; CAL. DV
CALL .24
OFF
POP2
SHLD 26
LHLD 35           ; GET DELAY TIME
SHLD 30           ; SAVE IT
LXI D,4           ; + 4 MV
LHLD 37
DAD D             ; VMAX
SHLD 41           ; - 4 MV
LXI D,177774
LHLD 37
DAD D             ; VMIN
SHLD 35           ; +122 MV
LXI D,310
LHLD 37
DAD D             ; VEXTR1
SHLD 43           ; - 122 MV
LXI D,177470
LHLD 37
DAD D             ; VEXTR2
SHLD 33           ; STATUS 0=END, 1=CONTINUE
MVI A,1
STA 32
LXI H,0
SHLD 45
SHLD 47
SHLD 51
SHLD 53
POP H
POP D
POP B
RET
:10 LDAX B          ; GET SIGN
CPI 0             ; NEGATIVE
JNZ .11
INX B
LDAX B            ; GET L BYTE
CMA
MOV E,A
INX B
LDAX B            ; GET H BYTE
CMA
MOV D,A
LXI H,1
DAD D
XCHG
:12 LXI H,4704
DAD D             ; CAL. 2.5-X
MVI B,7           ; *8
MOV E,L
MOV D,H
:13 DAD D
DCR B
JNZ .13
PUSH2
MVI A,47         ; RES. OF PG
ON
DIV
RET
:11 INX B
LDAX B
MOV E,A
INX B
LDAX B
MOV D,A

```

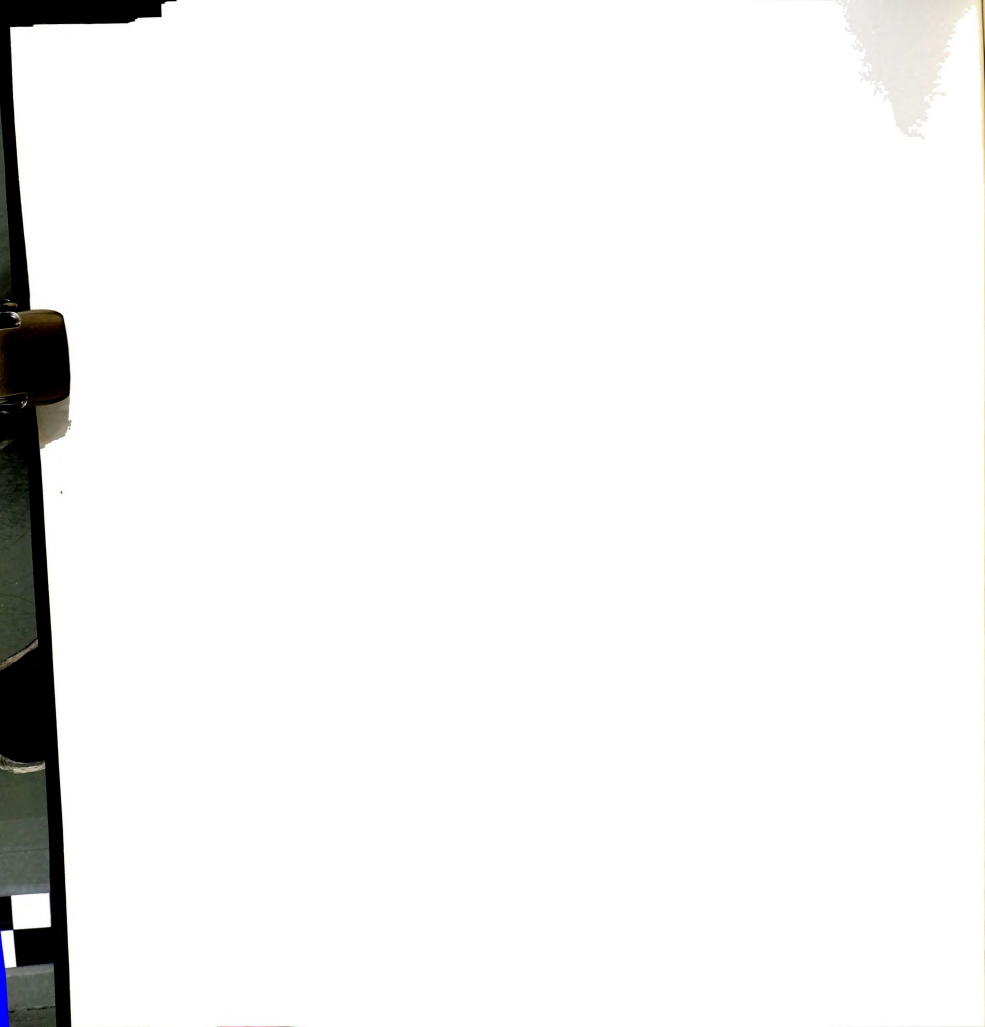


```

:20      JMP .12
        LDAX B
        CPI 0
        JNZ .21          ; NEGATIVE
        INX B
        LDAX B
        CMA
        MOV E, A
        INX B
        LDAX B
        CMA
        MOV D, A
        LXI H, 1
        DAD D
        XCHG
:23      LXI H, 4704
        DAD D
:24      MVI B, 10          ; 2.5-V
        MOV E, L          ; *9
        MOV D, H
:22      DAD D
        DCR B
        JNZ .22
        PUSH2
        MVI A, 13          ; RES. OF ADC*9000
        ON
        DIV
        RET
:21      INX B
        LDAX B
        MOV E, A
        INX B
        LDAX B
        MOV D, A
        JMP .23
<< VNEXT
        PUSH H
        PUSH D
        LHLD 37          ; GET VI
        XCHG
        LHLD 26          ; GET DV
        DAD D            ; VNEXT=VI+DV
        SHLD 37          ; SAVE IT
        LDA 25           ; GET VFIN H BYTE
        CMA
        MOV H, A
        LDA 24           ; GET VFIN L BYTE
        CMA
        MOV L, A
        LXI D, 1
        DAD D
        XCHG
        LHLD 37          ; -VFIN
        DAD D            ; GET VNEXT
        JC .1            ; VNEXT-VFIN VNEXT<VFIN CARRY=0
        LXI D, 4          ; VNEXT>/VFIN CARRY=1
        LHLD 37          ; CAL. NEW LIMITS
        DAD D
        SHLD 41          ; VMAX
        LXI H, 177774
        XCHG
        LHLD 37
        DAD D            ; VMIN
        SHLD 35
        LXI D, 310
        LHLD 37
        DAD D            ; VEXTR1
        SHLD 43
        LXI H, 177470
        XCHG
        LHLD 37
        DAD D            ; VEXTR2
        SHLD 33
        LXI H, 0
        SHLD 47
        SHLD 51
        SHLD 53
        POP D
        POP H
        RET
:1      MVI A, 0
        STA 32          ; STATUS =0

```

>> POP D
POP H



APPENDIX B

DATA ANALYSIS PROGRAMS

The programs used in the PDP-11/40 minicomputer to analyze the acquired data are listed here.




```

C
C      VCELL. FTN
C
C      THIS PROGRAM READS A DATA FILE AND
C      CREATES A STD C. G. ENKE FILE FOR PLOTING
C
      INTEGER COUNT, OBS, VOLT(1024)
      BYTE DATA(3000), IFILE(24), OFILE(24)
      DIMENSION YDATA(1024), VOLT(1024), X(1024)
100    WRITE(6, 900)
      READ(6, 901) IFILE
      IERR=0
      CALL FORPIP(IFILE, IERR)
      IF(IERR.EQ.1) GO TO 110
      WRITE(6, 902) IFILE
      GO TO 100
110    CALL UNFMD(IERR, IFILE, 0, 1)
      COUNT=3000
      CALL UNFMRW(IERR, DATA, COUNT)
      IF(IERR) 200, 210, 220
210    CALL UNFMC(IERR)
      WRITE(6, 904)
      GO TO 100
220    CALL UNFMC(IERR)
      WRITE(6, 903)
      GO TO 100
200    CALL UNFMC(IERR)
      CALL FMESG(NOBS, DATA, COUNT, VOLT )
      DO 10 I=1, NOBS
      YDATA(I)=2.5-VOLT(I)*0.001221
      X(I)=I*1.0
      CONTINUE
10    C
      C
      C      OPTIONS
      C
400    WRITE (6, 911)
      READ(6, 912) IFLG
      IF(IFLG.EQ.1) GO TO 300
      IF(IFLG.EQ.2) GO TO 40
      IF(IFLG.EQ.3) GO TO 100
      WRITE(6, 913)
      GO TO 400
300    DO 20 I=1, NOBS
      WRITE(6, 914) X(I), YDATA(I)
20    CONTINUE
      GO TO 400
40    WRITE (6, 906)
      READ (6, 901) OFILE
      IERR=0
      CALL FORPIP(OFILE, IERR)
      IF (IERR) 50, 70, 60
50    WRITE (6, 903)
      GO TO 40
60    WRITE (6, 907)
      GO TO 40
70    CALL ASSIGN (4, OFILE, 24, IERR)
      IF (IERR.EQ.0) GO TO 80
      WRITE (6, 908)
      GO TO 40
80    DO 30 I=1, NOBS
      WRITE(6, 909) X(I), YDATA(I)
30    CONTINUE
      ENDFILE 4
      WRITE (6, 910)
      GO TO 100
C
C
C      FORMATS
900    FORMAT('$FILE: ')
901    FORMAT(24A1)
902    FORMAT(1X, 24A1/ 'DOES NOT EXIST')
903    FORMAT(1X, 'FILE ERROR')
904    FORMAT(1X, 'TOO MANY POINTS')
905    FORMAT(/, 4X, I5, 4X, I5, 4X, F9. 6, 4X, F9. 6)
906    FORMAT ('$OUTPUT FILE: ')
907    FORMAT ('FILE ALREADY EXISTS')
908    FORMAT ('ASSIGN ERROR')
909    FORMAT ( 'RD', 2G15. 6)
910    FORMAT ( 'CONVERSION COMPLETE')
911    FORMAT(4X, '1 SCREEN ?', /, 4X, '2 SAVE ?', /, 4X,
1'3 GO BACK ?', /)
912    FORMAT(I1)
913    FORMAT(4X, 'INV. CMD. ')

```

```
914      FORMAT(4X, F15. 6, 4X, F15. 6)  
      END
```



```

C
C
C
C
C
C
POLAR. FTN

THIS PROGRAM CALCULATES VA, VC, AND CURRENT
AND SENDS THE RESULTS TO THE SCREEN
OR TO THE FLOPPY

INTEGER COUNT, VOLT(1024)
BYTE DATA(3000), IFILE(24), OFILE(24)
DIMENSION VOLT(1024), V(5, 1024), X(1024), Y(1024)
100 WRITE(6, 900)
READ(6, 901) IFILE
IERR=0
CALL FORPIP(IFILE, IERR)
IF(IERR.EQ.1)GO TO 110
WRITE(6, 902) IFILE
GO TO 100
110 CALL UNFMD(IERR, IFILE, 0, 1)
COUNT=3000
CALL UNFMRW(IERR, DATA, COUNT)
IF(IERR)200, 210, 220
210 CALL UNFMC(IERR)
WRITE(6, 904)
GO TO 100
220 CALL UNFMC(IERR)
WRITE(6, 903)
GO TO 100
200 CALL UNFMC(IERR)
CALL FMESS3(NOBS, DATA, COUNT, VOLT)
WRITE (6, 915)
READ(6, 916) CI
WRITE(6, 917)
READ(6, 916) VP
J=1
DO 10 K=0, NOBS
I=4*K+1
V(4, J)=VOLT(I)*1.0
J=J+1
10 CONTINUE
J=1
DO 20 K=0, NOBS
I=4*K+2
V(5, J)=VOLT(I)*1.0
J=J+1
20 CONTINUE
DO 21 J=1, NOBS
V(1, J)=V(4, J)*VP*CI/V(5, J)
21 CONTINUE
J=1
DO 30 K=0, NOBS
I=4*K+3
V(2, J)=2.5-VOLT(I)*0.001221
J=J+1
30 CONTINUE
J=1
DO 40 K=0, NOBS
I=4*K+4
V(3, J)=2.5-VOLT(I)*0.001221
J=J+1
40 CONTINUE
C
C
C
C
OPTIONS
300 WRITE(6, 908)
READ(6, 906) JFLG
IF(JFLG.EQ.1)GO TO 310
IF(JFLG.EQ.2)GO TO 320
IF(JFLG.EQ.3)GO TO 100
WRITE(6, 907)
GO TO 300
C
C
C
C
310 WRITE(6, 918)
READ(6, 906) IFLG
IF(IFLG.EQ.0)GO TO 311
IF(IFLG.GT.3)GO TO 311
DO 11 J=1, NOBS
WRITE (6, 909) J, V(IFLG, J)
11 CONTINUE
GO TO 300
311 WRITE (6, 907)

```

```

GO TO 310
C
C
C
320  WRITE(6,905)
      READ(6,906) IFLG
      IF(IFLG.EQ.1)GO TO 340
      IF(IFLG.EQ.2)GO TO 350
      IF(IFLG.EQ.3)GO TO 360
      IF(IFLG.EQ.4)GO TO 370
      IF(IFLG.EQ.5)GO TO 380
      IF(IFLG.EQ.6)GO TO 100
      WRITE (6,907)
      GO TO 320
340  DO 341 J=1,NOBS
      X(J)=V(2,J)
      Y(J)=V(1,J)
341  CONTINUE
      GO TO 330
350  DO 351 J=1,NOBS
      X(J)=V(3,J)
      Y(J)=V(1,J)
351  CONTINUE
      GO TO 330
360  DO 361 J=1,NOBS
      X(J)=V(3,J)
      Y(J)=V(2,J)
361  CONTINUE
      GO TO 330
370  DO 371 J=1,NOBS
      X(J)=V(2,J)
      Y(J)=V(5,J)
371  CONTINUE
      GO TO 330
380  WRITE(6,920)
      READ(6,919) VD
      DO 381 J=1,NOBS
      Y(J)=ALOG10((VD-V(1,J))/V(1,J))
      X(J)=V(2,J)
381  CONTINUE
      GO TO 330
330  WRITE(6,910)
      READ(6,901)OFILE
      IERR=0
      CALL FORPIP(OFILE,IERR)
      IF(IERR)50,70,60
50    WRITE(6,903)
      GO TO 330
60    WRITE(6,911)
      GO TO 330
70    CALL ASSIGN(4,OFILE,24,IERR)
      IF(IERR.EQ.0)GO TO 80
      WRITE (6,912)
      GO TO 330
80    DO 12 J=1,NOBS
      WRITE(4,913) X(J),Y(J)
12    CONTINUE
      ENDFILE 4
      WRITE(6,914)
      GO TO 300
C
C
C
      FORMATS
900  FORMAT('$FILE: ')
901  FORMAT(24A1)
902  FORMAT(1X,24A1/'DOES NOT EXIST')
903  FORMAT(1X,'FILE ERROR')
904  FORMAT(1X,'TOO MANY POINTS')
905  FORMAT(4X,'1 CURRENT VS VA ?',/,4X,'2 CURRENT VS
      1 VC ?',/,4X,'3 VA VS VC ?',/,4X,'4 TIME VS VA ?',
      2/,4X,'5 LOGDI/I VS VCELL ?',/,4X,' 6 GO BACK ?',/)
906  FORMAT(I1)
907  FORMAT(4X,'INV. COMD. ')
908  FORMAT(4X,'1 SCREEN ?',/,4X,'2 SAVE ?',/,4X,'3 GO
      1BACK ?',/)
909  FORMAT(4X,I5,4X,F9.6)
910  FORMAT('$OUTPUT FILE: ')
911  FORMAT('FILE ALREADY EXISTS')
912  FORMAT('ASSIGN ERROR')
913  FORMAT('RD',2G15.6)
914  FORMAT('CONVERSION COMPLETE')
915  FORMAT(4X,'CIN(UF)='/,/)
916  FORMAT(F9.2)

```

```

917 FORMAT(4X, 'VPULSE(MV)=',/)
918 FORMAT(4X, '1 CURRENT ?',/,4X, '2 VA ?',/,4X, '3 VC ?',/)
919 FORMAT(F7.5)
920 FORMAT(4X, 'LIMITED CURRENT (UA) =',/)
END

```

```

. TITLE FILTER
. GLOBL FMESG
TPS=177564
TPB=177566
. MCALL .F4DEF
. F4DEF 0
;
;
CALL FMESG(NOBS, DATA, COUNT, IVOLT)
;
; R1=NOBS
; R2=COUNT
; R3=DATA
; R4=IVOLT
;
FMESG: MOV R0, -(SP)
MOV R1, -(SP)
MOV R2, -(SP)
MOV R3, -(SP)
MOV R4, -(SP)
CLR R1
CLR @2(R5)
MOV @6(R5), R2
MOV 4(R5), R3
MOV 10(R5), R4
CLR R2
A: MOV B (R3)+, R0 ; SEND TEXT TO THE TTY
CMPB #3, R0
BEQ B
JSR R5, WRITE
JMP A
B: BISB (R3)+, R1 ; GET # OF POINTS
SWAB R1
BISB (R3)+, R1
MOV R1, @2(R5)
C: BISB (R3)+, R2 ; GET POINTS
SWAB R2
BISB (R3)+, R2
MOV R2, (R4)+
CLR R2
SOB R1, C
MOV (SP)+, R4
MOV (SP)+, R3
MOV (SP)+, R2
MOV (SP)+, R1
MOV (SP)+, R0
RTS R5
;
;
WRITE: TSTB TPS
BPL WRITE
MOV B R0, TPB
RTS R5
. END

```



```

        .TITLE FILT3
        .GLOBL FMESS3
        TPS=177564
        TPB=177566
        .MCALL F4DEF
        .F4DEF 0
;
;
;       CALL FMESSG(NOBS, DATA, COUNT, IVOLT)
;               R1=NOBS
;               R2=COUNT
;               R3=DATA
;               R4=IVOLT
;
FMESS3: MOV R0, -(SP)
        MOV R1, -(SP)
        MOV R2, -(SP)
        MOV R3, -(SP)
        MOV R4, -(SP)
        CLR R1
        CLR @2(R5)
        MOV @6(R5), R2
        MOV 4(R5), R3
        MOV 10(R5), R4
        CLR R2
A:       MOV B (R3)+, R0
        CMPB #3, R0
        BEQ B
        JSR R5, WRITE
        JMP A
B:       BISB (R3)+, R1
        SWAB R1
        BISB (R3)+, R1
        MOV R1, @2(R5)
C:       JSR R5, READD
        CLR R2
        JSR R5, READD
        CLR R2
        MOV R1, -(SP)
        CLR R0
        CLR R1
        BISB (R3)+, R1
        SWAB R1
        BISB (R3)+, R1
        BISB (R3)+, R0
        SWAB R0
        BISB (R3)+, R0
        BISB (R3)+, R2
        SWAB R2
        BISB (R3)+, R2
        DIV R2, R0
        MOV R0, (R4)+
        MOV (SP)+, R1
        CLR R2
        JSR R5, READD
        CLR R2
        SOB R1, C
        MOV (SP)+, R4
        MOV (SP)+, R3
        MOV (SP)+, R2
        MOV (SP)+, R1
        MOV (SP)+, R0
        RTS R5
;
;
;
WRITE:   TSTB TPS
        BPL WRITE
        MOV B R0, TPB
        RTS R5
READD:   BISB (R3)+, R2
        SWAB R2
        BISB (R3)+, R2
        MOV R2, (R4)+
        RTS R5
        .END

```




APPENDIX C

MICROCOMPUTER TO MINICOMPUTER COMMUNICATION PROGRAMS

The programs used in the PDP-11/40 minicomputer for the mini-to-microcomputer communication are listed here.

```

C      PROGRAM LINK.FTN
C      FINAL FORM OF THE LINK
C
C      INTEGER COMMND,COMLST(4)
C      BYTE ACK,NAK,BEL
C      DATA NCOM/4/
C      DATA ACK,NAK,BEL/6,21,7/
C      DATA COMLST/2HMN,2HMA,2HUN,2HUA/
C
C      CLEAR MDB RACK
C
C      600 CALL CMICRO
C
C      CHECK TO SEE IF ANY MICRO ASKED FOR SERVICE
C      IF YES SEE WHICH MICRO IT WAS AND SEND ACK-EOT
C
C      CALL WAITM(MICRON,MASK)
C
C      GET COMMAND
C
C      CALL RAMICR(IERR,COMMND,COUNT)
C
C      CHECK THE LIST OF COMMANDS
C
C      DO 100 I=1,NCOM
C      IF(COMMND.NE.COMLST(I))GO TO 100
C
C      IF ONE IS FOUND SEND BEL-EOT
C
C      CALL MSMICR(BEL)
C      GO TO(110,120,130,140)I
C      100 CONTINUE
C
C      IF NOT FOUND SEND NAK-ERROR MESSAGE
C
C      CALL MSMICR(NAK,'INV. CMD')
C      GO TO 600
C      110 CALL MINCSR(I)
C          GO TO 600
C      120 CALL MINCSR(I)
C          GO TO 600
C      130 CALL UICCSR(I)
C          GO TO 600
C      140 CALL UICCSR(I)
C          GO TO 600
C      END

```

```

C
C
C      UICCSR.FTN
C
C      THIS SUBROUTINE SENDS AN UNFORMATTED BINARY
C      OR A FORMATTED ASCII FILE TO MICRO
C
C      SUBROUTINE UICCSR(I)
C      INTEGER COUNT
C      BYTE IDATA(510), IFILE(24), NAK, ACK, BEL, EOT, ENG, SOH
C      DATA NAK, ACK, BEL, EOT, ENG, SOH/21, 6, 7, 4, 5, 1/
C
C      GET THE NAME OF THE FILE
C
C      CALL RAMICR(IERR, IFILE, COUNT)
C      IERR=0
C
C      CHECK TO SEE IF THIS FILE EXISTS
C      OR IF THERE IS ANY ERROR
C
C      CALL FORPIP(IFILE, IERR)
C      IF(IERR.EQ.1)GO TO 300
C      IF(IERR.LT.0)GO TO 350
C      CALL MSMICR(NAK, 'FILE DOES NOT EXIST')
C      RETURN
350    CALL MSMICR(NAK, 'FILE ERROR')
C      RETURN
300    CALL MSMICR(SOH)
C
C      WHAT TYPE OF FILE? BINARY OR ASCII?
C
C      IF(I.EQ.4)GO TO 400
C
C      OPEN THE FILE (UNFORMATTED BINARY)
C
C      CALL UNFMO(IERR, IFILE, 0, 1)
C
C      READ THE FILE
C      IF THERE IS ONLY ONE PAGE(255 BYTES)      IERR=0
C      IF THERE ARE MORE THAN ONE PAGES          IERR=-1
C      IF THERE IS AN ERROR                        IERR=+1
C
360    COUNT=255
C      CALL UNFMRW(IERR, IDATA, COUNT)
C      IF(IERR)310, 320, 330
320    CALL WNMICR(IERR, IDATA, COUNT)
C      IF(IERR.EQ.0)GO TO 360
C      IF(IERR.EQ.1)GO TO 340
C      IF(IERR.EQ.2)GO TO 370
340    CALL UNFMC(IERR)
C      CALL MSMICR(NAK, 'CHECKSUM ERROR')
C      RETURN
370    CALL UNFMC(IERR)
C      CALL MSMICR(NAK, 'NOT AN ACK OR NAK AFTER CHECKSUM')
C      RETURN
330    CALL UNFMC(IERR)
C      COUNT=0
C      CALL MSMICR(NAK, 'FILE ERROR')
C      RETURN
310    CALL WNMICR(IERR, IDATA, COUNT)
C      COUNT=0
C      CALL WNMICR(IERR, IDATA, COUNT)
C      CALL UNFMC(IERR)
C      RETURN
C
C
C      OPEN THE FILE (FORMATTED ASCII)
C
C      CALL UNFMO(IERR, IFILE, 0, 2)
C
C      READ THE FILE
C      IF THERE IS ONLY ONE PAGE(255 BYTES)      IERR=0
C      IF THERE ARE MORE THAN ONE PAGES          IERR=-1
C      IF THERE IS ANY ERROR                      IERR=+1
C
C
460    COUNT=255
C      CALL UNFMRW(IERR, IDATA, COUNT)
C      IF(IERR)410, 420, 330
420    CALL WAMICR(IERR, IDATA, COUNT)
C      IF(IERR.EQ.0)GO TO 460
C      IF(IERR.EQ.1)GO TO 340
C      IF(IERR.EQ.2)GO TO 370
410    CALL UNFMC(IERR)

```

```
C
C MINCSR.FTN
C
C READS A FILE FROM MICRO AND STORES IT IN
C UNFORMATTED BINARY FORM(A FILE IMAGE) OR
C IN FORMATTED ASCII FORM
C
SUBROUTINE MINCSR(I)
INTEGER COUNT
BYTE IDATA(510), IFILE(24), NAK, ACK, BEL, EOT, ENG
DATA NAK, ACK, BEL, EOT, ENG/21, 6, 7, 4, 5/
C
C GET THE NAME OF THE FILE
C
CALL RAMICR(IERR, IFILE, COUNT)
IERR=0
C
C CHECK TO SEE IF THIS FILE ALREADY EXISTS
C OR IF THERE IS ANY ERROR
C
CALL FORPIP(IFILE, IERR)
IF(IERR.EQ.0)GO TO 200
IF(IERR.LT.0)GO TO 250
CALL MSMICR(NAK, 'FILE ALREADY EXISTS')
RETURN
250 CALL MSMICR(NAK, 'FILE ERROR')
RETURN
200 CALL MSMICR(ENG)
C
C WHAT TYPE OF TRANSFER? BINARY OR ASCII ?
C
IF(I.EQ.2)GO TO 260
C
OPEN THE FILE (UNFORMATTED BINARY)
C
CALL UNFMO(IERR, IFILE, 1, 1)
C
READ THE FILE.
IF THERE IS ONLY ONE PAGE(255 BYTES)      IERR=0
IF THERE ARE MORE THAN ONE PAGES          IERR=-1
IF THERE IS AN ERROR                      IERR=+1
240 IERR=0
CALL RNMICR(IERR, IDATA, COUNT)
IF(IERR)210, 220, 210
220 CALL UNFMRW(IERR, IDATA, COUNT)
GO TO 240
210 CALL UNFMC(IERR)
RETURN
C
OPEN THE FILE(FORMATTED ASCII)
C
CALL UNFMO(IERR, IFILE, 1, 2)
C
READ THE FILE
IF THERE IS ONLY ONE PAGE (255 BYTES)      IERR=0
IF THERE ARE MORE THAN ONE PAGES          IERR=-1
IF THERE IS AN ERROR                      IERR=+1
270 IERR=0
CALL RFMICR(IERR, IDATA, COUNT)
IF(IERR)280, 290, 280
290 CALL UNFMRW(IERR, IDATA, COUNT)
GO TO 270
280 CALL UNFMC(IERR)
RETURN
END
```

```

.TITLE MML1
.GLOBL CMICRO
.GLOBL WAITM
.GLOBL MSMICR
.GLOBL RAMICR
.GLOBL RNMICR
.GLOBL WNMICR
.GLOBL WAMICR
.GLOBL RFMICR
FLGREG=100010
MDB=165000
IMDB=165002
.MCALL F4DEF
.F4DEF 0

;
;
PUSH

.MACRO PUSH
MOV RO,-(SP)
MOV R1,-(SP)
MOV R2,-(SP)
MOV R3,-(SP)
MOV R4,-(SP)
.ENDM

;
;
POP

.MACRO POP
MOV (SP)+,R4
MOV (SP)+,R3
MOV (SP)+,R2
MOV (SP)+,R1
MOV (SP)+,R0
.ENDM

;
;
CMICRO
CMICRO: MOV #40,165004          ;TURN ON MDB
        MOV #100007,MDB       ;ENABLE INTERRUPTS
        CLR MDB               ;TURN OFF MDB
        MOV #0,165004
        RTS R5

;
;
WAITM
WAITM:  PUSH                    ;SAVE REGISTERS
A:      CLR R0
        CLR R1
        CLR R2
        MOV #40,165004        ;TURN ON MDB
        MOV #FLGREG,MDB
        MOVB IMDB,R0          ;CHECK IF ANY MICRO ASK FOR
        CMPB #7,R0            ;SERVICE
        BEQ A                  ;IF NOT CHECK AGAIN
B:      BIT #1,R0              ;CHECK THE FIRST BIT AT R0
        BEQ C                  ;IF IT IS NOT ZERO ROTATE
        ASRB R0                ;RO RIGHT UNTIL YOU FIND
                                ;A ZERO
C:      JMP B
        MOV R1,R2              ;SAVE R1
        ADD #100000,R2         ;CREATE INDIRECT MICRO ADDR
        MOV R2,MICRON
        MOV R2,@2(R5)
        MOV #1,R0              ;SET MICRO MASK(FLAG)
        ASH R1,R0
        MOV R0,MASK
        MOV R0,@4(R5)
        JSR R5,READ            ;GET THE BYTE
        CMPB #6,R0            ;IS IT AN ACK?
        BNE A                  ;IF NOT START AGAIN
        MOV #6,R0              ;SEND ACK
        JSR R5,WRITE
        MOV #4,R0              ;SEND EOT
        JSR R5,WRITE
        POP
        RTS R5

;
;
MSMICR SUBROUTINE: SENDS AN ASCII MESSAGE TO MICRO
MSMICR: PUSH
        MOVB (R5),R2           ;GET LOW BYTE OF R5
        MOV 2(R5),R3           ;GET ADDR. OF FIRST BYTE
        MOVB (R3),R0

```



```

        JSR R5,WRITE          ; SEND THE BYTE
        CMPB #1,R0           ; SOH?
        BEQ EXITT
D:      DEC R2                ; CHECK IF MORE BYTES
        BEQ EXIT1
        MOV 4(R5),R3         ; GET ADDR. OF NEXT BYTE
DD:     MOVB (R3)+,R0
        BEQ EXIT1           ; CHECK IF ZERO
        JSR R5,WRITE        ; SEND IT
        BR DD
EXIT1:  MOV #4,R0            ; SEND AN EOT
        JSR R5,WRITE
EXITT:  POP
        RTS R5
;
;      RAMICR SUBROUTINE: READS AN ASCII MESSAGE FROM MICRO
;
RAMICR: PUSH
        CLR R2
        MOV 4(R5),R3
F:      JSR R5,READ          ; GET BYTE
        CMPB #4,R0          ; CHECK IF EOT
        BEQ CEOT
        MOVB R0,(R3)+       ; STORE BYTE
        INC R2
        JMP F
CEOT:   MOV R2,@6(R5)        ; COUNTS
        POP
        RTS R5
;
;      RNMICR SUBROUTINE: READS A FORMATTED BINARY FILE
;                          FROM MICRO
;
;
RNMICR: PUSH
        MOV 4(R5),R3
        CLR R4
        JSR R5,READ          ; GET # OF COUNTS
        MOV R0,R2
        MOV R0,@6(R5)       ; SAVE # OF COUNTS
        TST R2              ; CHECK IF COUNTS=0
        BGT LOOP
        JMP TEL             ; IF YES GO TO TEL
LOOP:   JSR R5,READ          ; GET THE BYTE
        MOVB R0,(R3)+       ; STORE IT
        XOR R0,R4           ; UPDATE CHECKSUM
        SOB R2,LOOP         ; END?
CHECKS: JSR R5,READ          ; GET CHECKSUM
        CMP R0,R4           ; CHECK IF THE SAME
        BNE ERROR1
        MOV #6,R0           ; IF YES SEND ACK
        JSR R5,WRITE
        MOV #4,R0           ; SEND EOT
        JSR R5,WRITE
        MOV #0,@2(R5)       ; SET IEER=0
        JMP EXIT2
ERROR1: MOV #25,R0           ; SEND NAK
        JSR R5,WRITE
        MOV #4,R0           ; SEND EOT
        JSR R5,WRITE
        MOV #1,@2(R5)       ; SET IERR=1
        JMP EXIT2
TEL:    MOV #-1,@2(R5)      ; SET IERR=-1
EXIT2:  POP
        RTS R5
;
;      RFMICR SUBROUTINE: READS A FILE FROM MICRO AND
;                          ADDS A LF TO ANY CR
;
RFMICR: PUSH
        CLR R1
        CLR R4
        MOV 4(R5),R3
        JSR R5,READ          ; GET COUNTS
        MOV R0,R2           ; SAVE COUNTS
        TST R2
        BGT ALOOP
        JMP TEL             ; IF COUNT=0 EXIT
ALOOP:  JSR R5,READ          ; GET THE BYTE
        MOVB R0,(R3)+       ; STORE THE BYTE
        XOR R0,R4           ; UPDATE CHECKSUM
        INC R1
        CMPB #15,R0         ; CR?

```




```

BB:      BEQ AA
        SOB R2, ALOOP                ; END?
        MOV R1, @6(R5)
        JMP CHECKS
AA:      MOVB #12, (R3)+
        INC R1
        BR BB
;
;      WNMICR SUBROUTINE: SENDS A FORMATTED BINARY
;      FILE TO MICRO
;
WNMICR:  PUSH
        CLR R2
        CLR @2(R5)                  ; CLR ERROR CODE
        MOV @6(R5), R2              ; GET BYTE COUNT
        MOV 4(R5), R3               ; GET SRC ADDR.
CONT:    CLR R4
        MOV R2, R0                  ; SEND BYTE COUNT
        JSR R5, WRITE
        TST R2                      ; CHECK IF BYTE COUNT=0
        BGT XLOOP
        JMP CONT2
XLOOP:   MOVB (R3)+, R0
        XOR R0, R4                  ; UPDATE CHECKSUM
        JSR R5, WRITE              ; SEND THE DATA
        SOB R2, XLOOP              ; END?
        MOV R4, R0
        JSR R5, WRITE              ; SEND CHECKSUM
        JSR R5, READ               ; GET MICRO'S ANSW.
        CMPB #6, R0                ; IS IT AN ACK?
        BEQ CONT1
        CMPB #25, R0               ; IS IT A NAK?
        BEQ ERROR2
        JMP ERROR3
CONT1:   JSR R5, READ               ; GET EOT
CONT2:   MOV #0, @2(R5)             ; SET IERR=0
        JMP EXIT3
ERROR2:  JSR R5, READ
        MOV #1, @2(R5)             ; SET IERR=1
        JMP EXIT3
ERROR3:  JSR R5, READ
        MOV #2, @2(R5)             ; SET IERR=2
EXIT3:   POP
        RTS R5
;
;      WAMICR SUBROUTINE: SENDS AFORMATTED ASCII
;      FILE TO MICRO
;
WAMICR:  PUSH
        CLR R4
        CLR R3
        CLR R2
        CLR R1
        CLR @2(R5)                  ; CLR ERROR CODE
        MOV @6(R5), R2              ; GET BYTE COUNT
        MOV 4(R5), R3               ; GET SRC ADDR.
        MOV #DATABF, R1            ; GET ADDR. OF STORAGE BUFFER
        TST R2                      ; CHECK IF BYTE COUNT=0
        BGT YLOOP
        JMP CONT
YLOOP:   MOVB (R3)+, R0              ; GET THE BYTE
        CMPB #12, R0               ; CHECK IF IT IS LF
        BEQ CC                     ; IF YES GET NEXT BYTE
        MOVB R0, (R1)+             ; IF NOT STORE THE BYTE
        INC R4                     ; INCREMENT NEW BYTE COUNT
        SOB R2, YLOOP              ; END?
CC:      MOV R4, R2                 ; GET NEW BYTE COUNT
        MOV #DATABF, R3            ; GET NEW SRC ADDR.
        JMP CONT
;
;      LOCAL SUBROUTINES
;
WRITE:   MOV MICRON, MDB             ; SET UP INDIRECT ADDR.
        MOVB R0, IMDB              ; SEND DATA
        MOV #FLGREG, MDB           ; POINT TO FLAG REGISTER
FLAG1:  BIT #400, IMDB              ; BUFFER EMPTY?
        BEQ FLAG1
        RTS R5
;
;

```

```

READ:    MOV #FLGREG, MDB
READ1:   BIT MASK, IMDB           ; DATA AVAILABLE?
        BNE READ1
        MOV MICRON, MDB         ; POINT TO MICRO
        MOV IMDB, RO           ; GET THE BYTE
        RTS R5

;
;   STORAGE
;
MICRON:  .WORD 0
MASK:    .WORD 0
DATABF:  .BLKB 777
        .END

```

002

003

REFERENCES

REFERENCES

1. E. P. Parry and R. A. Osteryoung, Anal. Chem. 37, 1634 (1965).
2. D. E. Burge, J. Chem. Ed. 47(2), A81 (1970).
3. J. B. Flato, Anal. Chem. 44, 75A (1972).
4. P. E. Sturrock and R. J. Carter, CRC Critical Reviews in Analytical Chemistry, July 1975, p. 201.
5. P. E. Sturrock, J. L. Hughey, B. Vandrenil, G. E. O'Brien, and R. H. Gibson, J. Electr. Soc. 122, 1195 (1975).
6. J. H. Christie, J. A. Turner, and R. A. Osteryoung, Anal. Chem. 49, 1899 (1977).
7. G. L. Booman and W. B. Holbrook, Anal. Chem. 35, 1793 (1963).
8. "Symposium on Operational Amplifiers", Anal. Chem. 35, 1770 (1963).
9. "Symposium on Electroanalytical Instrumentation", Anal. Chem. 38, 1106 (1966).
10. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Chapter 5, John Wiley and Sons, NY 1974.
11. J. S. Mattson, H. B. Mark, Jr., H. C. MacDonald, Jr., Eds., "Computers in Chemistry and Instrumentation", Chapter 10, Vol. 2, Dekker, NY 1972.
12. G. Lauer, H. Schlein and R. A. Osteryoung, Anal. Chem. 35, 1789 (1963).
13. C. G. Enke and R. A. Baxter, J. Chem. Ed. 41, 202 (1964).
14. D. E. Bartak, H. K. Huudley, M. VanSwaay, and M. D. Hawley, Chem. Instrum. 4, 1 (1972).
15. Chia-yu Li, D. Ferrier, and R. R. Schroeder, Chem. Instrum. 3, 333 (1972).
16. S. O. Farwell and R. D. Geer, Chem. Instrum. 5, 199 (1973).

17. L. Ramaley, Chem. Instrum. 6, 119 (1975).
18. P. Delahay, Anal. Chim. Acta 27, 90 (1962).
19. P. Delahay, Anal. Chim. Acta 27, 400 (1962).
20. P. Delahay, Anal. Chem. 34, 1267 (1962).
21. P. Delahay and Y. Ide, Anal. Chem. 34, 1580 (1962).
22. P. Delahay, Anal. Chem. 34, 663 (1962).
23. A. Aramata and P. Delahay, Anal. Chem. 35, 1117 (1963).
24. J. M. Kudirka, R. Abel, and C. G. Enke, Anal. Chem. 44, 425 (1972).
25. M. Astruc, J. Bonastre, and R. Royer, J. Electroanal. Chem. 33, 211 (1972).
26. M. Astruc, and J. Bonastre, J. Electroanal. Chem. 40, 311 (1972).
27. B. K. Hahn, "Computer-Based Coulostatic System for Electrochemical Analysis", Ph.D. Dissertation, Michigan State University, 1974.
28. J. M. Katzenberger, and P. H. Daum, Anal. Chem. 47, 1887 (1975).
29. W. W. Goldsworthy and R. G. Clem, Anal. Chem. 44, 1360 (1972).
30. G. Lauer, Anal. Chem. 38, 1277 (1966).
31. J. E. Davis and N. Winograd, Anal. Chem. 44, 2152 (1972).
32. J. E. Hornshush, Ph.D. Dissertation, Michigan State University, 1978.
33. E. M. Carlson, Ph.D. Dissertation, Michigan State University, 1978.
34. Program written by T. V. Atkinson, Department of Chemistry, Michigan State University.
35. I. M. Kolthoff and J. J. Lingane, "Polarography" Second Edition, Interscience Publishers, NY 1952.
36. P. Znmay and I. M. Kolthoff, Eds., "Progress in Polarography", Interscience Publishers, NY, 1962.

37. R. W. Murray and C. N. Reilley, "Electroanalytical Principles", Interscience Publishers, NY, 1963.
38. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Chapter 7, John Wiley and Sons, NY 1974.
39. Data sheet on AD7522 D/A Converter, Analog Devices.
40. Intel Corporation, Intel Data Catalog, Santa Clara, CA, 1977.
41. S. P. Perone "Digital Computers in Scientific Instrumentation. Applications to Chemistry", McGraw-Hill, NY, 1973.
42. J. W. Cooper, "The Minicomputer in the Laboratory", John Wiley and Sons, Inc., NJ, 1973.
43. J. S. Mattson, M. B. Mark, Jr., H. C. MacDonald, Jr., Eds., "Computer Fundamentals for Chemists", Vol. 1, Marcell Dekker, Inc., NY, 1973.
44. J. W. Frazer, Anal. Chem. 40, 27A (1968).
45. G. Lauer, and R. A. Osteryoung, Anal. Chem. 40, 30A (1968).
46. G. P. Hicks, A. A. Eggert, and E. C. Torey, Jr., Anal. Chem. 42, 729 (1970).
47. G. I. Connor, G. H. Boehme, C. J. Johnson and K. H. Pool, Anal. Chem. 45, 437 (1973).
48. G. Lauer, R. Abel and F. C. Anson, Anal. Chem. 39, 765 (1967).
49. S. P. Perone, J. E. Harrar, F. B. Stephens and R. E. Anderson, Anal. Chem. 40, 899 (1968).
50. D. O. Jones and S. P. Perone, Anal. Chem. 42, 1151 (1970).
51. F. B. Stephens, F. Jakob, L. P. Rigdon, and J. E. Harrer, Anal. Chem. 42, 764 (1970).
52. L. B. Sybrondt and S. P. Perone, Anal. Chem. 43, 382 (1971).
53. H. E. Keller and R. A. Osteryoung, Anal. Chem. 43, 342 (1971).

54. L. Kryger, D. Jagyer and H. J. Skov, Anal. Chim. Acta 78, 241 (1975).
55. L. Kryger and D. Jagner, Anal. Chim. Acta 78, 251 (1975).
56. M. Bos, Anal. Chim. Acta, 81, 21 (1976).
57. G. A. Kory, "Microprocessors and Small Digital Computer Systems for Engineers and Scientists", McGraw-Hill, New York, 1977.
58. L. Altman, Ed., "Microprocessors", McGraw-Hill, NY 1975.
59. L. Altman, S. E. Scrupski, Eds., "Applying Microprocessors", McGraw-Hill, NY, 1976.
60. R. E. Dessy, P. Vuurem and J. A. Titus, Anal. Chem. 46, 917A (1974).
61. H. D. Toong, Scientific American 237, 146 (1977).
62. D. H. Chung, Electronic Design, 12, 133 (1976).
63. A. J. Weissberger, Computer Design, 151 (June 1977).





MICHIGAN STATE UNIV. LIBRARIES



31293107477014