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REAL-TIME COMPUTER OPTIMIZED SCANNING POTENTIAL COULOMETRY
FOR MULTI-COMPONENT TRACE ANALYSIS

A Dissertation
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

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by

Norman W. Petty

August 1977

This dissertation, by Norman W. Petty, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

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I. INTRODUCTION

Coulometry is an electroanalytical method capable of greater accuracy and precision than classical volumetric or gravimetric methods, primarily because electric currents can be controlled and measured with greater precision than can volumes of standard solutions (1,2). Coulometry offers the further advantage of permitting a chemical analysis to be made in terms of fundamental physical and electrical constants. The concentration of a substance in solution can be calculated from the following equation:

$$C = \frac{Q}{nFV} \quad (1)$$

where C is the formal concentration of the substance, Q is the total charge, in coulombs, n is the number of equivalents per mole of substance, F is the faraday, and V is the volume of the solution that is analyzed. Other quantitative methods use as their basis for measurement a comparison of some physical or chemical property of the sample with a similar property of another chemical substance. Calibration standards are required to obtain quantitative results. The quantities in Equation (1) are not defined or determined in such a manner. Each is a fundamental physical or electrical quantity. The charge is the electrical current integrated over the time of analysis. The faraday is

equal to the product of the atomic mass of the proton and its gyromagnetic ratio divided by the magnetic moment of the proton in units of the nuclear magneton. These constants can be determined by omegatron measurements and by resonance mass spectrometry (3-5).

Constant current coulometric methods are relatively simple and capable of extreme accuracy. An accuracy approaching 0.01% is easily reached under ordinary laboratory conditions. Precisions approaching 0.001% are attained by the National Bureau of Standards using constant current coulometric methods in the assay of some of their Standard Reference Materials (5-8). These precisions were obtained for the analysis of 0.25 to 2.5 milliequivalents of sample.

Constant current titrations, like classical volumetric and gravimetric titrations, are not highly specific (8). This often necessitates a chemical separation of the desired sample constituent prior to the analysis. Controlled potential coulometric methods are more selective, and thus more applicable to complex mixtures. An accuracy and precision of 0.1% are easily obtained with these methods.

In controlled potential coulometry, the substance being determined is electrolyzed at a working electrode at a potential which is controlled or maintained constant with respect to a reference electrode by means of a potentiostat. The current is integrated by means of an electronic integrator or coulometer. The counter electrode is placed in a separate cell compartment connected to the solution to be analyzed through a semipermeable

separator to prevent the reaction which is occurring at the working electrode from being reversed at the counter electrode. The working electrode potential is chosen to achieve a quantitative electrolysis and to avoid the effects of interferences by other constituents which also might be electrolyzed. A formal potential separation of more than 354 mV is required between equal molar electroactive sample constituents with one equivalent per mole in order to obtain 0.1% accuracy (2,9-11). If there are two equivalents per mole for each constituent, a formal potential separation greater than 177 mV is required. If the interfering substance is in greater concentration than the substance being determined, the formal potential separation must be proportionately greater. Controlled potential coulometric methods are generally used for the analysis of major constituents in a sample, or for the analysis of minor constituents when the major sample constituents are inactive electrochemically (11). These methods are conveniently used for the analysis of 1 microequivalent to 10 milliequivalents of substance. Solution volumes are in the range of 1-25 ml and solution concentrations in the 10^{-4} M to 10^{-2} M range (11,12). The upper limit depends chiefly on the voltage and current that can be obtained from the potentiostat. The lower limit is determined by the ratio of the current due to electrolysis of sample constituents to background current.

Conventional voltammetric methods are capable of resolving constituents with half-wave potentials 30 to 40 millivolts apart (12,13). These methods are best suited to the determination of constituents in the concentration range of 10^{-5} to 10^{-3} M.

Relative errors of the order of 2 to 5% are usually obtained. Below the lower limit the background current becomes a substantial fraction of the total current. Because the background currents have a relatively constant slope, a background correction can be made and analyses of 10^{-6} M solutions can be made with relative errors around 10% (13). Because voltammetric methods are not highly accurate, they are used primarily for the analysis of minor constituents.

Scanning potential coulometry combines the sensitivity and selectivity of voltammetry with the accuracy and absolute nature of controlled potential coulometry. An early attempt to perform a coulometric analysis during a potential scan was made by Samuel S. Lord and co-workers for the analysis of 10^{-5} M silver (14). The procedure required a cathodic deposition of the silver for a constant time at a constant potential followed by anodic dissolution at a potential that varied linearly with respect to time. The current during dissolution was integrated and was proportional to the concentration of silver in solution. Because a quantitative deposition was not performed the results were obtained relative to standards which were prepared. Since the results were not obtained in terms of absolutely defined quantities as are coulometric determinations, (1,2,9,11-13) this technique should not be considered a coulometric determination. Because of its relative nature this method should be considered anodic stripping voltammetry with integration of peak areas.

The use of scanning potential coulometry was originated by Scott and others for the analysis of traces of iron (15). The

sample to be analyzed was first oxidized at a constant potential until the current diminished to a small constant value. The potential on the working electrode was then scanned cathodically at a constant rate, and the current was plotted against time. Results obtained used analytical calculations based on measurements of the height of the current peak above a relatively flat background. The detection limit was determined to be 10^{-7} M (5×10^{-4} microequivalents of iron in 5 milliliters of solution). A standard deviation of 4×10^{-4} microequivalents was obtained for samples containing up to 0.1 microequivalents of iron.

Scanning potential coulometry was further developed by Propst (16), who developed an instrument with automatic background correction and a scan rate that varies in inverse proportion to the magnitude of the electrolysis current. The instrument provided a readout of the working electrode potential and the charge for plotting a coulogram. This instrument was used for the direct titration of 2 to 5 micrograms of plutonium in irradiated nuclear fuel with a precision of 2.1% (16). This instrument has also been used for the analysis of microgram quantities of polonium, americium, and neptunium (17-19). In the analysis of 0.4 to 4 micrograms of polonium, relative standard deviations of 5% were obtained (17). A precision of 1.5% was obtained in the analysis of 30 micrograms of americium (18). In each of these analyses solution volumes were between 5 and 10 milliliters, and the concentration ranged from 10^{-6} M for polonium to 10^{-4} M for americium. A thin-layer conducting glass electrode cell was used for the analysis of neptunium (19). The solution volume was 6.8 microliters and the concentration

ranged from 1.5×10^{-4} M to 5×10^{-4} M. The standard deviations for these analyses were 1.5×10^{-5} M.

Because scanning potential coulometry yields well defined waves, Propst and co-workers have used this method to study the electrochemistry of various electroactive species. Electrochemical studies were made on silver (20), californium in aqueous solution (21), ruthenium in perchloric acid solution (22), and berkelium in acidic aqueous solution (23).

Other workers have used a linear scan in scanning potential coulometry because the method used by Propst required that one know, prior to the analysis, the behavior of the background throughout the scan. Oglesby and co-workers (24) used scanning potential coulometry to determine equimolar copper, lead, cadmium, and zinc mixtures. The relative inaccuracy for 10^{-2} M solutions ranged from 0.5% for cadmium to 8.1% for zinc. Half-height potential separations for adjacent ions were large enough that overlapping waves were not a problem. These ranged from 190 millivolts for lead and cadmium to 480 millivolts for copper and lead. Halide mixtures were also analyzed. For 5×10^{-3} equimolar chloride, bromide, and iodide the relative inaccuracy ranged from 1.8% for iodide to 18% for chloride. I. S. Sklyarenko and co-workers (25) used this method for the analysis of 10^{-5} M iron with relative precisions of 5%.

Many analytical methods have been improved by application of computers for data analysis and by real-time control and data acquisition. Since its advent, the computer has been used to analyze experimental data (26). The large volumes of raw data

generated by modern instrumental techniques have made computer analysis an absolute necessity. Initially, the only computing facilities available were at large central processing centers. Because the researcher was limited by the relatively slow batch turn-around time of these centers, real-time control of experiments was impossible. The processing of data as they are being acquired is referred to as a real-time operation. The processing can be simple data collection and storage or complex data analysis and experiment control, but for real-time operations the processing must be completed before the next data point is to be taken. By 1966 small laboratory computer systems, which could be connected on-line to the experiment, became available. The earliest extensive use of these on-line computers was in the field of nuclear chemistry (27,28).

The early on-line computers were used to automate data collection and to perform simple data analysis (29-32). No significant control of the experiment was involved. One of the first applications of an on-line computer in chemistry was for an electrochemical system (29). The computer was used to initiate chronocoulometric experiments, to acquire and store the data and to perform a functional analysis on the stored data. This system was used later for the study of anion-induced adsorption of cadmium on mercury from iodide and bromide solutions (30).

Other experimenters have used an on-line computer either to increase the number of experimental runs that one could perform (31) or decrease the time required to do an electrochemical analysis (32). Perone and others (31) describe the use of an on-line

digital computer for data acquisition and analysis in fast-sweep derivative polarography. The computer could be programmed to average data for up to 2048 repetitive sweeps on the same sample. The averaging technique provided an enhanced signal-to-noise ratio and an order of magnitude increase in sensitivity. Stephens and co-workers have used a real-time computer to predict the final value of charge in a controlled potential coulometric determination (32). This system gave analytical results in one-third the electrolysis time required for conventional controlled-potential coulometry.

Lauer and Osteryoung (33) describe a laboratory computer system which includes general-purpose data-acquisition, timing, interfacing, and digital control features with a great deal of flexibility for application to a variety of electroanalytical methods. The approach described by the authors was to program the computer to generate all the control functions for the various electroanalytical techniques. The authors have applied the system to the various electroanalytical methods of chronocoulometry, pulse polarography, ac polarography, chronopotentiometry, and cyclic voltammetry. A program was written to generate the control functions for each method. To change the method one need only change the control program. Keller and Osteryoung (34) have used this system for pulse polarographic experiments at a hanging mercury-drop electrode. Signal averaging was applied to increase sensitivity. This approach gives a researcher virtually unlimited flexibility. Since no hardware change is required for a different method, new and innovative methods can be quickly investigated.

A real-time computer which can interact with the experiment under its control can often enhance experimental measurements. Perone, Jones, and Gulknecht used a real-time computer to optimize, in real-time, polarographic measurements at a stationary electrode (35). The computer was used to control the sweep on an electrochemical cell. The computer caused a temporary interruption of a linear scan after each reduction step to allow time for the reducible species to dissipate in the diffusion layer and minimize interference with succeeding reduction steps. The investigators reported that this interactive approach gave a hundredfold increase in the quantitative resolution capabilities over the conventional polarographic method.

The work reported here used a real-time computer for data acquisition and experiment control in scanning potential coulometry. The scan consists of a series of computer-controlled 1-millivolt potential steps. The electrolysis current is integrated by a digital coulometer which is read by the computer at regular intervals. Based on the collected data, the computer determines if near-equilibrium conditions exist. If near-equilibrium conditions do exist, then the electrolysis current is due to a background current and its contribution is subtracted from the accumulated charge. The computer then generates the next 1-millivolt potential step for the scan. If near-equilibrium conditions do not exist then the potential is not stepped and the computer continues to collect the data. This technique automatically scans at the optimum rate to maintain equilibrium conditions closely. The method reported by Propst (16) also maintained equilibrium

conditions closely, but required that one know prior to the scan the behavior of the background throughout the scan in order to obtain accurate results. The method reported here has no such requirement since the background is measured throughout the scan. Non-linear least squares curve fitting techniques are used to resolve overlapping peaks and background. These techniques have further increased the sensitivity, selectivity, and precision of the method.

II. INSTRUMENTATION AND APPARATUS

Digital data accumulation and processing permit a high rate of data collection and greater accuracy, resolution, and precision than can be obtained from analog readout devices such as servo-recorders and meters (36). Data collected in the digital form is suitable for further data processing by a computer, thereby expanding the scope and complexity of the experiment undertaken. On-line computers have improved several electroanalytical techniques by automating experimentation, data assimilation, and data processing (29-32). Virtually unlimited flexibility in electroanalytical experimentation has been demonstrated by using an on-line computer to control the experimental parameters (33,34). These approaches ultimately are limited by the inherent limitations of a particular measurement technique. To take full advantage of the on-line computer, one should use its capabilities for rapid "intelligent" feedback, and incorporate the computer into the experimental control loop (35,37). The computer could monitor the experiment, process the data in real-time as the experiment progresses, and, based on the results of the data processing, modify the course of the experiment to provide optimum measurement conditions. For the work reported here, a real-time interactive computer maintained optimum scanning and measurement conditions for scanning potential coulometry used for multi-component trace analysis.

Figure 1 is a block diagram of the instrumentation and apparatus used for real-time computer-optimized scanning potential coulometry. The computer interface, data acquisition and control unit, potentiostat and potential reference control, and coulometer are all general purpose devices. Virtually any voltammetric or controlled potential coulometric analysis can be performed by changing only the control program and possibly the electrolysis cell. In addition, the computer interface and the data acquisition and control unit are general purpose units capable of real-time operations in a variety of different chemical experiments using different instruments. A PDP-11/20 mini computer from Digital Equipment Corporation with 24K of core memory from Standard Memories is used as the real-time control computer. An International Memories Data Miser disc controller and a Wanco cartridge disc drive with one removable and one nonremovable disc cartridge is used for program and data storage. A Computer Operations C-3000 Link Tape system and a Digital Equipment Corporation high speed paper tape reader/punch are used for auxiliary data and program storage. A Tektronix 4010-1 graphics terminal is used as the console terminal to control the operation of the computer operating system (RT-11) and to plot the data from experimental scans and data analysis. Hard copy plots are obtained from a Tektronix 4662 plotter, and hard copy printouts of the results and the programs are printed using a General Electric Terminet terminal.

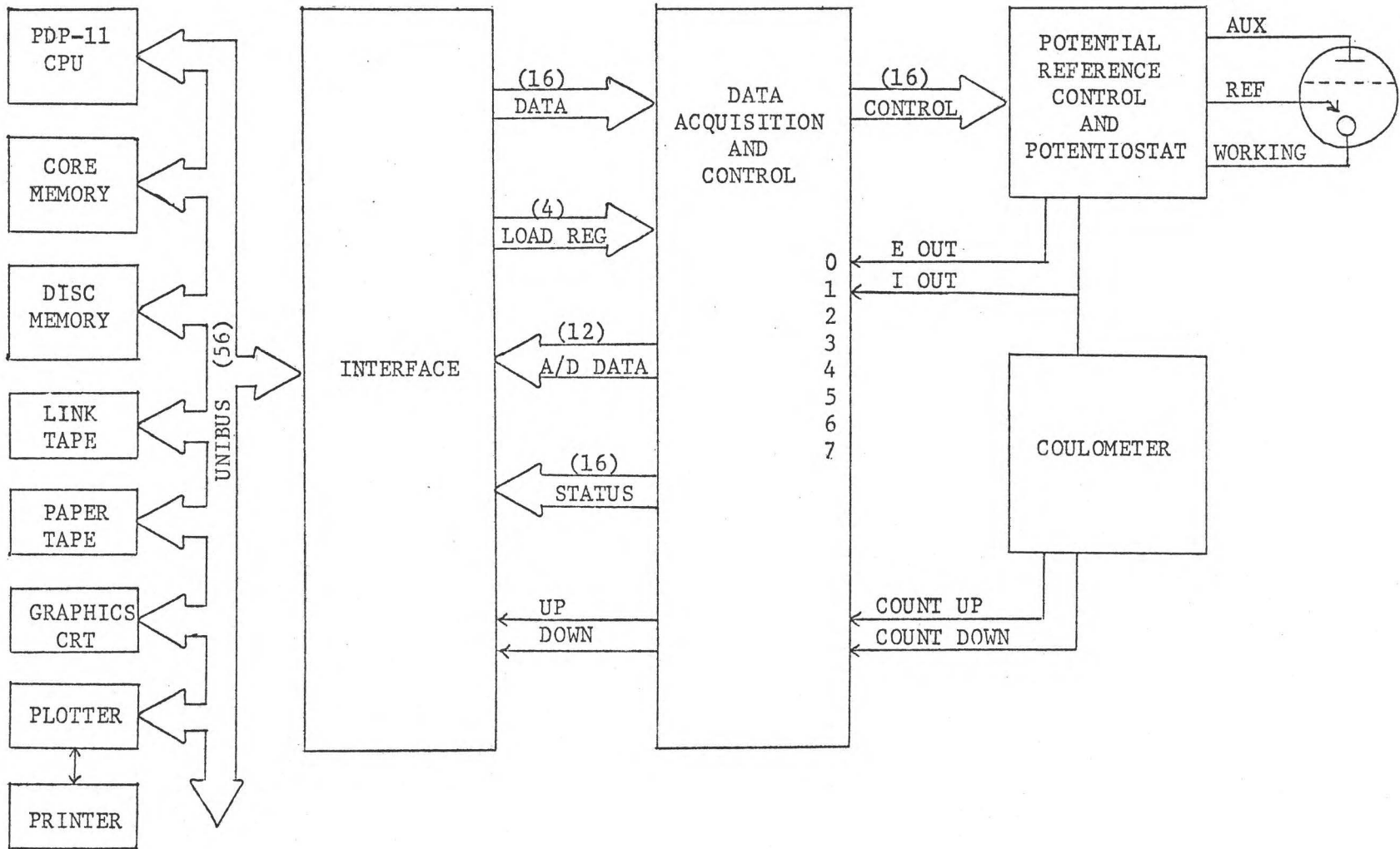


Figure 1. Block diagram of instrumentation for computer controlled scanning potential coulometry.

The Computer Interface

A block diagram of the computer interface is shown in Figure 2. This interface was constructed using standard TTL (Transistor-Transistor Logic) for control, input, and gating. Open collector TTL interface circuits were used to interface to the UNIBUS. The interface provides the control and interfacing logic to the PDP-11 UNIBUS for the computer to load four 16-bit registers in the data acquisition and control unit to control the various programmable functions in this unit, and to read four additional 16-bit registers. Two of these registers are in the data acquisition and control unit; one 12-bit register contains the digital output of the analog to digital converter and one 16-bit register contains the status information of various functions in the data acquisition and control unit. The other two registers, which can be read by the computer, are in the computer interface itself. The one register is a 16-bit general purpose register for reading 16 bits of digital information from any device with digital outputs. The other register is a special purpose 16-bit up/down counter which is used in conjunction with the coulometer. After each read operation, this counter is automatically cleared. This enables the computer to read the total accumulated counts (either positive or negative) since the last time the counter was read. The counter was placed in the computer interface for two reasons. First, it is capable of handling a pulse rate that is too fast for the computer, (up to 20 MHz), and second, it requires only two signal lines to the experiment instead of the sixteen that would be required if the counter were external to the interface. The interface also contains interface arbitration and control logic

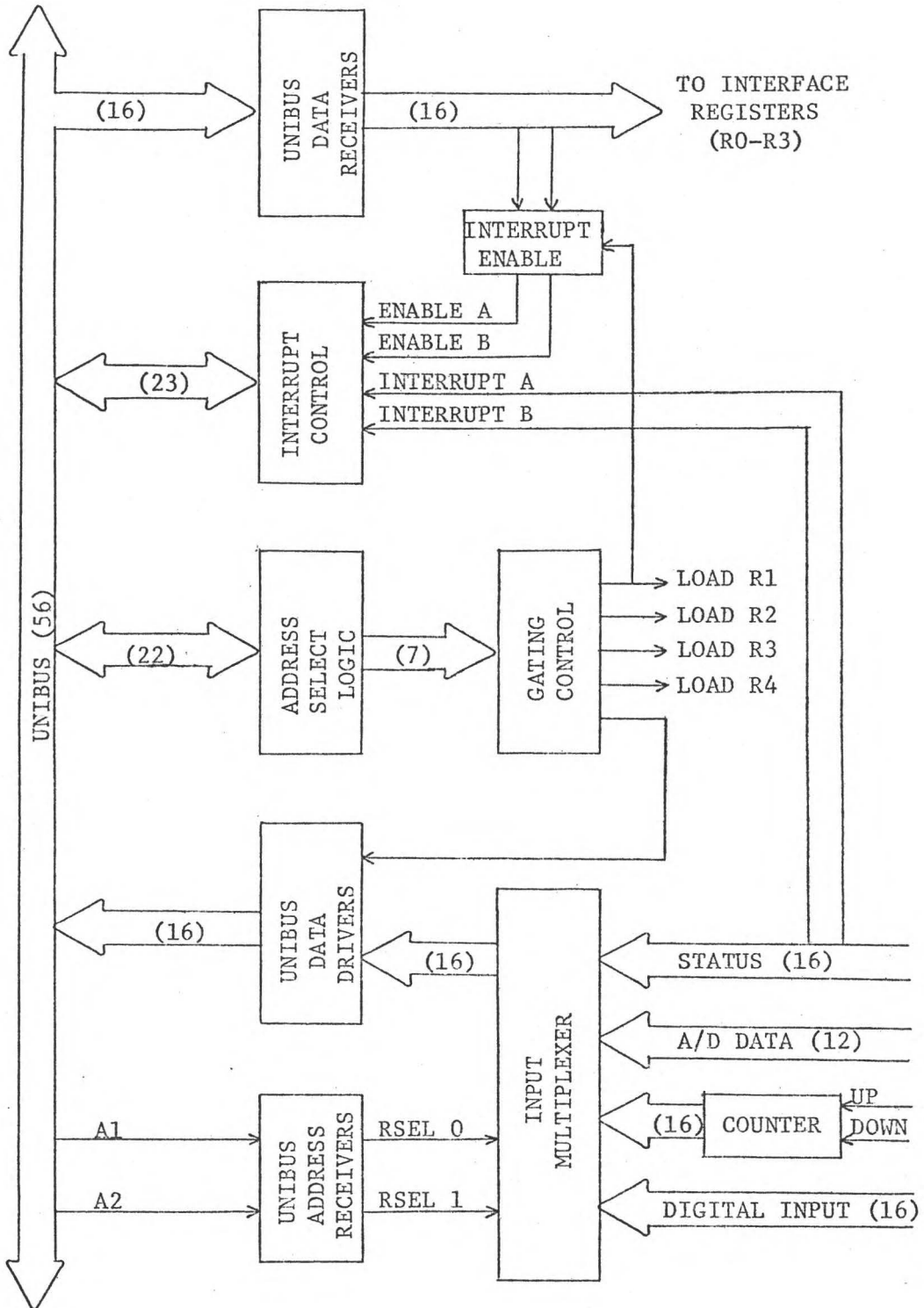


Figure 2. Block diagram of the PDP-11 computer interface to the data acquisition and control unit. See text for explanation.

for two different interface devices and interrupt vectors. When a device requests an interrupt, priorities permitting, the processor interrupts current processing and saves the location of the interrupted routine in memory. The processor then relinquishes UNIBUS control to the interrupting device, which sends the processor an interrupt command and a unique address of a memory location that contains the starting address of the device service routine. The processor then executes the device service routine, and, when this routine is complete, transfers control back to the interrupted routine at the point of interruption. One interrupt in the interface is initiated when the data acquisition and control unit has completed a new analog to digital conversion so a new datum is available. The other interrupt is initiated when the control sequence and decision logic in the data acquisition and control unit determines that new controls are needed. A complete description of the theory, operation, and interfacing to the PDP-11 UNIBUS can be found in manuals published by Digital Equipment Corporation (38,39).

The Data Acquisition and Control Unit

A block diagram of the data acquisition and control unit is shown in Figure 3. Schottky TTL circuits are used for the control and sequence logic to permit this unit to operate at high speed. Standard TTL circuits are used for the other digital functions and the registers in this unit. Sixteen bits of data are sent from the computer interface to four 16-bit registers in the data acquisition and control unit. Each of these registers is loaded individually by the four load register lines. The output of each of these registers

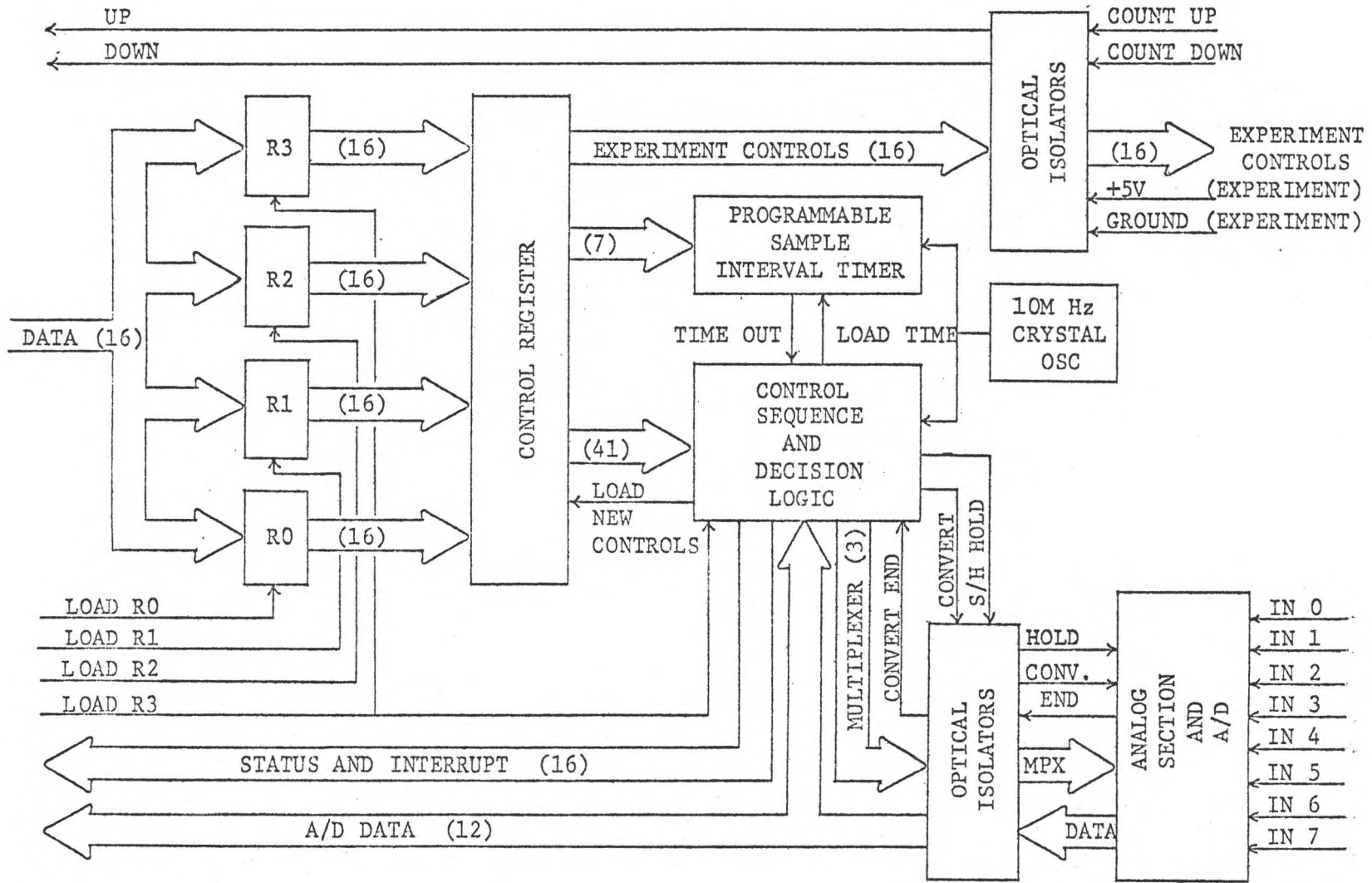


Figure 3. Block diagram of data acquisition and control unit. See text for explanation.

is connected to the input of a 64-bit control register. This arrangement of two register sets insures that new controls for the programmable functions and the experiment controls are available when the control sequence and decision logic requests new controls, rather than requiring the data acquisition and control unit to wait for the computer to load new controls. The computer can then load the next controls while the new controls are operational. The control sequence and decision logic will request new controls when the requested number of samples, programmable between 1 and 4095, has been taken or the most recent digitized datum, when compared with a programmable 12-bit value, meets one of the following programmable conditions: the datum is greater than the test value, the datum is greater than or equal to the test value, the datum is equal to the test value, the datum is less than or equal to the test value, the datum is less than the test value, or the datum is not equal to the test value.

There are a number of other programmable functions in the data acquisition and control unit. There are 16 optically isolated programmable control lines to the experiment. The sample interval is programmable between 5 microseconds and 160 seconds. The reference oscillator for the sample interval logic is a crystal oscillator stable to 0.001%. There is a programmable gain amplifier providing gains of 1, 4, 16, 64, 256, 1024. Any one of eight analog channels can be selected under program control either sequentially or randomly. If the channels are selected sequentially, the beginning and ending channels are also selected under program control.

The analog section is optically isolated from the digital section to prevent any digital noise in the analog section. The controls to the experiment, the count-up signals from the experiment, and the count-down signals from the experiment are also optically isolated. Optical isolation of all digital signal lines to and from the experiment prevents instrumentation at the experiment, having common analog and digital ground systems, from externally connecting the analog and digital ground systems in the data acquisition and control unit. Hewlett Packard 5082-4370 high gain optically coupled isolators are used to connect to the experiment controls, and Hewlett Packard 5082-4360 high speed optically isolated gates are used for the optical isolation of the analog section, the count-up signals, and the count-down signals.

An Analog Devices MPX 8A multiplexer is used to input analog signals. The multiplexer system is designed to input one of eight single-ended analog signals or one of four differential analog signals. The mode of operation is selected by a switch on the data acquisition and control unit. The programmable gain amplifier is constructed using two Analog Devices 605L instrumentation amplifiers and two Analog Devices AD7510KD CMOS switches to select the proper gain-resistors. These resistors are carefully trimmed to provide an accuracy of 0.02% for each of six programmable gains. An Analogic MP270 sample and hold amplifier and an Analogic MP2912A high speed 12-bit analog-to-digital converter complete the analog and analog-to-digital-conversion section. This section is capable of digitizing any one of eight analog signals either randomly or sequentially every five microseconds with 12-bit accuracy, (one part in 4096).

The digital output of the analog-to-digital converter is optically coupled to a 12-bit register. The output of this register is sent to the control and decision logic for comparison and to the computer interface for further data processing. Status and interrupt signals are also sent to the computer interface. The status register indicates the status of the input and the output registers, the multiplexer, and the error register. The data acquisition and control unit is connected to the computer interface through multiple, individually shielded signal lines to provide a powerful and versatile system for data acquisition, experiment control, and interactive experiment control.

The Potentiostat Potential Control And Potential Reference

A schematic diagram of the potentiostat potential control and potential reference is shown in Figure 4. Control signals from the data acquisition and control unit (CO-C11) are used to control the output of the potentiostat potential control. Twelve 7408 TTL AND gates are used to buffer the control signals to the Analog Devices AD562AD-BIN 12-bit digital-to-analog converter. The buffers present a minimum load to the control signals and to the digital-to-analog converter. A single TTL load is presented to each control line and to each input to the digital-to-analog converter. The output of the digital-to-analog converter is a current that is proportional to the binary value at the input. The output current of the digital-to-analog converter is also proportional to the current at the reference input of the converter. A constant current reference source was constructed using an Analog Devices AD580-KH low

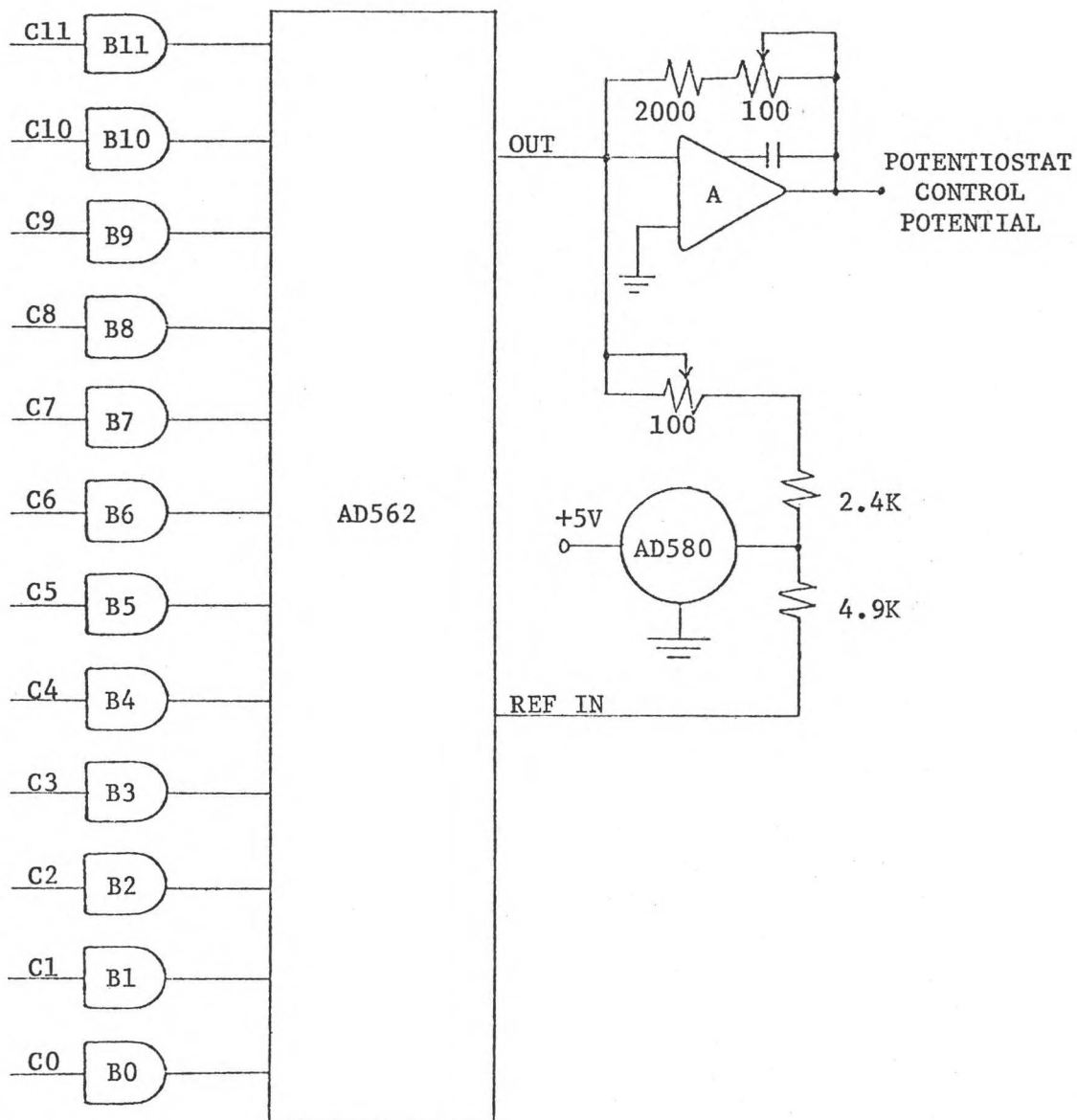


Figure 4. Schematic diagram of potentiostat potential control and reference. See text for explanation.

drift voltage reference source and a 4.9-kohm resistor. The use of a constant current source at the reference input insures that the output of the digital-to-analog converter is always proportional to the binary value at its input. Amplifier A is an Analog Devices AD504LH low drift, low noise operational amplifier used as a current follower to convert the output current of the digital-to-analog converter to a potential proportional to the current. The output potential is offset 2048 millivolts using the voltage reference source, a 2.4-kohm low-temperature-coefficient resistor, and a 100-ohm 10-turn trimpot to offset the input current. This provides an output potential range of -2.048 volts to +2.047 volts in one millivolt steps.

The Potentiostat

A schematic diagram of the potentiostat is shown in Figure 5. Amplifiers A1 and A2 are Analog Devices 234K chopper-stabilized operational amplifiers. Amplifier A3 is an Intech A186 ultra low drift operational amplifier. Amplifiers B1 and B2 are Intech A401 current boosters used to provide up to 100 milliamperes at the output of the control amplifier and the current follower amplifier. This configuration of amplifiers for potentiostatic control was first proposed by Deford (40) as an extension of the circuit developed by Booman in 1957 for coulometry (41). Amplifiers A1 and B1 are used together as the control amplifier. The control amplifier adjusts its current output to maintain the potential between the reference electrode and the working electrode at the control potential. The control amplifier summing network consists of the 99.18-kohm

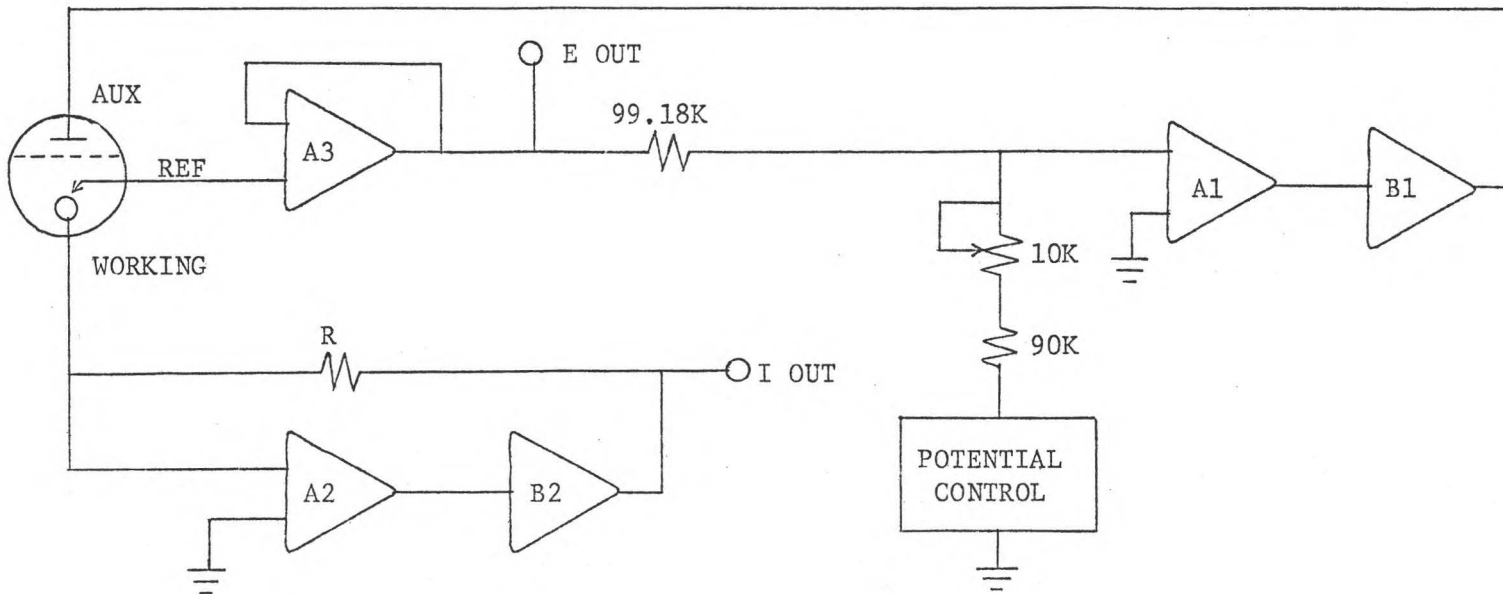


Figure 5. Schematic diagram of Potentiostat. See text for explanation.

resistor, the 90-kohm resistor, and the 10-kohm trimmer. Amplifier A3 is used as a voltage-follower to prevent loading of the reference electrode by the summing network of the control amplifier. Because of its high input impedance, this amplifier draws negligible current from the reference electrode. It also provides a low impedance output signal (E OUT) which is the potential of the reference electrode with respect to ground. Amplifiers A2 and B2 are used as the current follower amplifier. This amplifier generates a potential (I OUT) which is proportional to the current flowing in the cell. It also maintains the potential of the working electrode at virtual ground. Resistor R is a switch-selectable network of resistors in the feedback loop of the current follower providing six current ranges from 1 microampere full scale to 100 milliamperes full scale. Each current range provides a full scale output of 10 volts.

The Coulometer

A schematic diagram of the coulometer is shown in Figure 6. The coulometer consists of an absolute value and sign amplifier and a voltage-to-frequency converter which in conjunction with a counter effectively integrates the current. Amplifiers A1 and A2 are Analog Devices AD504JH low drift and low noise operational amplifiers which, in conjunction with diodes D1-D6 and resistors R1-R4, form the absolute value amplifier. The diodes are IN458 silicon diodes, and the resistors R1-R4 are an Analog Devices AD1830LD/10K thin film resistor network. In operation (42) amplifier A2, in conjunction with diodes D3-D6 and resistors R3-R4, behaves as an ideal diode to faithfully reproduce positive inputs and to provide a signal for

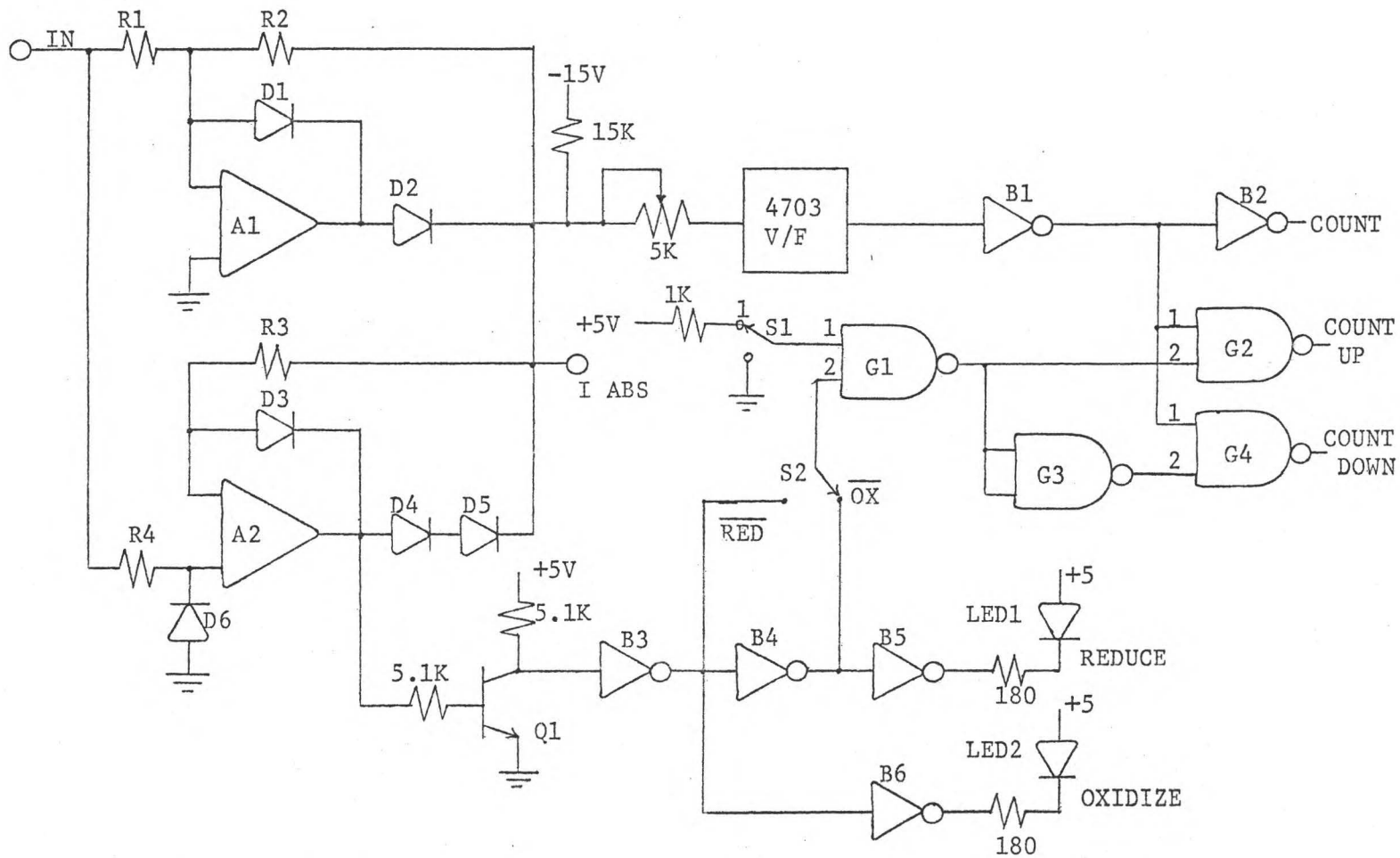


Figure 6. Schematic diagram of coulometer. See text for explanation.

transistor Q1, which indicates the sign of the input. Amplifier A1, in conjunction with diodes D1 and D2 and resistors R1 and R2, will invert negative inputs but not positive inputs. The output (I ABS) of the absolute value amplifier is connected to a Teledyne Philbrick 4703 voltage-to-frequency converter through a 5-kohm trimpot. This trimpot is used to adjust the output of the voltage-to-frequency converter during standardization. Transistor Q1 is a 2N3019 small signal switching transistor used to indicate the sign of the input signal. A 7406 TTL hex inverter is used for buffers B1-B6 and a 7400 TTL quad two-input NAND gate is used for gates G1-G4.

A positive signal at the input indicates that there is a reducing current at the working electrode. Transistor Q1 is turned on by amplifier A1 presenting a logic 0 signal at the input of B3 resulting in a logic 1 at the output of B3 ($\overline{\text{RED}}$) and a logic 0 at the output of B4 ($\overline{\text{OX}}$). If there is an oxidizing current at the working electrode, the transistor will be turned off resulting in a logic 0 at the output of B3 and a logic 1 at the output of B4. The output of the voltage-to-frequency converter is buffered by buffer B1. The output of B1 is connected to buffer B2 and to one input of gate G2 and one input of gate G4. Switch S1 determines if both count-up and count-down operations can occur. With switch S1 connected to a logic 1, the output of gate G1 is determined by the logic level at input 2 of G1. With S2 connected to $\overline{\text{OX}}$, the counter connected to the count-up and the count-down signals will count up with oxidizing current and count down with reducing current. The count rate will be proportional to the current. With switch S2 connected to $\overline{\text{RED}}$, the counter will count up with reducing current and

count down with oxidizing current. With switch S1 at a logic 0 level the output of G1 is always high and the output of G3 is always low so the counter will always count up.

Performance and Extensions of the Potentiostat,
The Potentiostat Potential Control,
And the Coulometer

The potentiostat potential control, the potentiostat, and the coulometer were all constructed in one enclosure to produce a single, self-contained instrument capable of a variety of controlled potential coulometric and voltammetric studies. A binary-coded decimal-to-offset binary code converter was constructed from standard TTL circuitry to provide the offset binary code for the potentiostat potential control when the instrument is not controlled by the computer. The binary-coded-decimal code is provided by thumbwheel switches on the front panel. In addition, another switch on the front panel can be used to select an external signal source as the potentiostat control potential. A six digit up/down counter and display are also incorporated into the front panel to provide a readout for the coulometer when the instrument is not used in conjunction with the computer. This is especially useful when performing conventional controlled-potential coulometric analyses.

The potentiostat potential control exhibits both long and short term stability. The control potential is always within 0.4 millivolt of the programmed control potential. The potentiostat is able to control the potential of the working electrode to within 0.1 millivolt of the control potential. The difference between the potential of the working electrode and the control value sent by the

computer is within 0.5 millivolt. This accuracy limitation is due primarily to the resolution limitations of the digital-to-analog converter. This inaccuracy is acceptable since the computer can set the control potential only to the nearest millivolt.

The current follower is accurate to 0.01% of the full scale reading on the three current scales used for scanning potential coulometry. The absolute value amplifier is accurate to 0.02% of the full scale range. The voltage-to-frequency converter has a linearity of 0.03% of the full scale range. Maximum accuracy is maintained by placing the follower on the most sensitive scale that will handle the maximum current during a scan. Controlled potential coulometric determinations precise to 1 part in 2500 are easily performed with this instrumentation.

The Scanning Potential Coulometric Cell

The platinum working electrode cell shown in Figure 7 was used for all the scanning potential coulometric scans reported in this work. This cell is similar in design to a cell described by L. P. Rigdon and J. E. Harrar (43). The cell used for this work has slightly smaller dimensions, uses a glass frit with a fumed silica gel salt bridge (44) for the counter electrode separator rather than a porous Vicor tube, and uses a larger magnetic Spinfin to effect better stirring.

Two other cells were constructed and the performance of each was investigated. The first cell is similar to one described by Scott, Perkema, and Connally (15). This cell has a glass frit bottom and two side arms connected to the main cell compartment

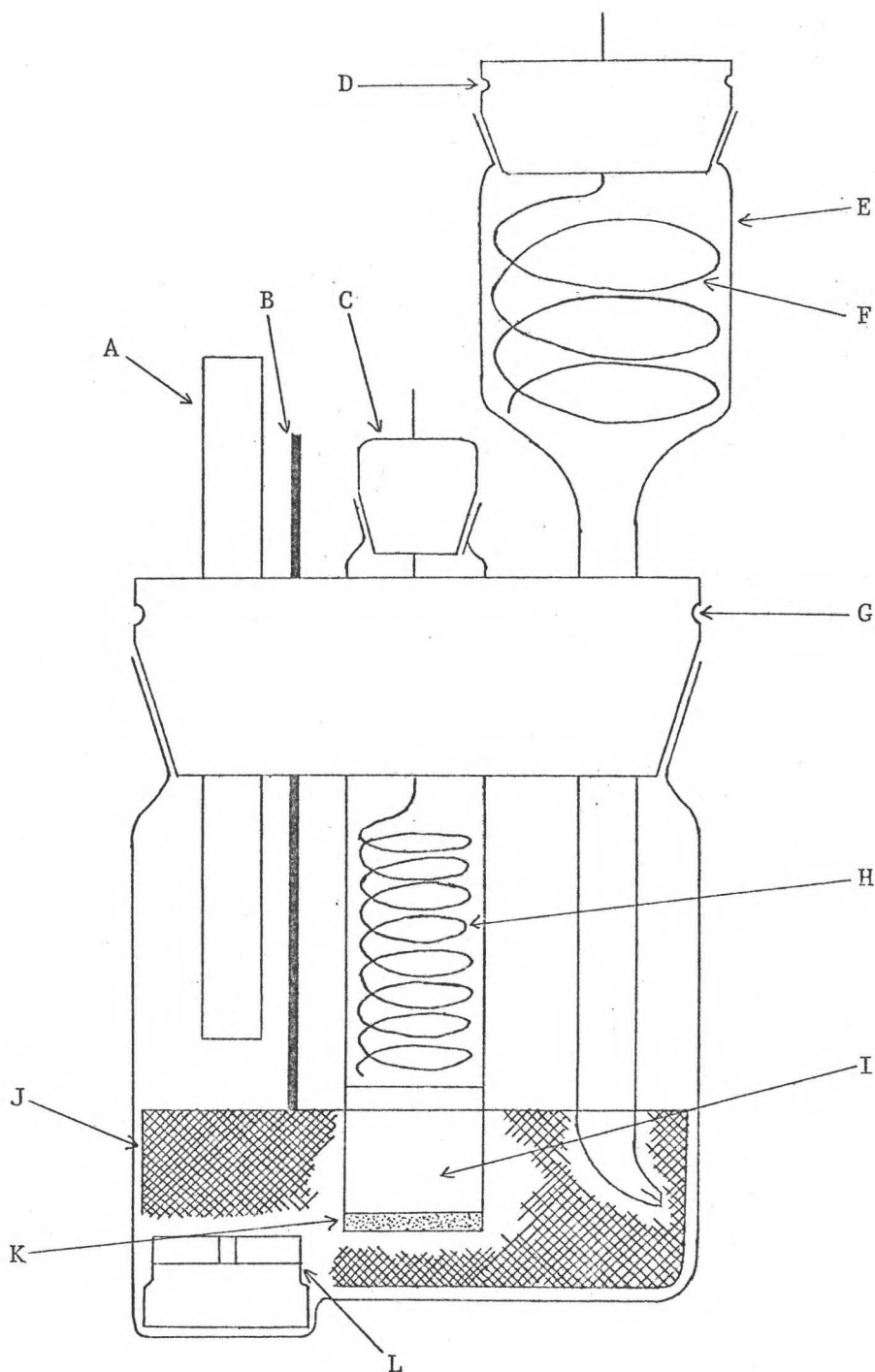


Figure 7. Coulometric cell. A--nitrogen gas inlet; B--connection to working electrode; C--polyethylene cap; D--Teflon cap; E--reference electrode compartment; F--Ag-AgCl reference electrode; G--Teflon cell cap; H--platinum counter electrode; I--fumed silica plug; J--platinum gauze working electrode; K--course glass frit; L--magnetic Spinfin.

through glass frits. The side arms contain the counter electrode and the reference electrode. Solution deoxygenation and stirring are accomplished by bubbling nitrogen through the glass frit on the bottom. This cell has nonuniform potential distribution due to geometrical effects (45,46) and has spray losses from deoxygenation and stirring that contribute to errors as high as 5%. The second cell tested is one similar in design to the rotated cells described by Clem and co-workers (47,48). A solid silver working electrode and a solid graphite working electrode are both used in the rotating cell. A coaxial reference/counter-electrode probe similar to the one described by Clem and co-workers is also used. Solution deoxygenation and analysis are rapid with this cell, but the solution spray at the probe tip results in solution loss and poor accuracy and precision.

The cell used in this work has good geometry, employs the simplicity of magnetic stirring, and permits deoxygenation by the gas-overflow method, which eliminates solution loss due to spray. The coaxial placement of the counter and working electrodes insures a uniform working-electrode potential from the standpoint of geometrical effects (45,46). The unsymmetrical stirring may cause some nonuniformity in the working electrode potential, but the control voltage will not be exceeded at any point of the working electrode because the reference electrode is placed in the region where the rate of mass transfer is the lowest.

The cell was constructed from a 40/50 Pyrex ground glass joint. The taper was cut to be 10-mm in length and a flat bottom was formed 50-mm from the bottom of the taper. The cylindrical

cavity for the magnetic Spinfin was formed by depressing a 1/2-inch-diameter graphite rod into the cell bottom while the cell bottom was still molten. The counter electrode compartment was formed by cutting off one end of a 10-mm course Pyrex sealing tube and joining the other end to a 10/14 Pyrex ground glass joint. The reference electrode compartment was constructed by joining a 14/20 Pyrex ground glass joint to a 6-mm OD tube. The Teflon cell cap was machined from 4-cm-diameter Teflon stock. Holes for the gas inlet, the counter electrode compartment, the wire to connect to the working electrode, a sample port, and the reference electrode compartment were drilled for a snug fit on all parts. The reference electrode compartment tip was formed with an asbestos fiber in the tip after it was inserted into the cell cap. The gas inlet tube is a firepolished piece of 6-mm OD Pyrex tubing. The working electrode was made from a piece of platinum gauze 12.2-cm x 4.3-cm. The platinum gauze was folded over in thirds and the ends were joined by weaving a length of 0.2-mm platinum wire through the joined ends. The counter electrode is a length of 0.2-mm platinum wire formed into a helix. The Ag-AgCl electrode is a length of 0.5-mm silver wire formed into a helix. The silver helix was oxidized electrochemically for 5 minutes in a 6F HCl solution to form a AgCl precipitate on the surface of the electrode. The Teflon cap to the reference electrode was machined from 2-cm Teflon stock, and the polyethylene cap to the counter electrode compartment is a standard polyethylene stopper that fits a 10/14 taper. The Spinfin was machined slightly so it will clear the

platinum gauze working electrode. The sample port is plugged with a polyethylene rod having a small hole in it to vent the nitrogen.

The Supporting Electrolyte Pretreatment Cell

Heavy metal impurities that can be reduced at a mercury cathode are removed from the supporting electrolyte by controlled-potential electrolysis (49) using the cell shown in Figure 8. The cell was designed to hold 2 liters of solution. The cell was constructed from a 6-inch diameter cylindrical jar and two Teflon stopcocks joined to the jar as shown in Figure 8. Cross contamination from the reference and the counter electrodes is prevented by the use of bridge tubes. These tubes were constructed by joining 24/40 Pyrex joints to 20-mm Pyrex sealing tubes and cutting the sealing tubes just below the glass frits. The cell cap was machined from 1/4-inch plexiglass, and the bridge tube caps are standard polyethylene stoppers. A saturated calomel electrode is used as the reference electrode, and a formed platinum gauze electrode is used as the counter electrode. The solution is deoxygenated by a steady flow of nitrogen through a gas dispersion tube. A tygon tube and a leveling bulb connected to stopcock L serve as the mercury reservoir. Mercury is introduced through this stopcock at the bottom of the cell to prevent any oxide, which has accumulated on the surface of the mercury in the reservoir, from entering the cell. The solution and mercury pool are stirred with a Teflon coated magnetic stirring bar. Contact to the mercury pool is made with a platinum wire sealed in a glass tube. A mercury pool in the glass tube makes electrical contact between the platinum wire and a copper wire connected to

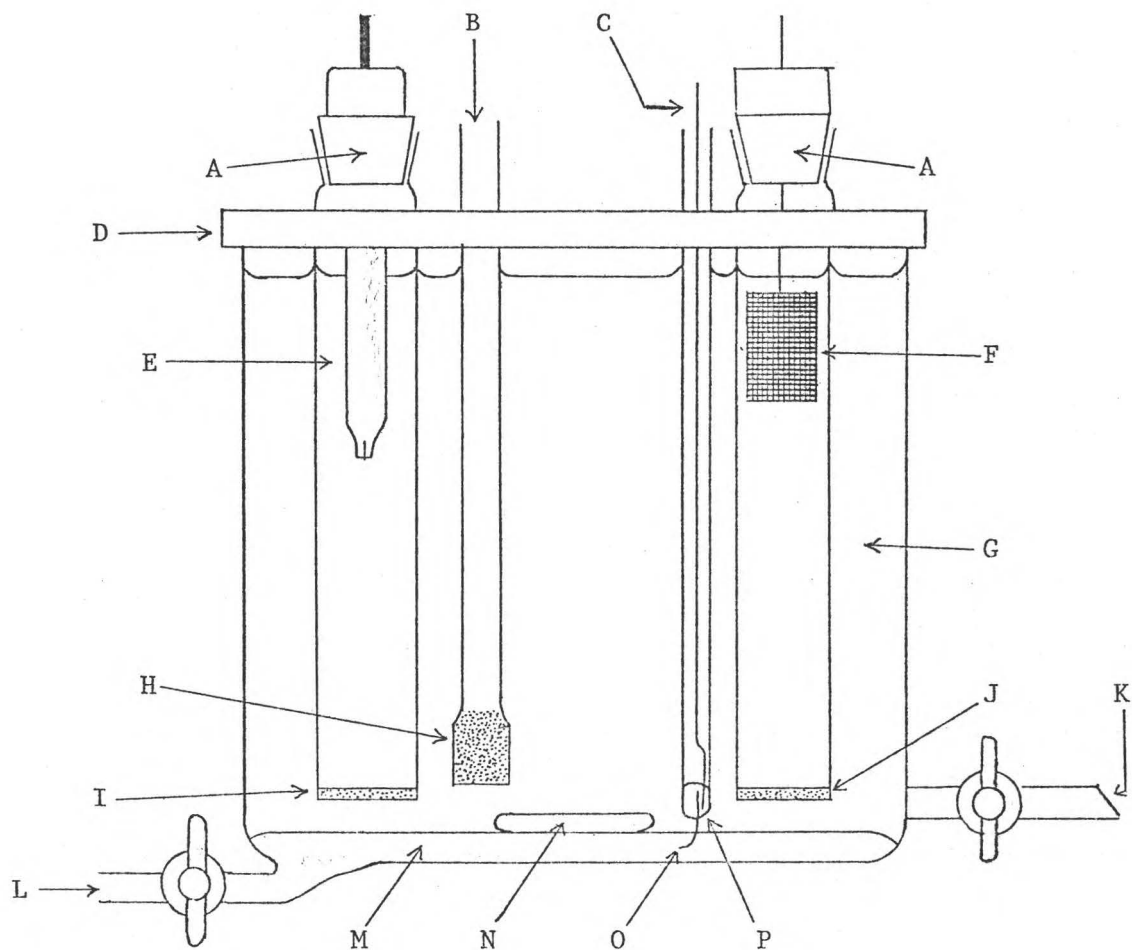


Figure 8. Supporting electrolyte pretreatment cell. A--polyethylene caps; B--nitrogen inlet; C--connection to mercury electrode; D--plexiglass cell cover; E--reference electrode; F--platinum gauze counter electrode; G--electrolyte solution; H--course gas dispersion tube; I--fine glass frit; J--medium glass frit; K--pretreated solution outlet; L--mercury inlet; M--mercury working electrode; N--magnetic stirring bar; O--platinum contact; P--platinum-glass seal with mercury contact to platinum and copper wire.

the potentiostat. The pretreated solution is drained into a clean container through the stopcock labeled K. Electrolysis is continued during draining to prevent spontaneous dissolution of impurities back into the pretreated solution.

III. EXPERIMENTAL

Instrumentation and Apparatus

The potentiostat, the potentiostat potential reference and control, the coulometer, the data acquisition and control unit, the computer interface and computer system, and the cells used for this work are described elsewhere in this dissertation. A Digitec model 269 multimeter was used to calibrate the potentiostat and the potentiostat potential reference and control. The current follower in the potentiostat was calibrated by adjusting the resistance in the feedback loop of the current follower to obtain a calibrated output. A constant potential from the potentiostat was applied across a Leeds and Northrup standard resistor to provide a constant current source for current follower calibration. The output potential of the current follower was measured by the Digitec model 269 multimeter. The calibrated output of the current follower was used to calibrate the coulometer. A Hewlett Packard model 5382A frequency counter was used to measure the output frequency of the voltage-to-frequency converter during calibration. A Tektronix model 7633 multimode storage oscilloscope with a 7A18 dual trace vertical amplifier and a 7B53A dual time base was used to observe current-time and current-potential relationships during potential scans. It was also used to study alternating current phase relationships of the periodic signal superimposed on the electrolysis current with respect

to the rotation of the magnetic stirrer and the 60 Hz AC line frequency. A Sargent model number S-76490 magnetic stirrer capable of 1200 RPM was used to rotate the magnetic Spinfin in the electrolysis cell, and a Precision Scientific Mag-Mix magnetic stirrer was used to rotate the stirring bar in the supporting electrolyte pretreatment cell.

Containers for Supporting Electrolyte And Standard Metal-Ion Solutions

Supporting electrolyte and standard metal-ion solutions were prepared and stored in polyethylene and polypropylene containers. All containers were soaked in a Radiacwash solution for at least 24 hours. "Radiacwash is a liquid compound that optimally combines a number of different chemical and physical principles causing it to act as a surface-wetting sequestering agent, chelater, carrier, ion-exchanger, emulsifier, solvent, complexer, peptizer, and detergent" (50). The containers were then rinsed with copious amounts of deionized distilled water and then left to dry in the air. Opaque polypropylene containers were used to store the standard silver ion solutions and the standard silver and iron ion mixtures. Polyethylene containers were used to store all solutions that did not contain any silver.

Preparation of Supporting Electrolyte And Standard Metal-Ion Solutions

Supporting electrolyte solutions were prepared by diluting reagent-grade perchloric acid with deionized distilled water. All supporting electrolyte solutions were 0.2 F in perchloric acid. Analysis of the supporting electrolyte by scanning potential

coulometry revealed impurities with concentrations ranging from 10^{-7} F to 10^{-5} F. Heavy metals which can be reduced to the metallic state at a mercury cathode were removed from solution by controlled potential electrolysis. The mercury cathode was held at -1.2 volts vs. the SCE. This potential was maintained at least 60 hours while the solution and the mercury cathode were stirred by the magnetic stirrer and nitrogen was bubbled through the solution. The solution was then drained into a clean polyethylene container while the control potential was still maintained to prevent spontaneous dissolution of the deposited heavy metal impurities into solution. Any impurities left in the pretreated supporting electrolyte were undetectable by scanning potential coulometry.

Standard metal-ion solutions were prepared gravimetrically by dissolving weighed quantities of reagent-grade materials in the pretreated supporting electrolyte solution. The standard iron solution was prepared by dissolving Baker analytical reagent iron wire in the pretreated supporting electrolyte. The solution was stirred constantly by placing the container on a vibrating magnetic stirrer. The iron wire dissolved in four days. The standard silver solution was prepared by dissolving Baker analytical reagent silver nitrate in the pretreated supporting electrolyte. Successive dilutions of standard metal-ion solutions with the pretreated supporting electrolyte were used to prepare standard metal-ion solutions and standard metal-ion mixtures. Successive dilutions were also carried out gravimetrically. All standard metal-ion solutions and successive dilutions were prepared using a Mettler model 315 kilogram

analytical balance. Standard solutions with metal-ion concentrations from 10^{-7} moles/kg to 10^{-4} moles/kg were prepared.

Electrolysis Cell Preparation and Storage

At the end of each day the main cell compartment and the magnetic Spinfin were rinsed with deionized distilled water and then left to soak in a Radiacwash solution overnight. The platinum gauze working electrode was rinsed with deionized distilled water and left to soak in 6 F nitric acid for one hour. The electrode was then rinsed with deionized distilled water and left to soak in a Radiacwash solution overnight. The outside of the reference electrode cell compartment and the outside of the counter-electrode cell compartment were rinsed with deionized distilled water and then allowed to dry overnight. Every 3 to 10 days both the reference electrode cell compartment and the counter electrode cell compartment were rinsed inside and out with deionized distilled water, left to soak in Radiacwash for at least four hours, rinsed with copious amounts of deionized distilled water, and then left to dry in the air. A fumed silica salt-bridge (44) for the counter-electrode cell compartment was prepared using fumed silica, trade named Cab-O-Sil, grade HS-5, by its manufacturer, the Cabot Corporation. The fumed silica was used in about 10% concentration by weight to cause the pretreated supporting electrolyte to gel. The gelatinous electrolyte was drawn into a 9-inch disposable Pasteur pipet with suction from an aspirator. The gelatinous electrolyte was then injected into the dry counter-electrode cell compartment by application of pressurized nitrogen on the pipet. The gelatinous electrolyte was

added to a depth of 1.5-cm in the counter-electrode cell compartment. Pressurized nitrogen was then applied to the top of the counter-electrode cell compartment until the bottom of the glass frit appeared wet. This last step was required to prevent separation of the gelatinous electrolyte from the glass frit. The counter-electrode cell compartment was then filled with the pretreated supporting electrolyte and the counter-electrode was placed in this compartment.

A small amount of the gelatinous electrolyte was injected into the tip of the reference electrode cell compartment. This was a precautionary measure to reduce cross contamination between the reference electrode cell compartment and the main cell compartment. This cell compartment was then filled with 1.000 F KCl, and the Ag-AgCl electrode was placed in this cell compartment. The reference electrode cell compartment will accommodate commercially available miniature electrodes, but none of these was used in the work reported here.

Procedure

The main cell compartment, the platinum working electrode, and the magnetic Spinfin were each rinsed with copious amounts of deionized distilled water. The working electrode and the magnetic Spinfin were then positioned in the main cell compartment using polypropylene forceps. About 15 grams of solution was poured directly into the electrolysis cell. The weight of the solution for analysis is determined by the weight difference of the solution container. The cell cap holding the counter and reference electrode

was then placed in the main cell compartment and the cell was mounted on a magnetic stirrer. The cell was connected to the potentiostat, which was set at a potential that would reduce the constituents to be analyzed. This reducing potential was maintained until the current decayed to a constant background. This required about 30 minutes. Oxygen in the solution was removed by passing nitrogen over the solution while it was being stirred. The nitrogen used was commercial "pure" nitrogen passed through a column of BASF BTS catalyst (51,52) that was purchased from BASF Wyandotte Corporation under the name of Catalyst R3-11. The catalyst is an activated form of finely divided copper on an inert support, and it removes oxygen that might be present in the nitrogen to below the 1-ppm level. The nitrogen was then bubbled through a pretreated supporting electrolyte solution. Nitrogen was passed over the solution and the solution was stirred both during the reduction step and during the potential scan.

When a constant background current is attained, the potential scan is started. The potential scan is controlled by the PDF-11/20 mini computer. The program to generate the potential scan and store the data is listed in Appendix A. This program will generate either linear or nonlinear scans. In the nonlinear scan mode the potential is stepped only when near equilibrium conditions exist. The accumulating charge is continuously monitored and rate of change of charge accumulation is tested by linear least squares for zero slope. When the slope is zero or very near zero the current is the result of faradaic background currents, and their

contribution is subtracted from the accumulated charge. The computer then generates the next potential step for the potentiostat.

The maximum scan rate, in potential regions where there is no electrolysis of sample, is limited to nine 1-mV steps-per-second. This is the maximum scan rate that permits accurate determinations of slope by linear least squares analysis. In potential regions where there is electrolysis of sample constituents the potential scan is stopped until the electrolysis current has decayed to the background. The computer thus maintains optimum scan-rate conditions throughout the scan. In the linear scan mode the charge at each potential step is collected and the next potential step is generated to maintain the chosen scan rate. This part of the program is not interactive nor does it subtract the background current. It maintains a linear scan rate without regard of the magnitude of the electrolysis current. In both the linear and non-linear scans the data from the scan are stored in core memory during the scan. When the scan is complete the data are transferred from the core memory to the disc memory for later data analysis. Two additional scans for each sample are generally run. The reduction step for each additional scan is accomplished in about 10 minutes. Because the first reduction step is combined with solution deoxygenation, it takes about 20 to 30 minutes longer than subsequent reduction steps.

Pretreatment of the platinum gauze electrode was necessary for accurate determinations of trace quantities of silver. The

rinsing, assembly, and set-up procedure that was followed for the analysis was followed for the working electrode pretreatment, with the exception that about 20 milliliters of 10^{-4} F silver-ion solution was poured into the cell. Neither the amount of silver solution added to the cell nor its concentration need be known accurately. A reducing potential of -0.1 V vs. the Ag-AgCl reference electrode was maintained on the working electrode until the electrolysis current decayed to a constant background. A control potential of 0.6 V was then maintained on the working electrode until the electrolysis current decayed to a constant background. This procedure was repeated two more times. The cell was emptied by inserting a polyethylene tube, which was connected to a suction flask, through the sample port into the solution. The oxidizing potential was maintained during solution removal to prevent spontaneous reduction of the silver ion onto the pretreated electrode. The cell and electrode were rinsed and assembled for sample analysis.

IV. RESULTS AND DISCUSSION

Discussion

Two electrochemical systems were studied in order to determine both the sensitivity and the resolution of computer controlled scanning potential coulometry. Iron and silver were chosen because they exhibit different electrochemical behavior. The iron exists as the ferrous and the ferric ions, both soluble species in solution. The silver exists as the soluble silver ion and as the insoluble metallic silver. Also, iron and silver are known to interfere in controlled potential coulometric determinations of each other (52-55). Silver interferes in controlled potential coulometric determinations of iron (53,54), and iron interferes in controlled potential coulometric determinations of silver (55,56). An indication of the resolving capability of computer controlled scanning potential coulometry can be obtained by analyzing for these constituents. The data obtained by scanning potential coulometry are analyzed by non-linear least squares curve fitting to resolve overlapping peaks and background. An equation that accurately describes the data is a necessary prerequisite for curve fitting. A listing of the analysis program can be found in Appendix B.

The charge required to reduce a constituent is expressed by the following equation:

$$Q_E = nFVC_r \quad (2)$$

where n is the number of equivalents per mole, F is the faraday, V is the volume of solution, and C_r is the concentration of the reduced form of the sample constituent produced in the reaction. Q_E is the charge required to reduce a sample constituent to produce VC_r moles of the reduced species when the concentration of the reduced species is zero at the beginning of the electrolysis. The concentration of the reduced species can also be expressed as

$$C_r = C - C_o \quad (3)$$

where C is the formal concentration of the sample constituent and C_o is the concentration of the oxidized species. Equation (2) can be rewritten as

$$Q_E = nFV (C - C_o) \quad (4)$$

by combining Equation (2) and Equation (3).

The Nernst equation describes the potential on an inert electrode for a reversible reaction involving only soluble ions

$$E = E^o - \frac{RT}{nF} \ln \frac{a_r}{a_o} \quad (5)$$

where E is the potential on the electrode, E^o is the standard potential, R is the ideal gas constant, T is the temperature, a_r is the activity of the reduced species and a_o is the activity of the oxidized species. Equation (5) can also be written as

$$E = E^o - \frac{RT}{nF} \ln \frac{y_r}{y_o} - \frac{RT}{nF} \ln \frac{C_r}{C_o} \quad (6)$$

where y_r is the activity coefficient of the reduced species, y_o is the activity coefficient of the oxidized species, C_r is the concentration of the reduced species, and C_o is the concentration of the oxidized species. The potential where the concentration of the oxidized and reduced species are equal can be expressed as

$$E_p = E^o - \frac{RT}{nF} \ln \frac{y_r}{y_o} \quad (7)$$

where E_p is the location of the peak for computer controlled scanning potential coulometry. Combining Equations (3), (6), and (7) one obtains an expression for potential in terms of concentration

$$E = E_p - \frac{RT}{nF} \ln \frac{C - C_o}{C_o} \quad (8)$$

Solving Equation (8) for C_o one obtains

$$C_o = \frac{1}{1 + e^{[(E_p - E) \frac{nF}{RT}]} \quad (9)$$

Substituting Equation (9) into Equation (4) one obtains

$$Q_E = nFVC \left[1 - \frac{1}{1 + e^{[(E_p - E) \frac{nF}{RT}]} \right] \quad (10)$$

The control program for computer controlled scanning potential coulometry stores the total charge collected during each millivolt step, and not the total accumulated charge during the potential scan. The charge collected during each 1-millivolt step is given in the following equation:

$$Q_{Es} = nFVC \left[\frac{1}{1 + e^{[(E_p - E_L) \frac{nF}{RT}]} - \frac{1}{1 + e^{[(E_p - E) \frac{nF}{RT}]} \right] \quad (11)$$

Q_{Es} is the charge collected during the 1-millivolt step at

potential E and E_L is defined as

$$E_L = E - .001S \quad (12)$$

where S is $+1$ or -1 depending on the scan direction.

The Nernst equation also describes the potential on an inert electrode for the reversible deposition of an insoluble substance. If the electrode is completely covered with at least a monolayer of the deposit the Nernst equation has the form

$$E = E^O - \frac{RT}{nF} \ln \frac{1}{a_o} \quad (13)$$

where the activity of the deposit is unity. When one is dealing with relatively large amounts of electroactive substance, an inert electrode is almost instantaneously covered with a deposit after passage of current (57,58).

Equation (13) can also be written as

$$E = E^O - \frac{RT}{nF} \ln \frac{1}{y_o} - \frac{RT}{nF} \ln \frac{1}{C_o} \quad (14)$$

If E_p is defined as

$$E_p = E^O - \frac{RT}{nF} \ln \frac{1}{y_o} \quad (15)$$

then one can write

$$E = E_p - \frac{RT}{nF} \ln \frac{1}{C_o} \quad (16)$$

Solving Equation (16) for C_o , one can write

$$C_o = \frac{1}{e^{[(E_p - E) \frac{nF}{RT}]} \quad (17)$$

During a potential scan the concentration of the oxidized species cannot exceed the formal concentration of the constituent.

Equation (17) would allow the concentration of the oxidized species to go to infinity. Delahay has solved this boundary condition (57). The boundary condition is a function of the complement of the error function and the fraction of substance reduced. Using Delahay's treatment of this boundary condition leads to the following equation

$$C_o = \frac{K}{e^{[(E_p - E) \frac{nF}{RT}]}} \operatorname{erfc} \left[\frac{e^{[(E_p - E) \frac{nF}{RT}]} }{C} \right] \quad (18)$$

where erfc is the complement of the error function and K is a constant. The charge at each 1-millivolt step is given by

$$Q_{Es} = nFVK \operatorname{erfc} \left[\frac{e^{[(E_p - E) \frac{nF}{RT}]} }{C} \right] \left[\frac{1}{e^{[(E_p - E_L) \frac{nF}{RT}]} } - \frac{1}{e^{[(E_p - E) \frac{nF}{RT}]} } \right] \quad (19)$$

The activity of trace amounts of a deposit on an inert electrode is not unity until the electrode is completely covered by the deposit (20, 56-65). Herzfeld (64) suggested that activity of the deposit would be proportional to the fraction of the electrode surface covered. Rogers and Stehney (59) have extended the concept of Herzfeld by making the following assumptions: (A) the activity of the deposit on an inert electrode is a product of the fraction of the electrode area covered by the deposit and the activity coefficient of the deposit; (B) a second layer of deposit is not formed until the surface of the electrode is covered with a monolayer of the deposit. Because of these assumptions the activity of the deposit on a partially covered inert electrode is given by

$$a_r = f_r y_r = \frac{N_r A_r y_r}{A_e} = \frac{(C - C_o) V N_a A_r y_r}{A_e} \quad (20)$$

where f_r is the fraction of the electrode covered by the deposit, N_r is the number of atoms deposited, A_r is the effective cross-sectional area of an atom of deposit, A_e is the area of the electrode, and N_a is Avogadro's number. Substituting Equation (20) into the Nernst equation one obtains

$$E = E^o - \frac{RT}{nF} \ln \frac{V N_a A_r y_r}{A_e y_o} - \frac{RT}{nF} \ln \frac{C - C_o}{C} \quad (21)$$

Assumption (A) used in the derivation of Equation (20) and (21) is a good assumption, but Assumption (B) is not a good assumption for the platinum gauze electrode used in this work. The electrode used in this work is platinum gauze folded over in thirds. Because of this electrode's geometry, some areas of the electrode have a higher probability of receiving a deposit than other areas. This increases the probability of some areas receiving more than a monolayer of deposit before the entire electrode is covered with a monolayer of deposit. This is consistent with the ideas proposed by Haissinsky (66). Haissinsky said that the degree of coverage on an electrode is not homogeneous, but varies from one point to another. He agreed that the activity of the deposit is proportional to the fraction of the electrode covered, but some areas will be covered with more than a monolayer of deposit before there is complete monolayer formation on the electrode. He introduced a term, which he called an energy transfer factor, to account for this non-homogeneous coverage. Introducing this factor into

Equation (21) one obtains

$$E = E^0 - \frac{RT}{nF} \ln \frac{VN A y_r}{A_e y_o} - \frac{RT}{nFB} \ln \frac{C - C_o}{C} \quad (22)$$

where B is the energy transfer factor. This factor is a function of the number of layers of deposit that are formed before there is a complete monolayer of deposit. B will change the shape of a curve, but it will not change the area under a curve.

Rogers, Krause, Griess, and Ehrlinger (60) found that the potential shift predicted by Equation (21) did not agree with their experimental results for the electrodeposition of traces of silver. They concluded that the silver and platinum formed an alloy on the surface of the electrode. They introduced another term which when added to Equation (22) gives

$$E = E^0 + E_a - \frac{RT}{nF} \ln \frac{VN A y_r}{A_e y_o} - \frac{RT}{nFB} \ln \frac{C - C_o}{C} \quad (23)$$

where E_a is the potential associated with the free energy of alloy formation.

Combining the first three terms in Equation (23) one obtains

$$E = E_p - \frac{RT}{nFB} \ln \frac{C - C_o}{C} \quad (24)$$

where E_p is given by

$$E_p = E^0 + E_a - \frac{RT}{nF} \ln \frac{VN A y_r}{A_e y_o} \quad (25)$$

Solving Equation (24) for C_o one obtains

$$C_o = \frac{C}{1 + e^{[(E_p - E) \frac{nFB}{RT}]}} \quad (26)$$

The charge at each 1-millivolt step is given by

$$Q_{Es} = nFVC \left[\frac{1}{1 + e^{[(E_p - E_L) \frac{nFB}{RT}]}} - \frac{1}{1 + e^{[(E_p - E) \frac{nFB}{RT}]}} \right] \quad (27)$$

The number of layers of a deposit on a partially covered electrode can change during a potential scan. B as a function of the potential is given by

$$B = B_1 + B_2 e^{[(E_p - E) \frac{nFB}{RT}]} \quad (28)$$

where B_1 is the number of layers of deposit on a partially covered electrode at the beginning of a potential scan and B_2 is a constant which determines the amount B will change during the scan.

The program used for data analysis is listed in Appendix B. Data analysis is accomplished by non-linear least squares to resolve overlapping peaks and background. This program calculates a curve using equations previously derived. The parameters in these equations are calculated by the program to generate a curve which will give the smallest deviation from the actual curve. The method used is a modification of an algorithm developed by Marquardt (67). This algorithm combines a gradient search with an analytical solution to a linearized form of the fitting function. This program converges in one iteration for linear parameters and within two to six iterations for nonlinear parameters.

The ratio of activity coefficients is assumed to be constant for the data analysis. E_p is calculated before the analysis program is run, and is recalculated by the program to give the best

value for E_p . This makes Equation (27) and Equation (11) equivalent if B in Equation (27) is equal to 1. Equation (27) is used to fit the charge contributions made by constituents with two soluble species and also the charge contribution made by constituents that form an insoluble deposit on a partially covered inert electrode. Equation (19) is used to fit the charge contribution of constituents that form an insoluble deposit on a completely covered electrode, where the activity of the deposit is unity. The faradaic background is assumed to be linear. The fitting function is a sum of all charge contributions made by the individual constituents and the charge produced by the background.

Discussion of Results

The results of computer controlled scanning potential coulometric analysis of single constituents and of mixtures are shown in Table 1. The data for individual scans and the curves, which were calculated by the computer to give the best fit to the data using the derived equations, are plotted in Figures 9 through 20. The data in these plots are the solid lines, the dashed lines are the computer-calculated curves, the dotted lines are the contribution due to each constituent, and the dot-dashed lines are the background. The silver peak is due to two different contributions, the stripping of silver from a completely covered electrode, and the stripping of silver from a partially covered electrode. These two contributions are fit separately during data analysis and added together after data analysis. The iron peak is due only to the oxidation of the ferrous ion to the ferric ion. A good fit is

indicated when the dashed lines follow the solid lines closely. A perfect fit is indicated when the dashed lines are exactly superimposed over the solid lines. The reported concentrations are the average of three values obtained from a single sample with the exceptions of Samples 7, 9, and 11. A single scan was run on Sample 7 and two scans each were run on Sample 9 and Sample 11.

Good results were obtained for the analysis of iron without any silver interference (Samples 1-3). Figures 9-11 show a platinum-iron overlap of charge for Samples 1-3. In all cases the relative inaccuracy was below 2%, demonstrating that the platinum-iron overlap of charge was resolved. If this overlap were not resolved the relative errors would be approximately 50%. The peak height for the 2×10^{-7} F (Figure 11) iron is not much greater than the random noise in the scanning potential coulogram. The sensitivity of this method would ultimately be limited by this random noise. The sensitivity could possibly be extended another order of magnitude, but unless the random noise were removed the sensitivity could not be extended further.

The electrolysis current was monitored with a Tektronix oscilloscope to determine the source of the random noise. A small periodic current was found superimposed on the electrolysis current. The magnitude and the frequency of this current decreased when the stirring rate was decreased. A small toroid was mounted on the magnetic stirrer and the leads were connected to one input of the dual trace amplifier in the oscilloscope. This allowed the study of the phase relationship between the periodic signal

superimposed on the electrolysis current and the rotation of the magnetic stirrer. The frequency of the signal superimposed on the electrolysis current was exactly 4 times the frequency of rotation. The periodic current was either induced by the magnetic stirrer or caused by some phenomenon related to the stirring. The latter conclusion was most likely because there are 4 fins on the magnetic Spinfin, and an induced current would be the same frequency as the stirrer rotation. The Spinfin was removed and the stirrer turned on in order to confirm this conclusion. No periodic signal was observed. This confirmed the conclusion that the periodic current was due to some phenomenon related to the stirring. A possible method to compensate for this noise would be to synchronize the sample rate with the periodic signal. If this signal remained relatively constant during the scan, it would add a constant to the background which could be removed by curve fitting during data analysis.

Good results were obtained from Samples 4-6 (Figures 12-14), but these results were not as accurate as the results obtained from the samples where iron was the only constituent. This indicates that silver does interfere with determinations of iron. Figures 12-14 show high computer-calculated curves for silver, especially at the beginning of the silver peaks. This should cause the reported values for silver to be high, but the reported values for silver are low in all three cases. Also, an analysis of 2.3×10^{-5} F silver (Sample 7 and Figure 15) was 86% low. No trace of silver could be found by scanning potential coulometric analyses of 10^{-6}

and 10^{-7} F silver. These results lead one to conclude that there is a loss of a relatively constant amount of silver somewhere in the system. Propst (20) and Rogers and co-workers (60) account for similar results as intermetallic bonding or alloy formation on the inert electrode. This author believes that the silver which was not reported by scanning potential coulometry goes to the formation of a platinum-silver intermetallic bond. The electrode pretreatment procedure described in the experimental section of this dissertation formed a layer of the platinum-silver intermetallic bond over the entire surface of the platinum electrode and was necessary to obtain accurate results for silver. This electrode pretreatment was used for Samples 8-11 (Figures 16-19). The data are fit more accurately and more accurate results are obtained from these scans than are obtained from the scans performed without the pretreatment, with the exception of Sample 11. The inaccuracies for samples analyzed after the pretreatment were less than 3% compared with an inaccuracy of 86% for a sample analyzed before pretreatment. Sample 11 was run using a linear scan with a scan rate of 0.03 V/min. This was the optimum scan rate for the 10^{-7} F silver, but not for the iron. Figure 19 shows that the data are lower than the predicted curve at the beginning of the oxidation of the iron. This is an indication that the scan rate is too rapid for near-equilibrium conditions to be maintained. This also caused the curve fitting program to place the background too low at the silver peak. This caused a high reported value for silver. A more accurate value for silver is obtained by fitting the silver peak alone (Figure 20).

Discussion of Results Obtained From Theoretically
Generated Scanning Potential Coulograms

The results obtained from the theoretically generated scanning potential coulograms are shown in Table 2. The coulograms are shown in Figures 21-31. These coulograms were generated to determine the theoretical resolution for computer controlled scanning potential coulometry. The worst case is the overlap of charge caused by two constituents with 1 equivalent per mole and the same formal potential. These cannot be resolved because the curve generated by the two constituents is identical to a curve generated by a single constituent with a concentration equal to the sum of the concentrations of each individual constituent.

Another case that was examined is that of one constituent having one equivalent per mole and the other having two equivalents per mole, but each having the same formal potential (Runs 1-7 and Figures 21-27). The data in Table 2 indicate more accurate results are obtained resolving a sharp peak (2 equivalents per mole) from a wide peak than can be obtained by resolving a wide peak from a sharp peak.

The last case tested was the resolving of two constituents, each with one equivalent per mole, but with a formal potential separation of 10-mV (Runs 8-11 and Figures 28-31). The inaccuracy of the least concentrated constituent is less than 2% for a 1 to 100 concentration ratio and the inaccuracy is 16% for a 1 to 1000 concentration ratio.

Conclusion

Computer controlled scanning potential coulometry is an accurate and sensitive method for trace analysis. This method is especially attractive since it requires little sample preparation and it requires no standards for accurate quantitative determinations. The sensitivity limit for the system as it is described in this work is approximately 10^{-8} F. The system could be made more sensitive if methods were employed which would reduce or compensate for the random noise on electrolysis current. A constant added to the electrolysis current will not affect the sensitivity because it will be subtracted as background during curve fitting. The linear scan is less sensitive to noise and therefore it can give more accurate and precise results than the computer optimized scan, if the scan rate is chosen to allow near equilibrium conditions to be maintained throughout the scan. However, a linear scan can require two to three times longer than a computer optimized scan.

This method is not well suited for the analysis of constituents that give an insoluble deposit on an inert electrode. Accurate determinations of silver were performed, but the time required for the electrode pretreatment and sample preparation allowed only for the analysis of one sample each day. Determinations of constituents that give an insoluble deposit would be practical only if the electrochemical behavior of the electrode-deposit intermetallic bond could be accurately described mathematically. Electrode pretreatment would no longer be necessary.

The method described in this work provides an accurate, and relatively rapid method for electrochemical analysis. The primary prerequisite for accurate determinations by this method is that one is able to describe accurately mathematically the electrochemical behavior of the sample constituent. This method could be extended to the determinations of metals at a mercury cathode because the mathematical behavior of the reduced species to form an amalgam is already known. The theoretical resolution of this method would allow complex mixtures to be analyzed accurately.

Table 1

Results Obtained Using Computer Controlled Scanning Potential Coulometry

Sample Number	Constituent	Formal Concentration for	Formal Concentration Found	% Inaccuracy	% Standard Deviation	Figure Number
1	Fe	1.395×10^{-5}	1.388×10^{-5}	0.478	0.146	9
2	Fe	2.898×10^{-6}	2.857×10^{-6}	1.43	0.433	10
3	Fe	2.176×10^{-7}	2.137×10^{-7}	1.80	0.682	11
4	Ag	2.589×10^{-4}	2.582×10^{-4}	0.276	0.186	12
	Fe	1.838×10^{-4}	1.814×10^{-4}	1.34	0.424	
5	Ag	2.855×10^{-4}	2.549×10^{-4}	10.7	5.89	13
	Fe	5.407×10^{-5}	5.371×10^{-5}	0.662	0.342	
6	Ag	2.920×10^{-4}	2.895×10^{-4}	0.861	0.266	14
	Fe	2.160×10^{-6}	2.012×10^{-6}	6.88	2.20	
7	Ag	2.299×10^{-5}	2.238×10^{-6}	85.9	-----	15
8	Ag	9.178×10^{-5}	8.992×10^{-5}	2.02	0.618	16
	Fe	1.375×10^{-4}	1.379×10^{-4}	0.290	0.118	
9	Ag	1.689×10^{-5}	1.738×10^{-5}	2.31	1.08	17
	Fe	1.547×10^{-4}	1.550×10^{-4}	0.200	0.096	
10	Ag	9.994×10^{-6}	1.001×10^{-5}	0.666	0.230	18
	Fe	1.307×10^{-5}	1.330×10^{-5}	1.74	0.539	
11	Ag	1.806×10^{-7}	2.177×10^{-7}	20.4	9.68	19
	Fe	1.164×10^{-5}	1.186×10^{-5}	1.86	0.891	
11	Ag	1.806×10^{-7}	1.857×10^{-7}	2.67	1.26	20

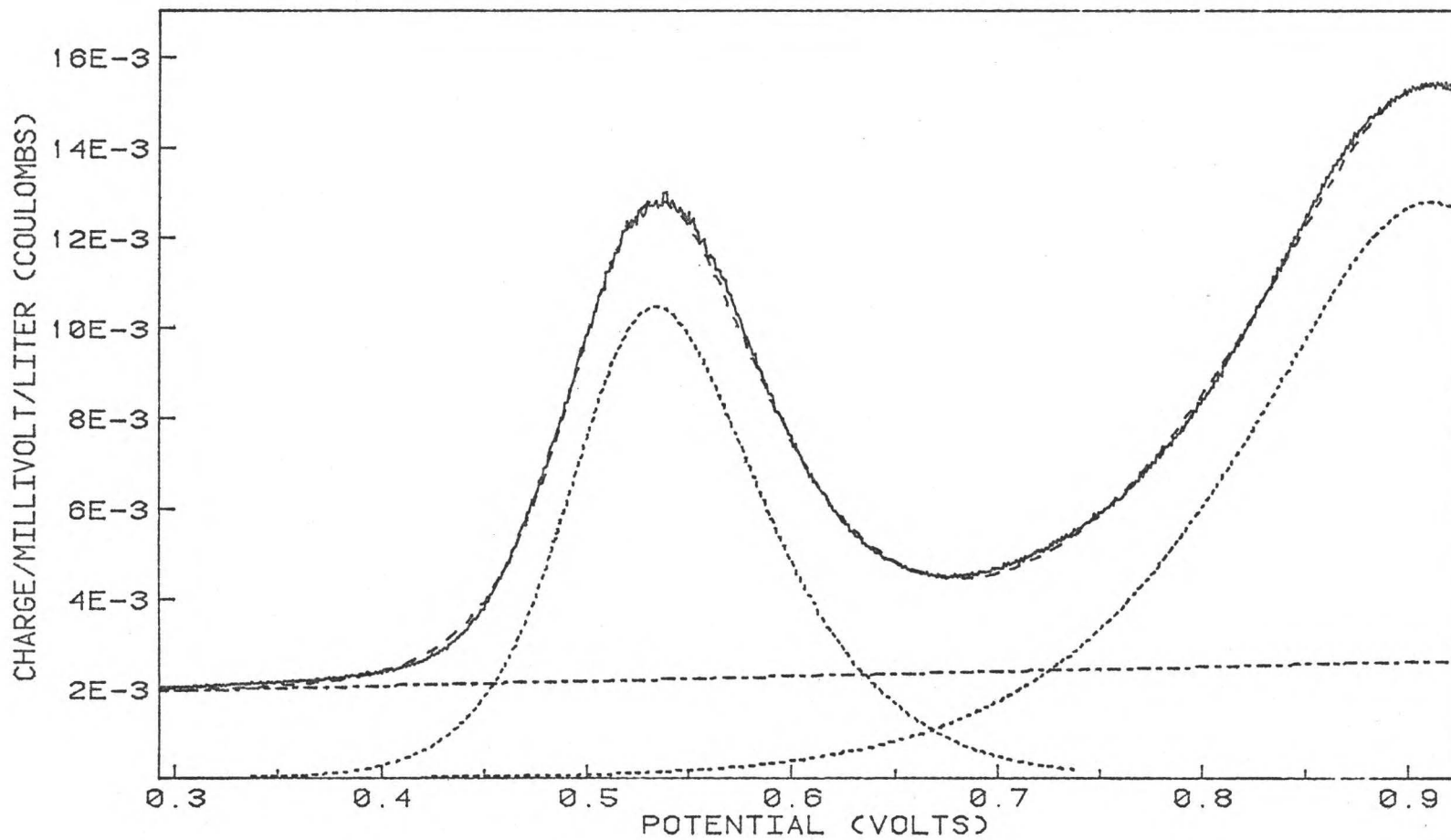


Figure 9. Scanning potential coulogram of 1.395×10^{-5} F iron.

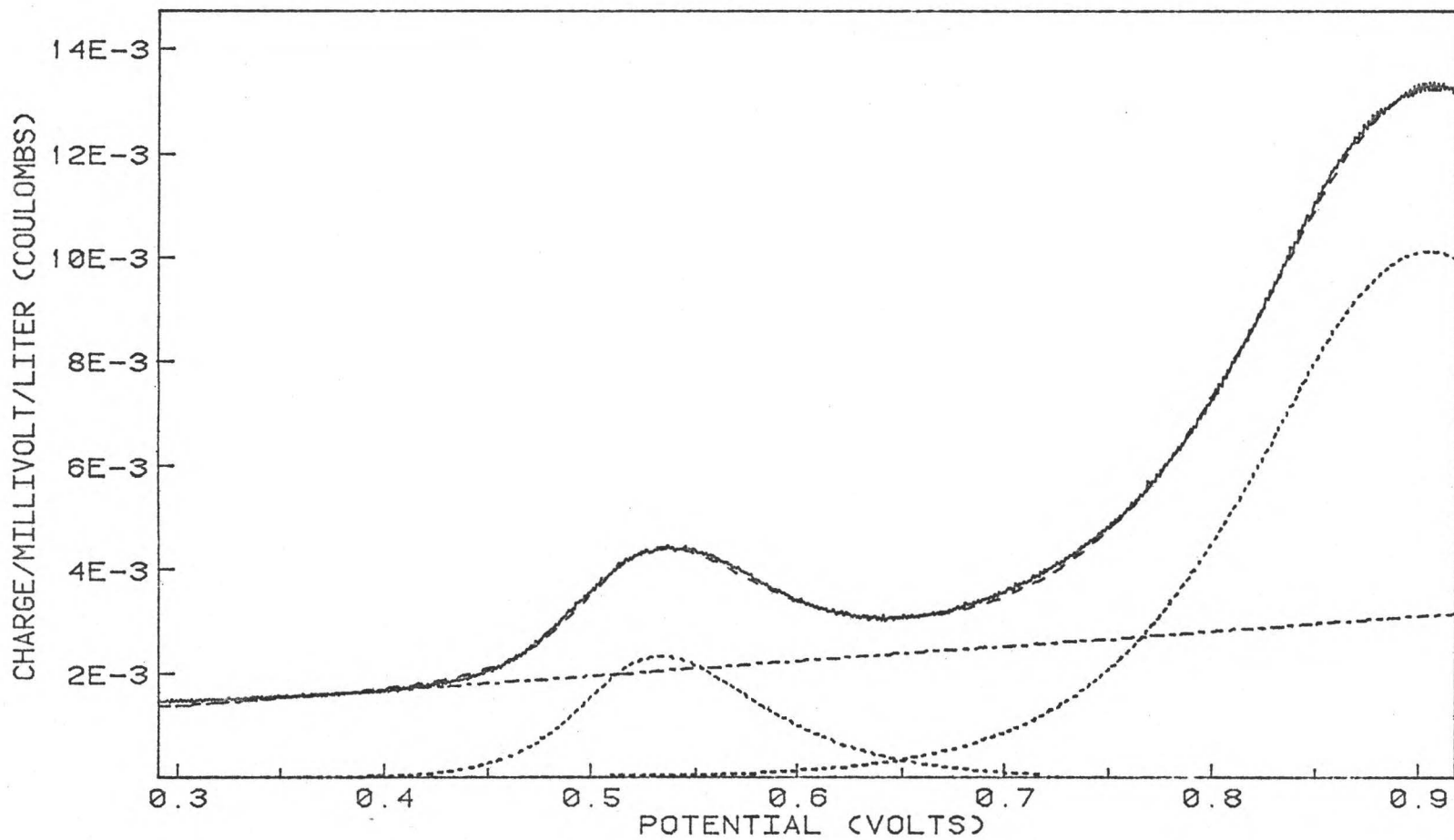


Figure 10. Scanning potential coulogram of 2.898×10^{-6} F iron.

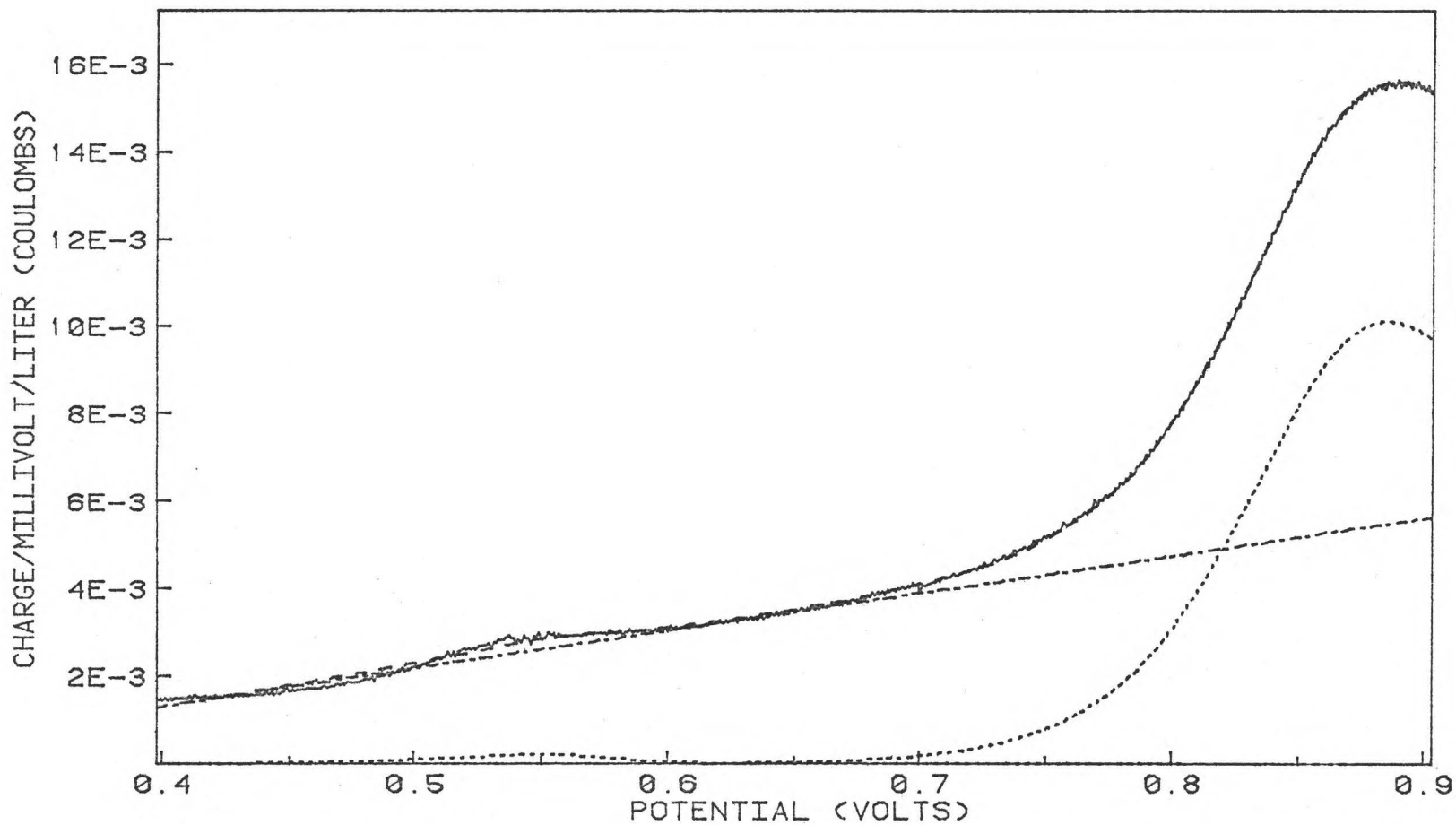


Figure 11. Scanning potential coulogram of 2.176×10^{-7} F iron.

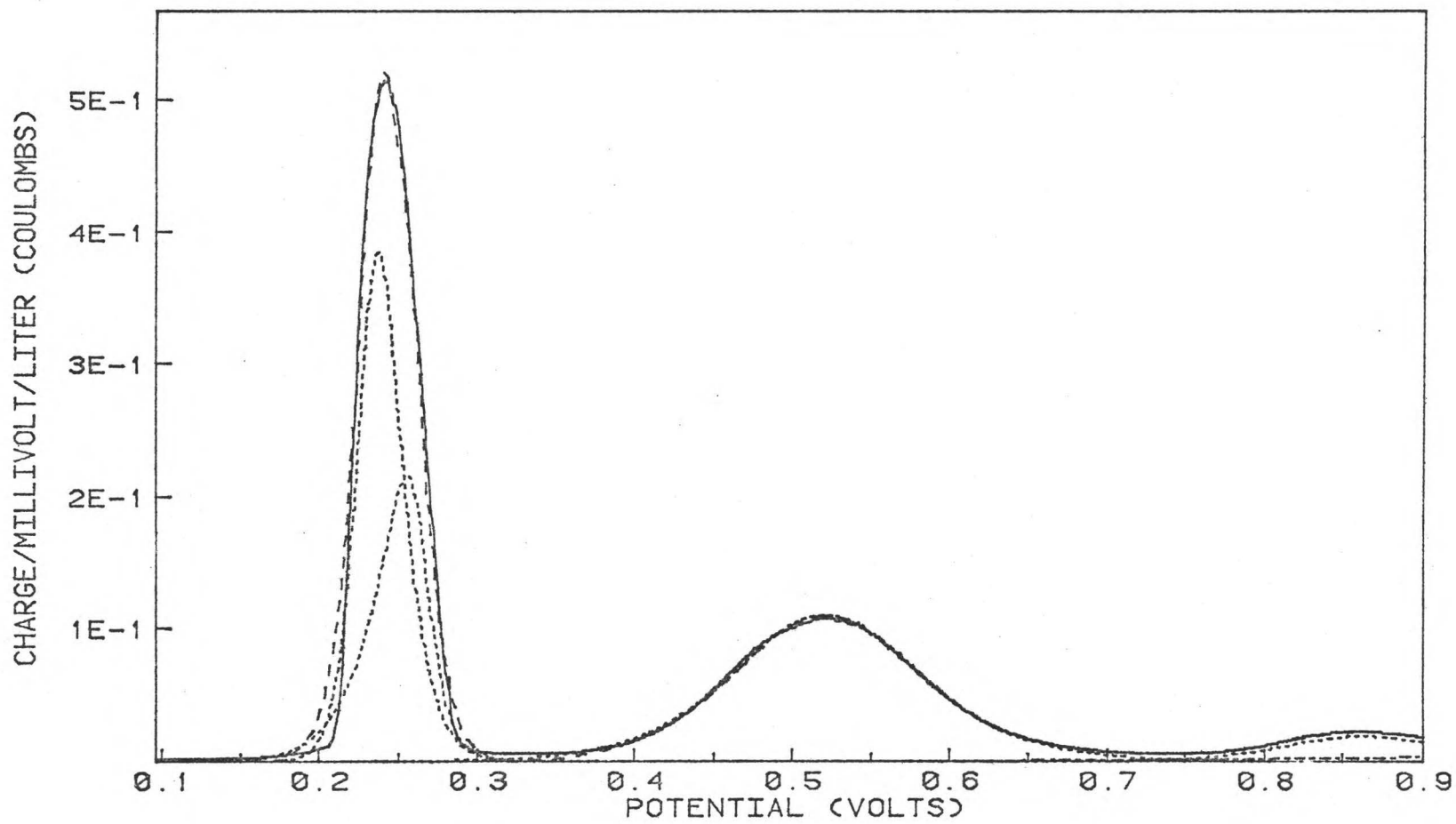


Figure 12. Scanning potential coulogram of 2.589×10^{-4} F silver and 1.838×10^{-4} F iron.

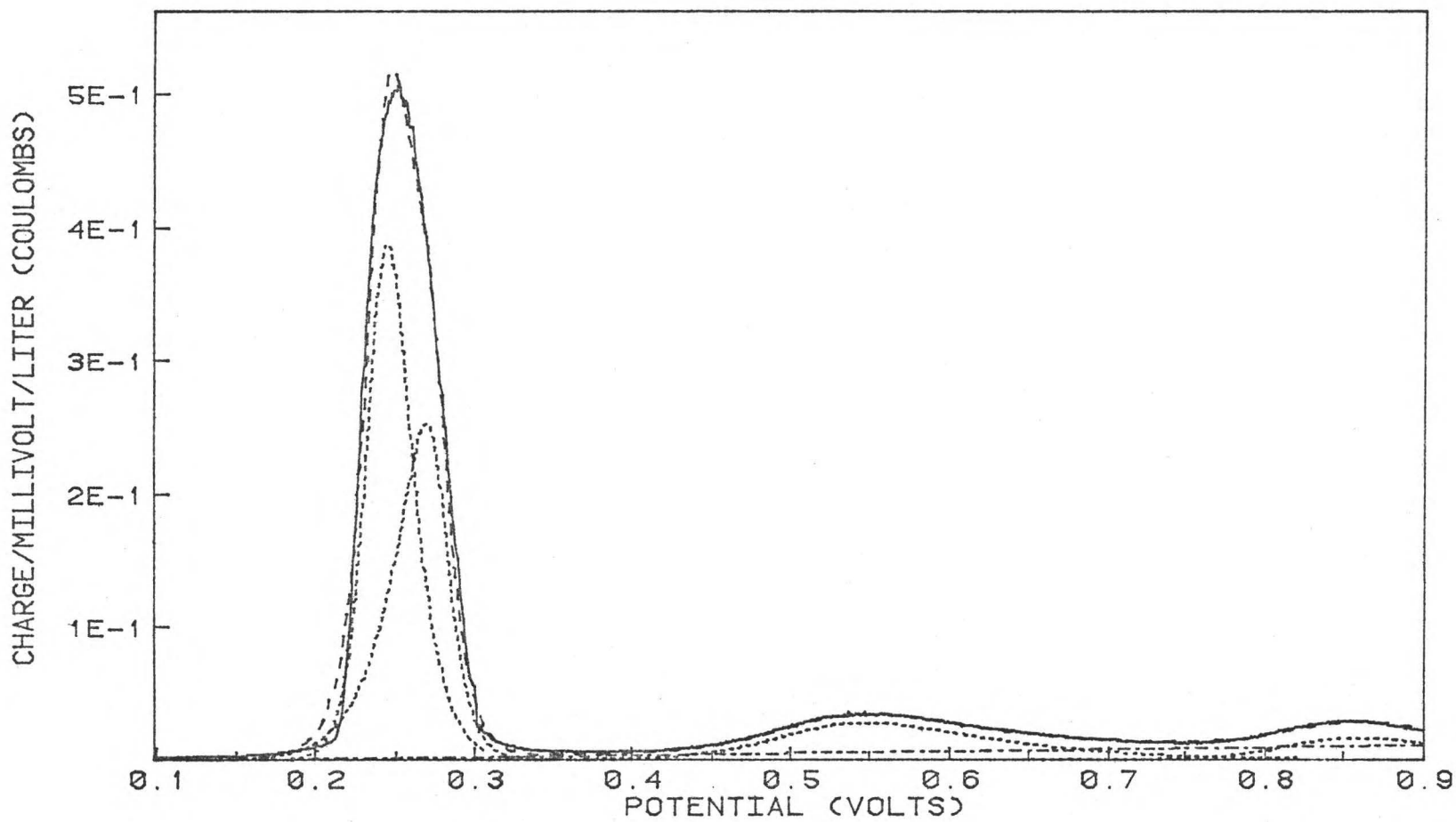


Figure 13. Scanning potential coulogram of 2.855×10^{-4} F silver and 5.407×10^{-5} F iron.

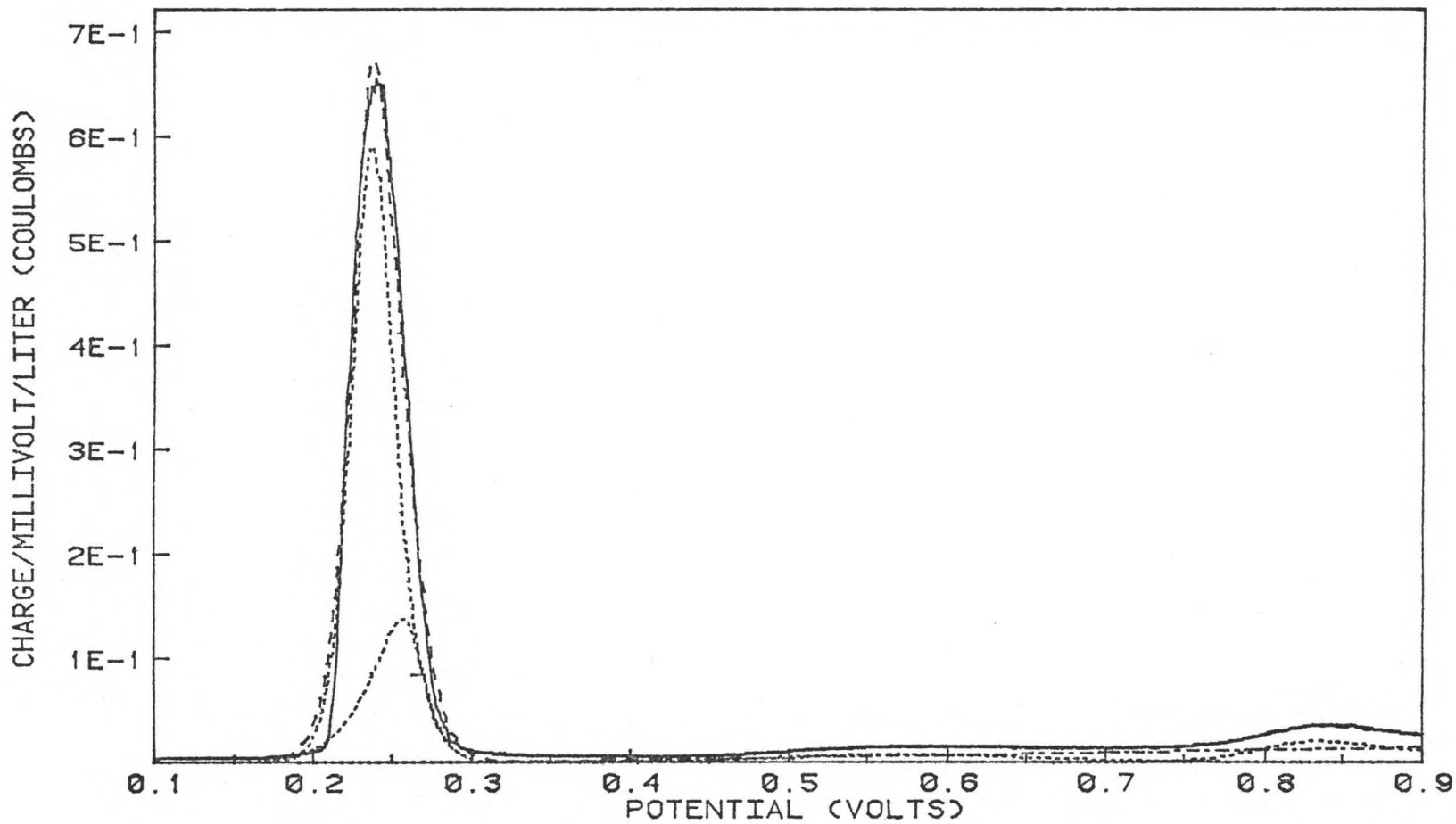


Figure 14. Scanning potential coulogram of 2.920×10^{-4} F silver and 2.160×10^{-6} F iron.

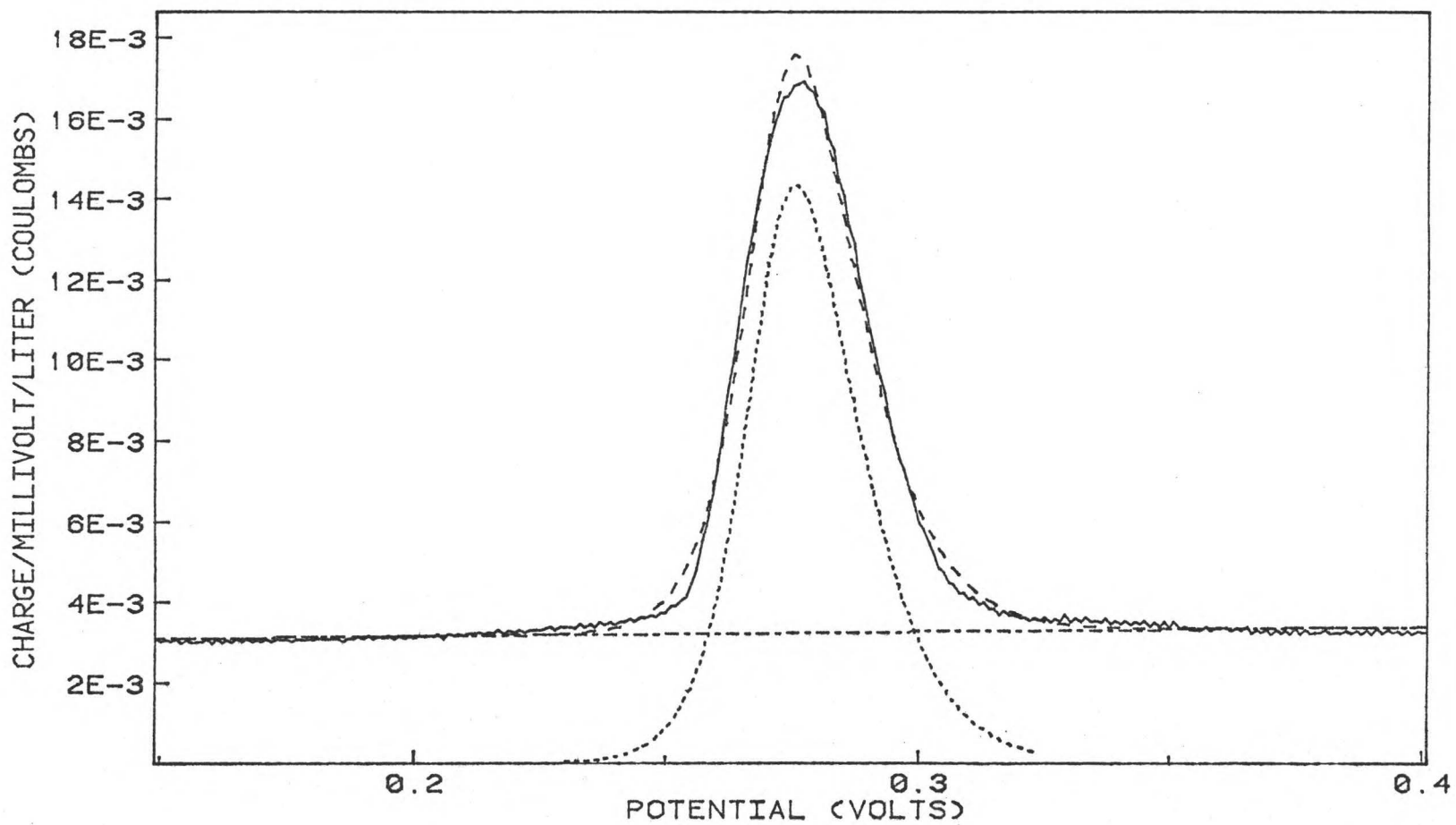


Figure 15. Scanning potential coulogram of 2.299×10^{-5} F silver.

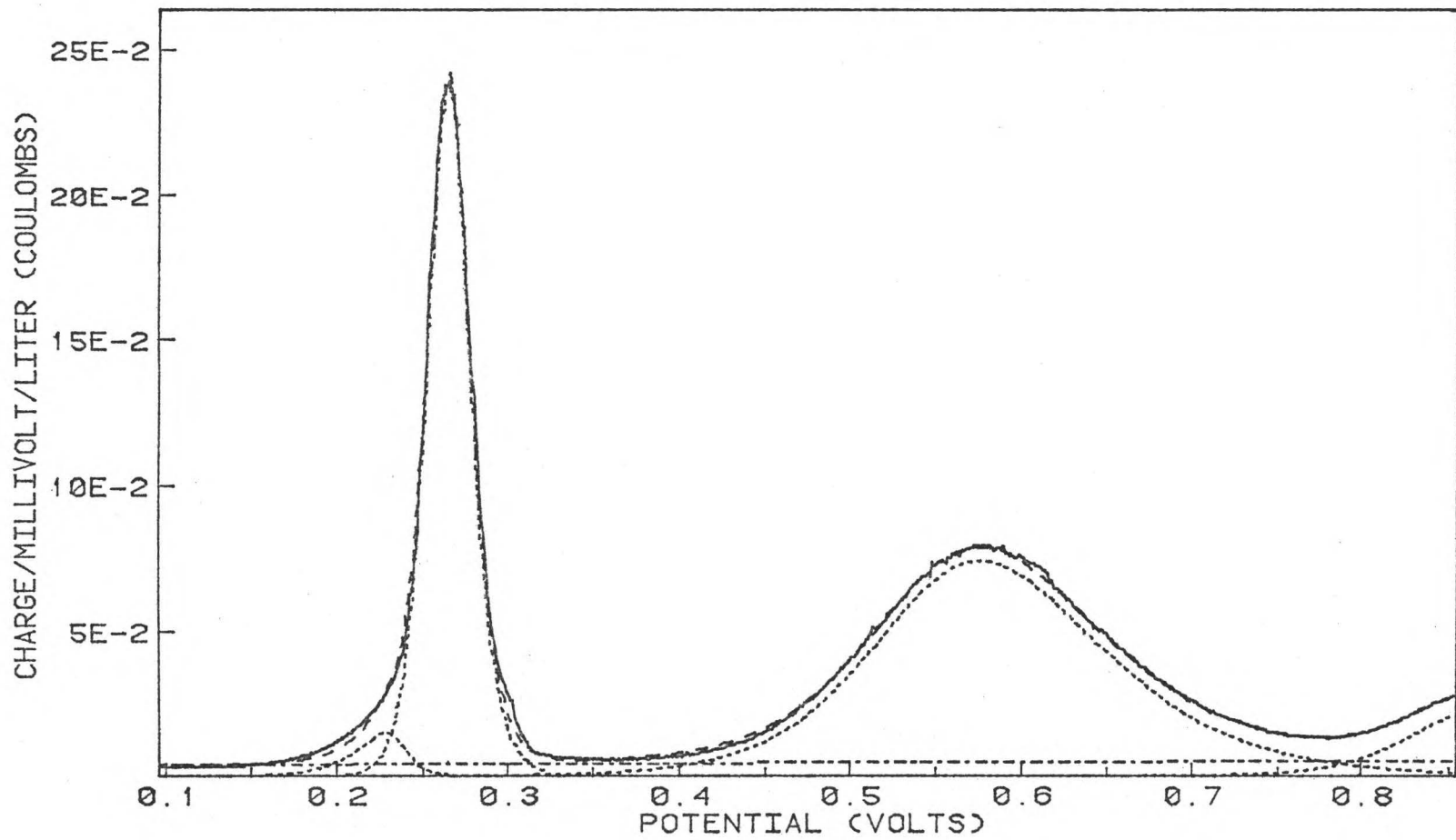


Figure 16. Scanning potential coulogram of 9.178×10^{-5} F silver and 1.375×10^{-4} F iron.

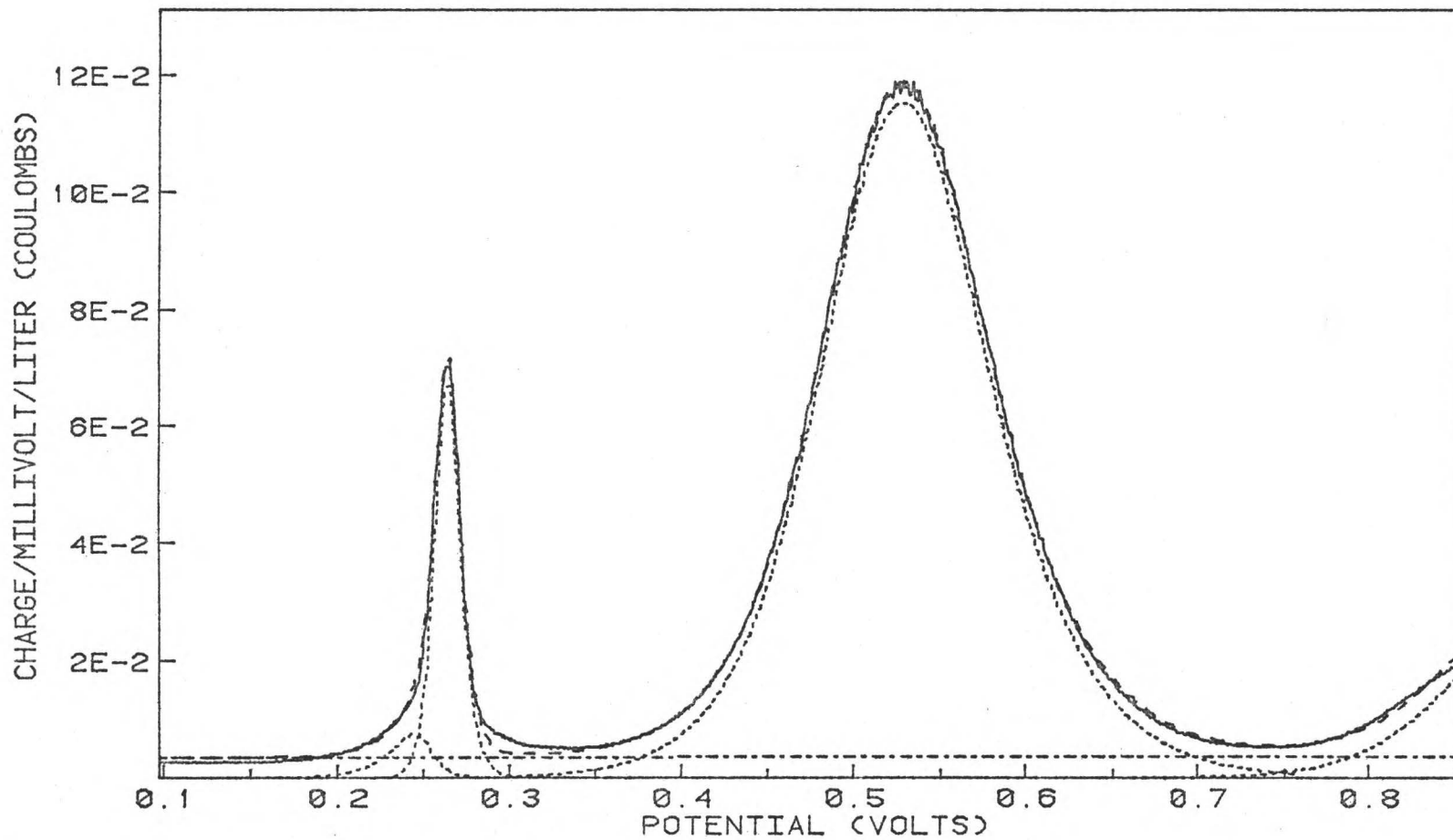


Figure 17. Scanning potential coulogram of 1.689×10^{-5} F silver and 1.547×10^{-4} F iron.

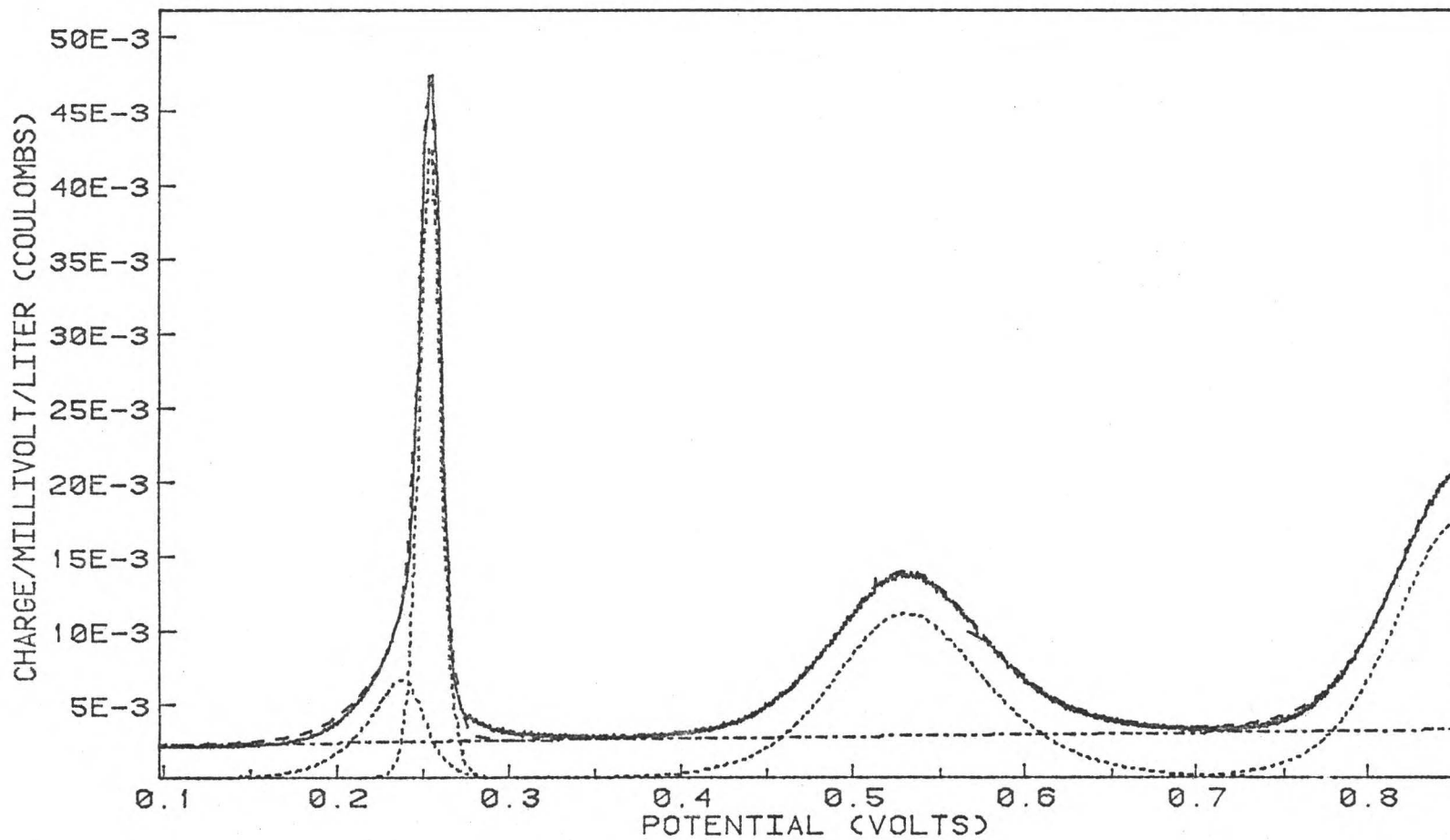


Figure 18. Scanning potential coulogram of 9.994×10^{-6} F silver and 1.307×10^{-5} F iron.

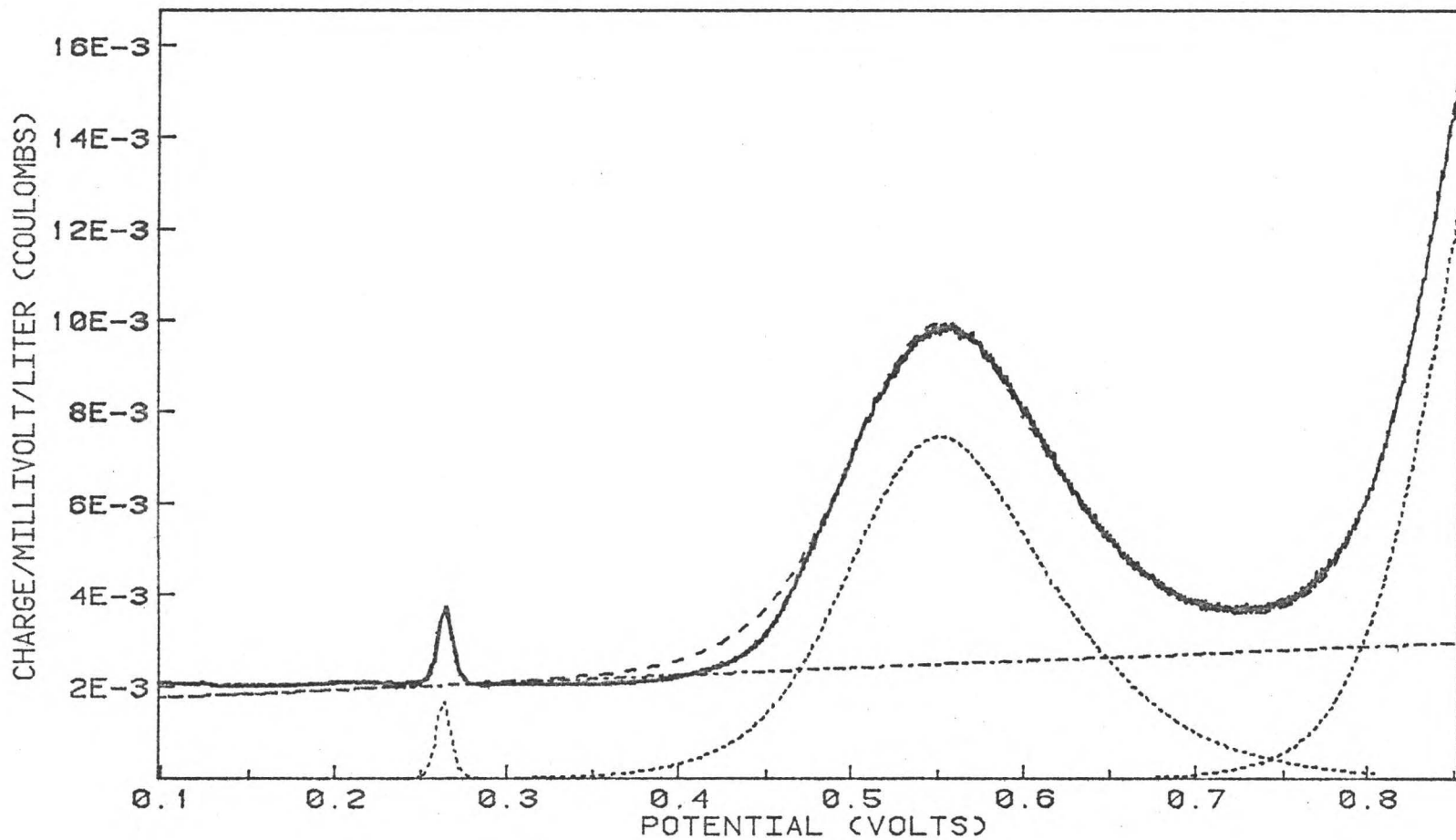


Figure 19. Scanning potential coulogram of 1.806×10^{-7} F silver and 1.164×10^{-5} F iron.

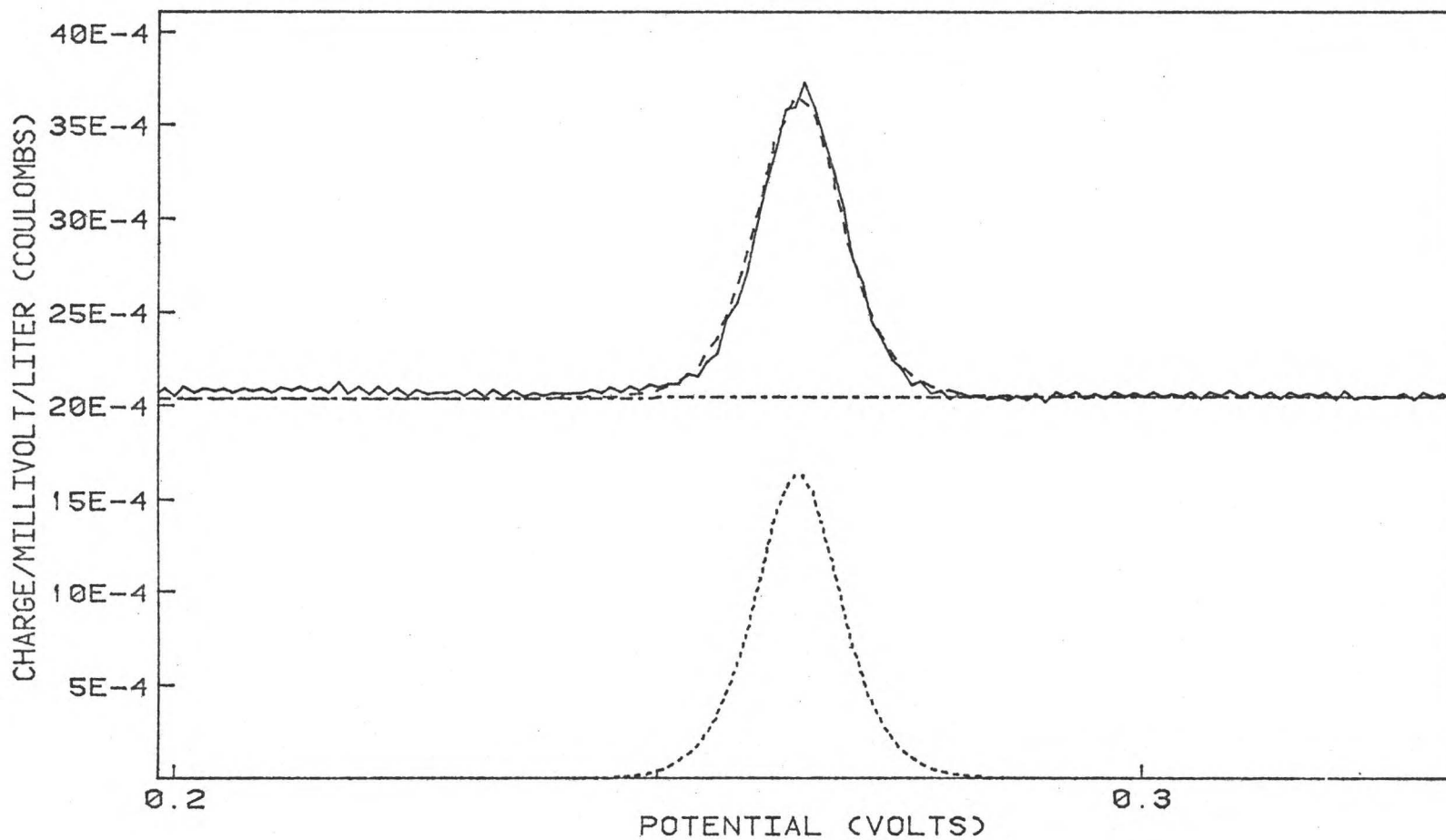


Figure 20. Scanning potential coulogram of 1.806×10^{-7} F silver.

Table 2

Results Obtained Using Theoretically Generated Scanning Potential Coulograms for Two Constituents

Run Number	Concentration Ratio in Equiv/1 1 to 2	E ⁰ Separation in Millivolts	Equivalent/mole Constituent		% Inaccuracy Constituent		Figure Number
			1	2	1	2	
1	1 - 1	0	1	2	0.00	0.00	21
2	1 - 10	0	1	2	0.01	0.00	22
3	1 - 100	0	1	2	0.20	0.00	23
4	1 - 1000	0	1	2	2.10	0.00	24
5	10 - 1	0	1	2	0.00	0.00	25
6	100 - 1	0	1	2	0.00	0.10	26
7	1000 - 1	0	1	2	0.00	1.30	27
8	1 - 1	10	1	1	0.00	0.00	28
9	1 - 10	10	1	1	0.15	0.01	29
10	1 - 100	10	1	1	1.56	0.02	30
11	1 - 1000	20	1	1	16.90	0.02	31

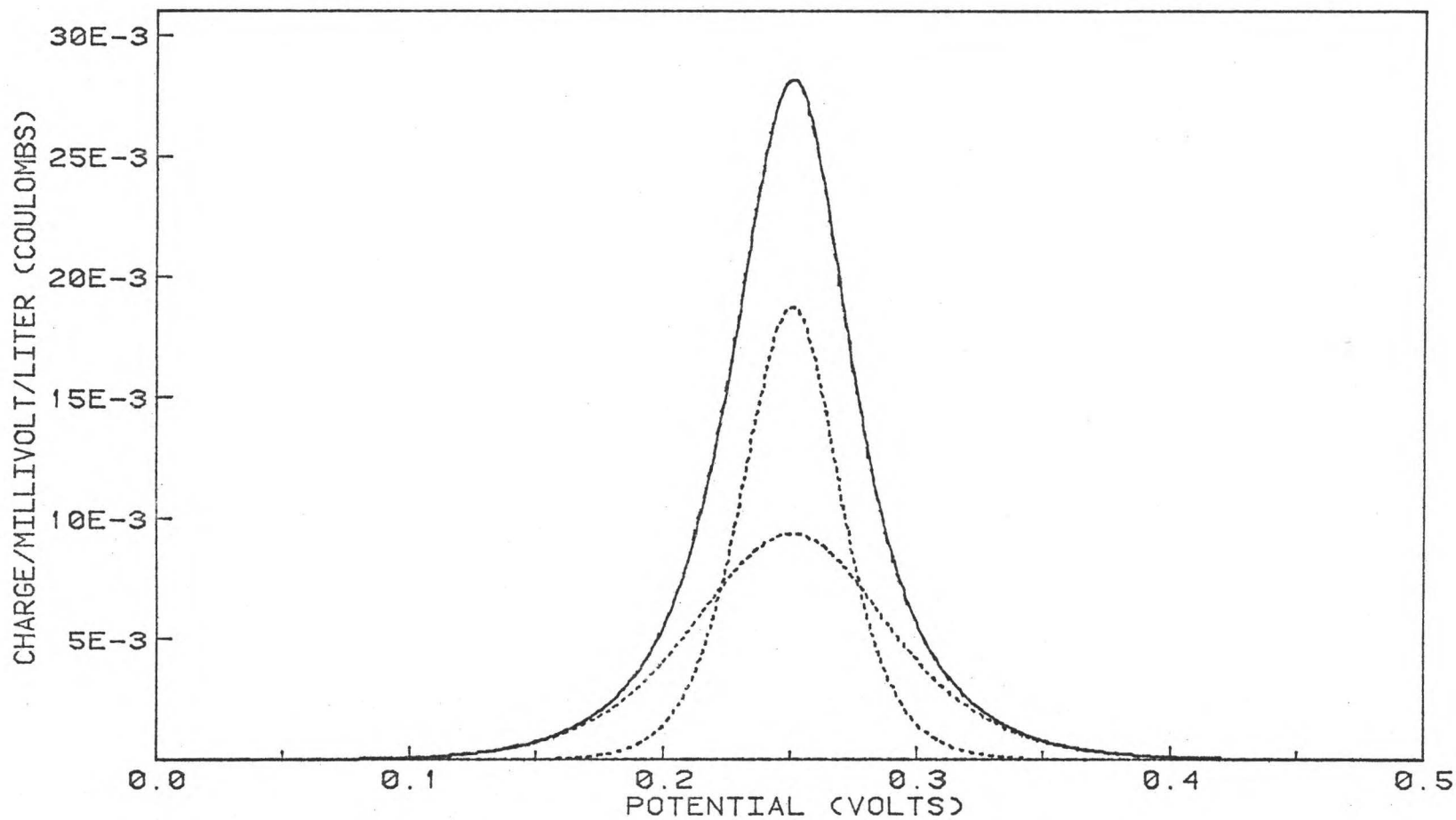


Figure 21. Theoretically generated scanning potential coulogram of a 1 to 1 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

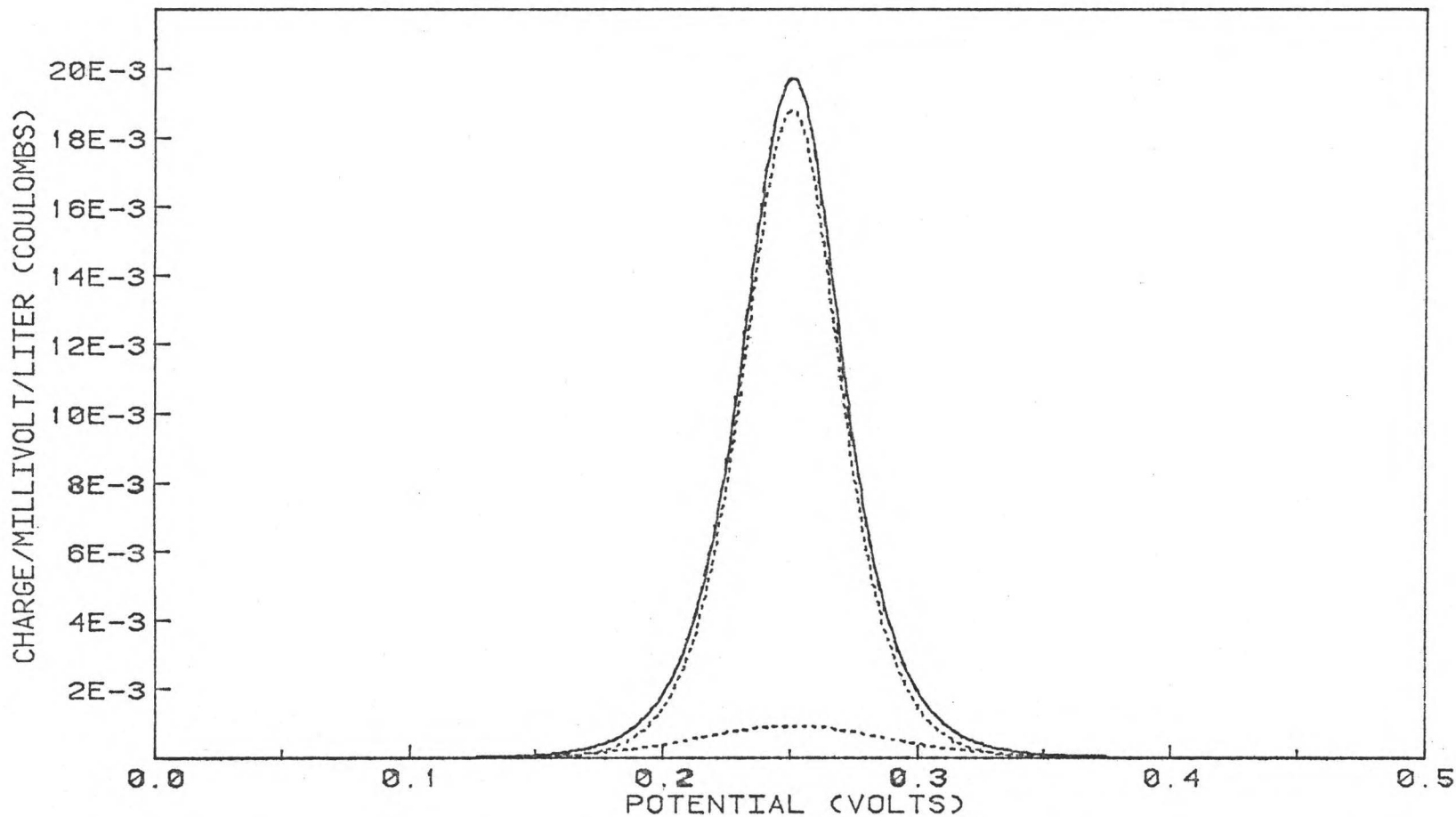


Figure 22. Theoretically generated scanning potential coulogram of a 1 to 10 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

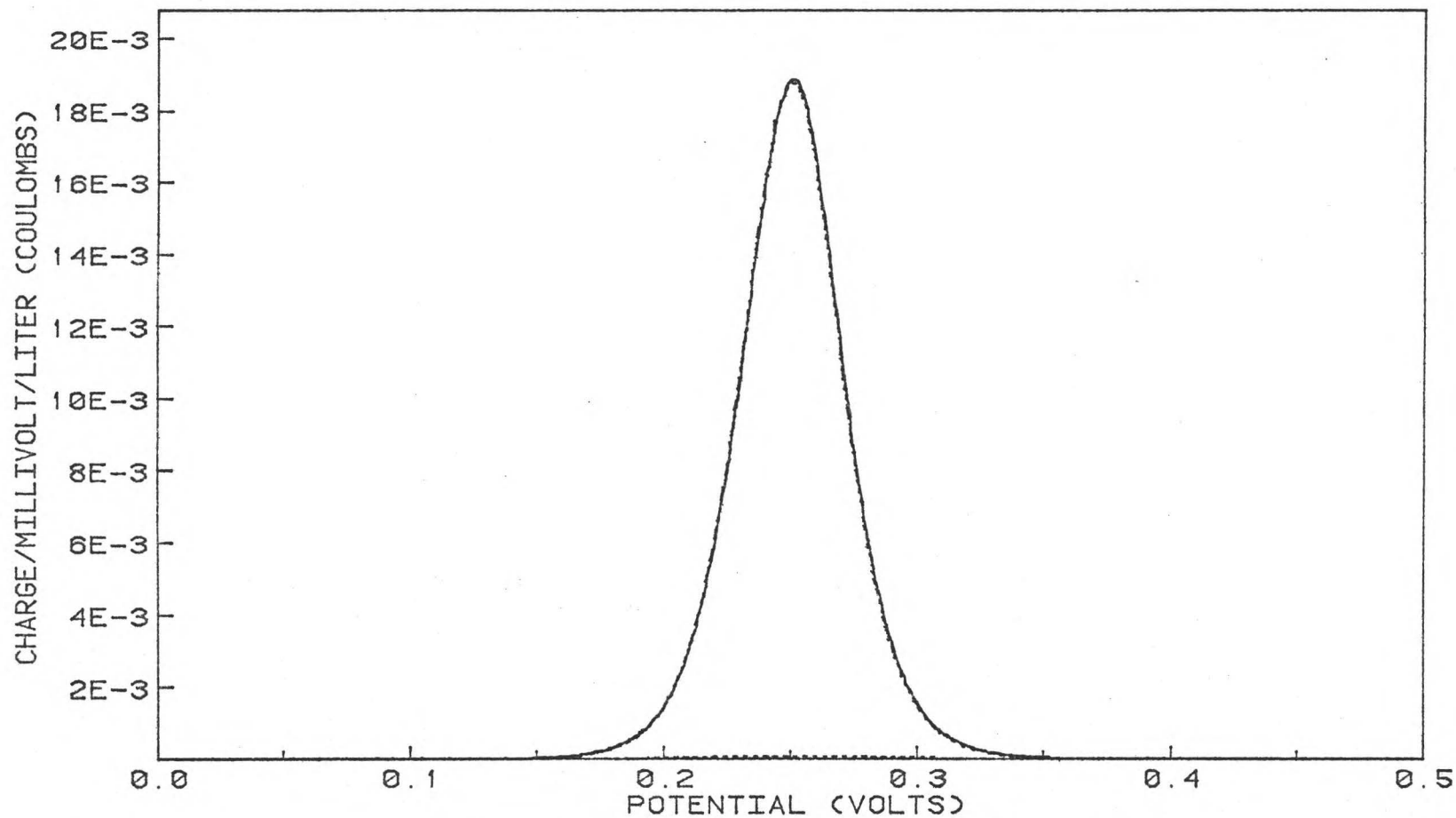


Figure 23. Theoretically generated scanning potential coulogram of a 1 to 100 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

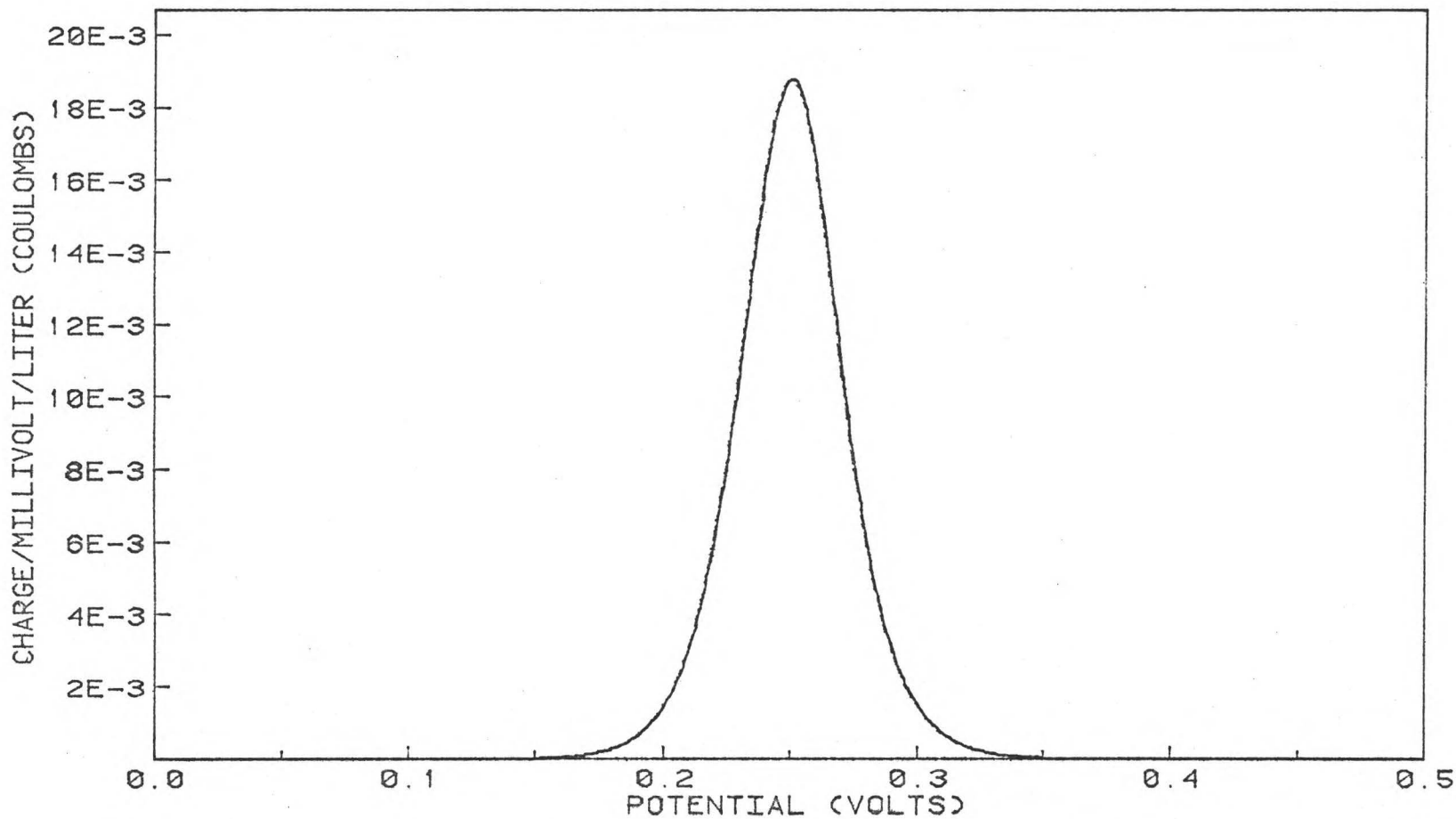


Figure 24. Theoretically generated scanning potential coulogram of a 1 to 1000 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

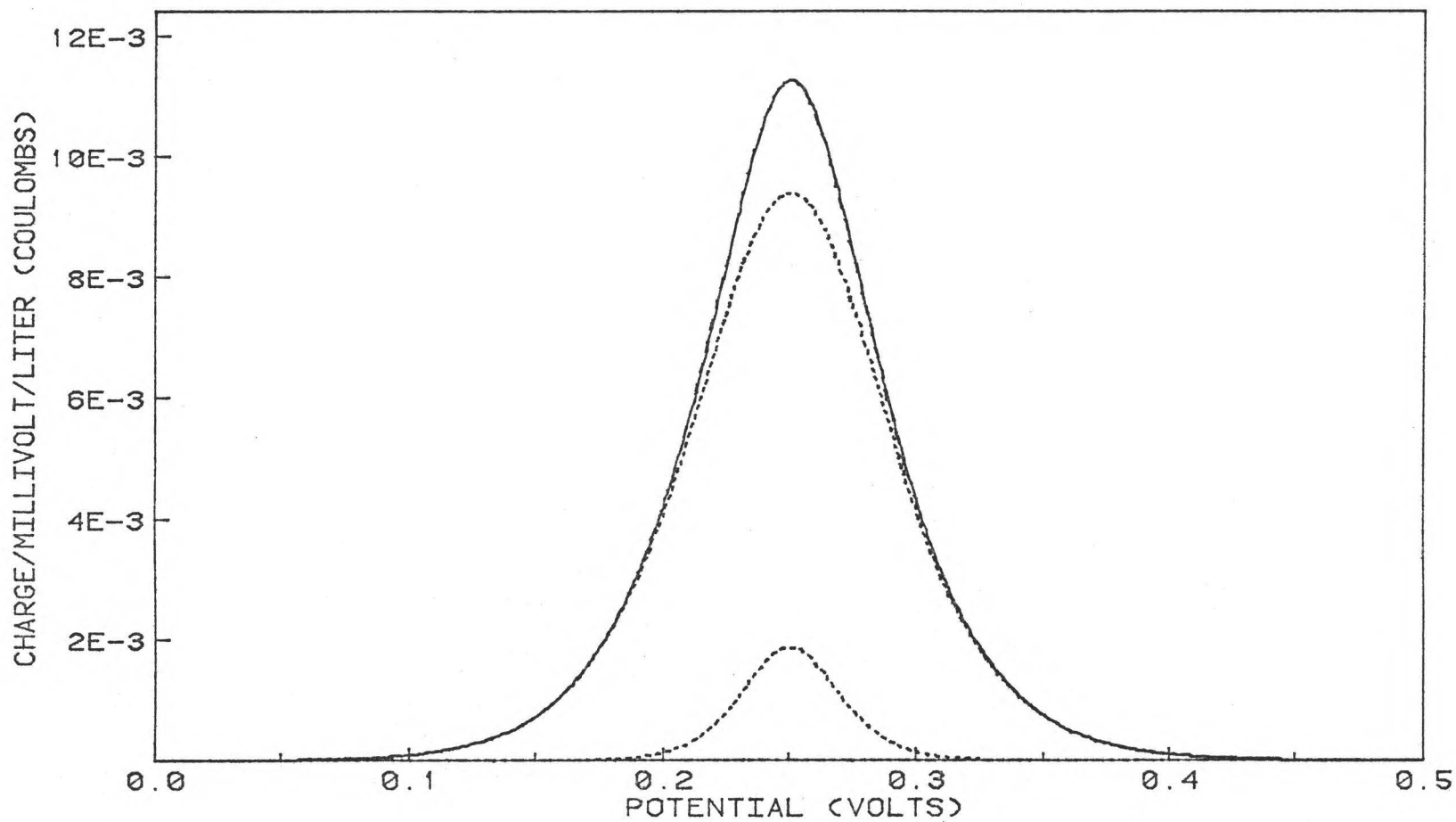


Figure 25. Theoretically generated scanning potential coulogram of a 10 to 1 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

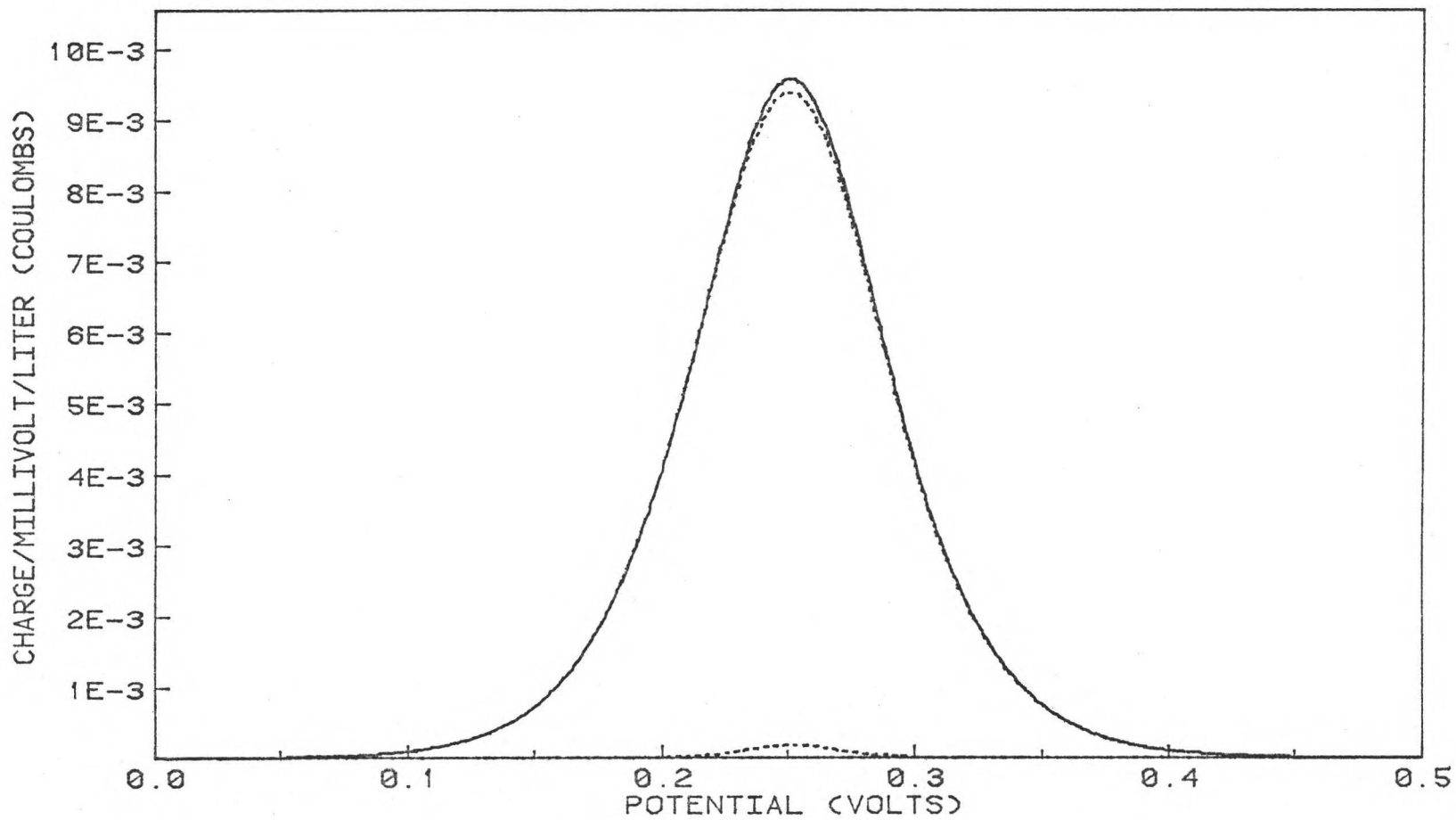


Figure 26. Theoretically generated scanning potential coulogram of a 100 to 1 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

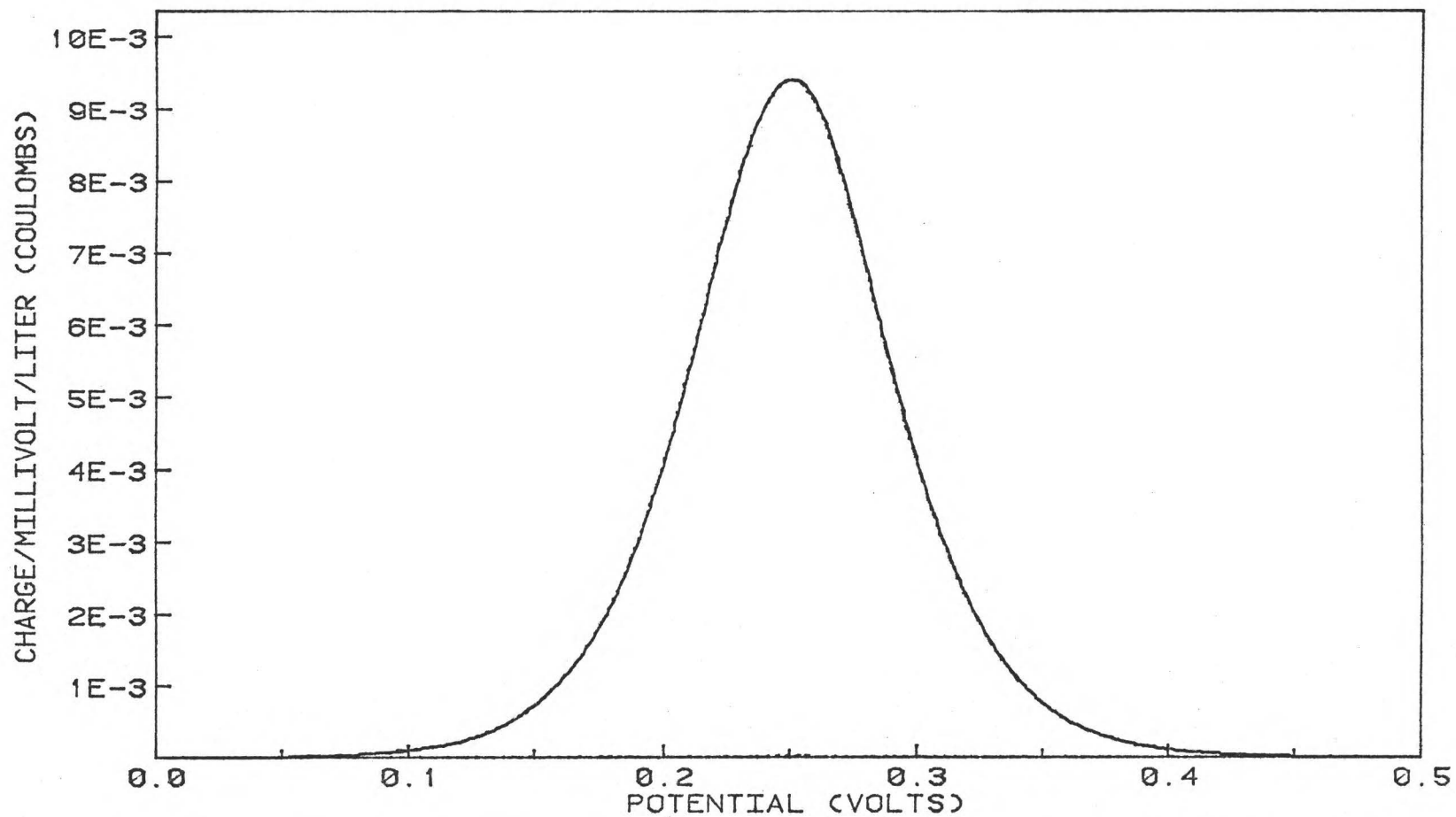


Figure 27. Theoretically generated scanning potential coulogram of a 1000 to 1 ratio mixture of two constituents; one with one equivalent per mole and one with two equivalents per mole. The formal potentials of the constituents are equal.

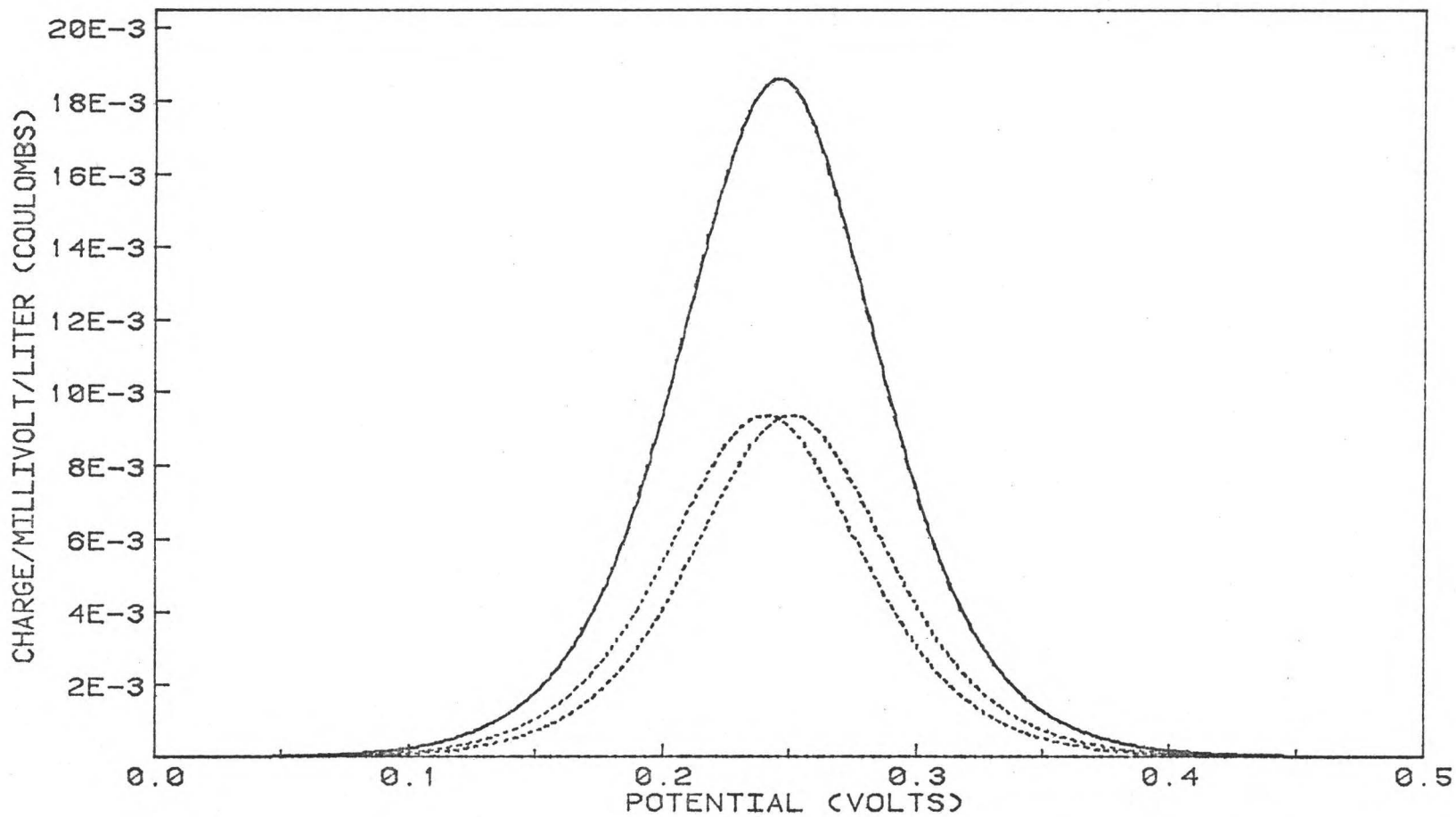


Figure 28. Theoretically generated scanning potential coulogram of a 1 to 1 ratio mixture of two constituents each with one equivalent per mole, but with a formal potential separation of ten millivolts.

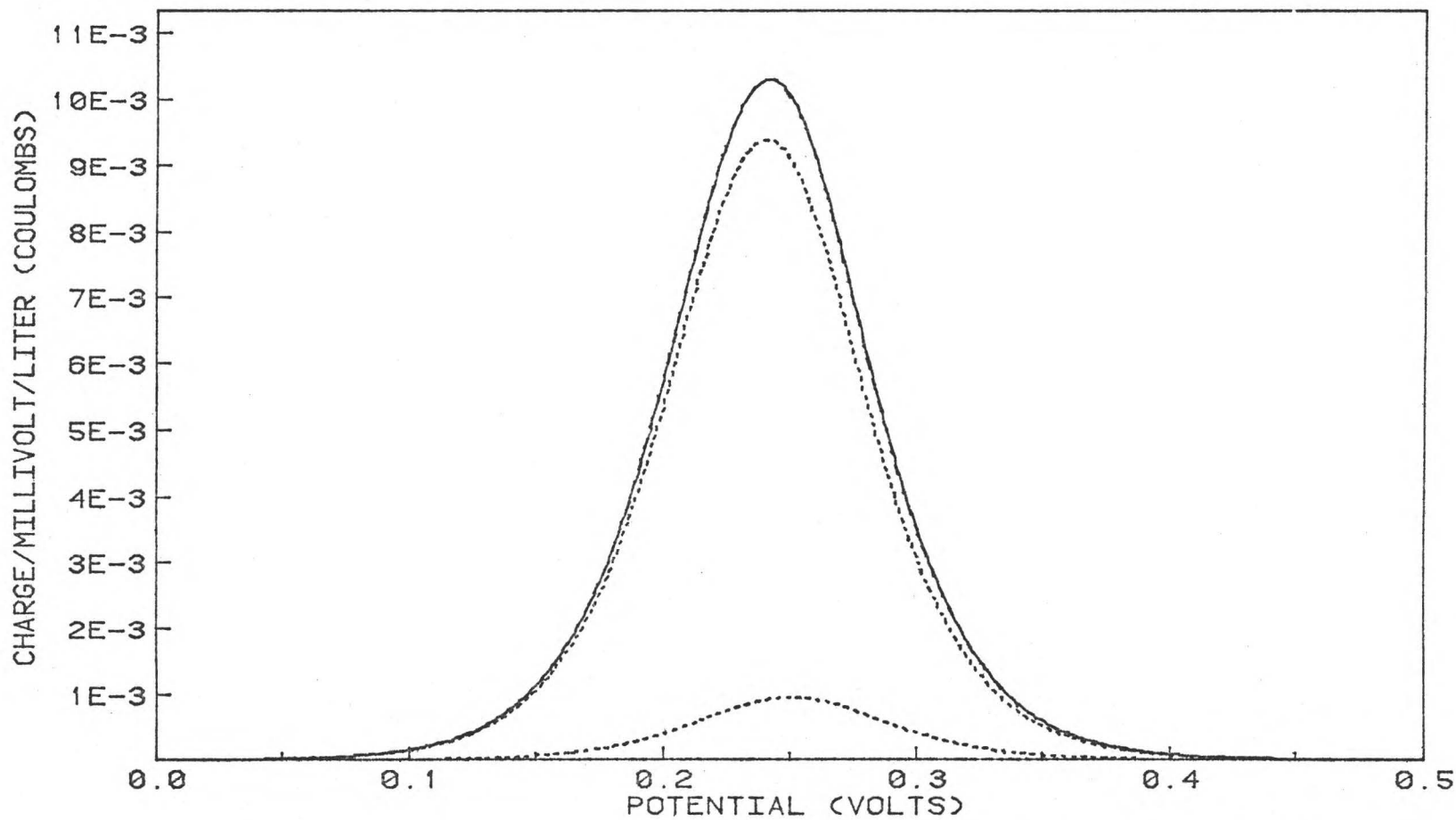


Figure 29. Theoretically generated scanning potential coulogram of a 1 to 10 ratio mixture of two constituents each with one equivalent per mole, but with a formal potential separation of ten millivolts.

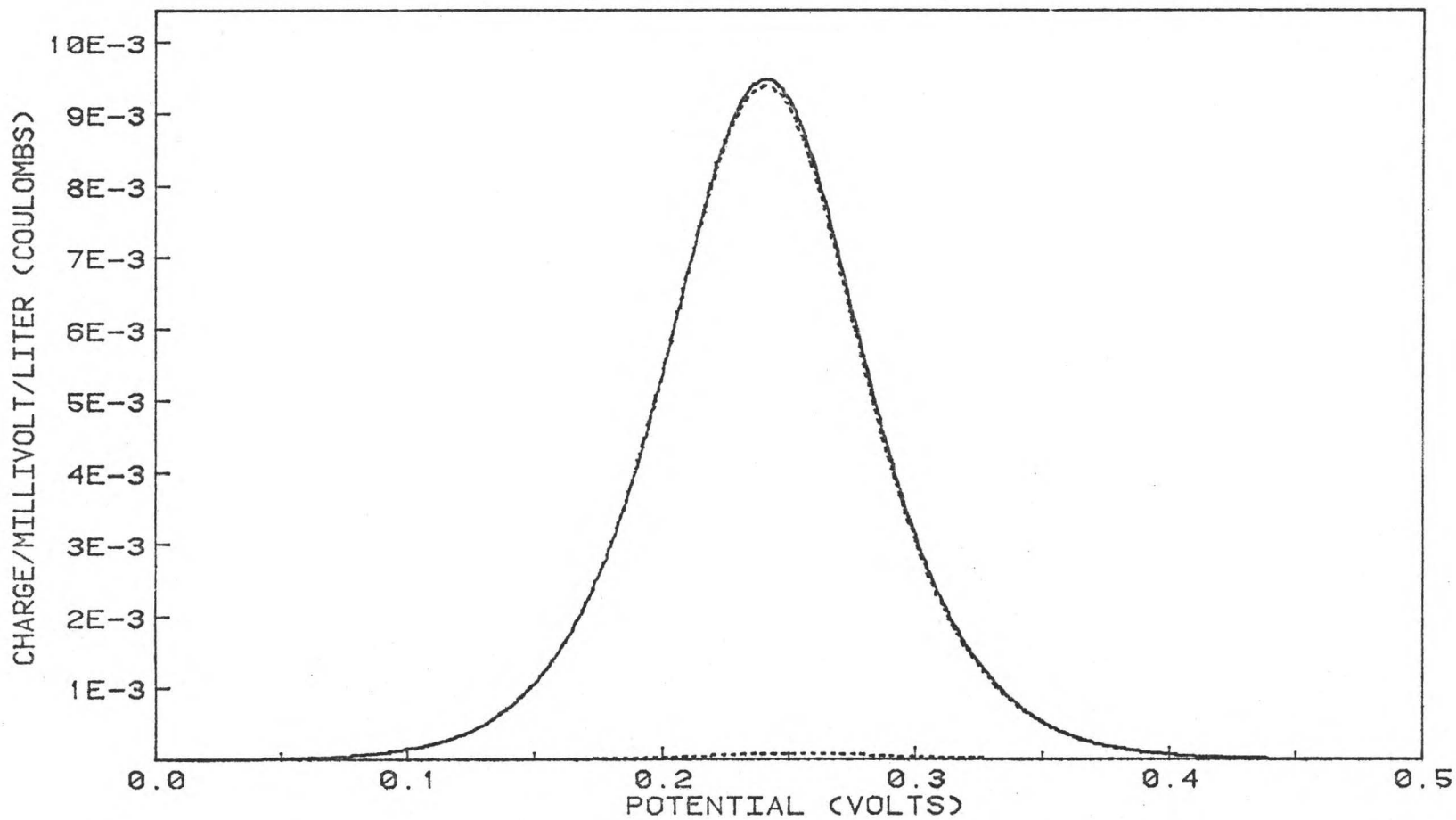


Figure 30. Theoretically generated scanning potential coulogram of a 1 to 100 ratio mixture of two constituents each with one equivalent per mole, but with a formal potential separation of ten millivolts.

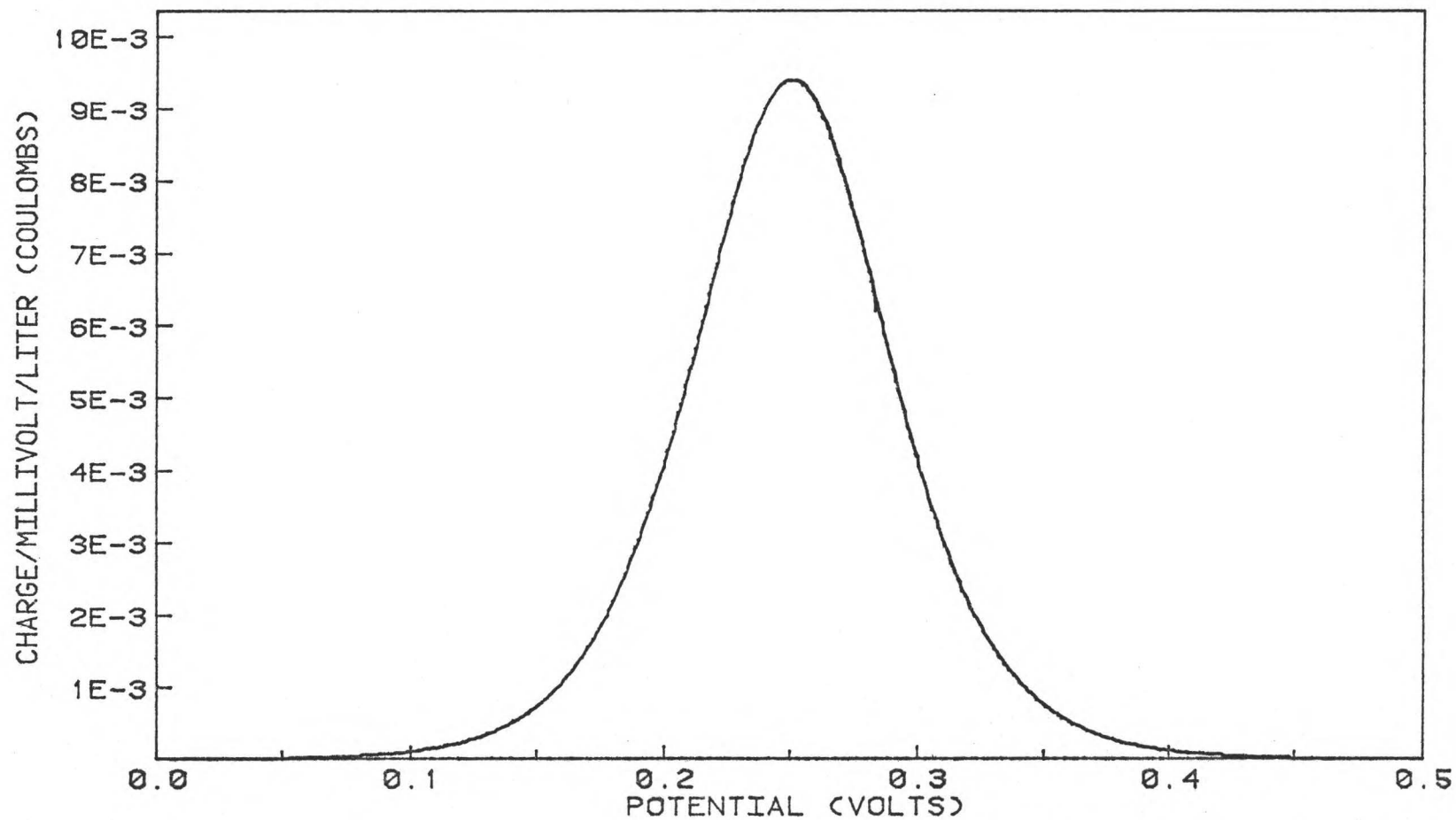


Figure 31. Theoretically generated scanning potential coulogram of a 1 to 1000 ratio mixture of two constituents each with one equivalent per mole, but with a formal potential separation of ten millivolts.

APPENDIX A

The Control Program

This program generates, in real-time, both linear and non-linear scans for real-time computer controlled scanning potential coulometry. The control routines and the data register read routines for the data acquisition and control unit are all written in PDP-11 assembly language. These routines are all general purpose routines and can be called from FORTRAN programs. The main program is written in FORTRAN, and it does all the file handling and calculations. During the scan, operations and calculations must be performed in real-time. Only subroutines that must be called to control or read data from the data acquisition and control unit are called during the scan. In order to avoid the time which would be required to make additional subroutine linkages, no other subroutines are used. When the entire scan is complete the data are written to disc memory for later data analysis. The data are also plotted on the Tektronix graphics terminal using subroutines listed in Appendix C.

```

C THIS PROGRAM GENERATES BOTH LINEAR AND NONLINEAR SCANS
C A LINEAR SCAN IS SELECTED BY A POSITIVE SCAN RATE AND A
C NONLINEAR SCAN IS SELECTED BY A NEGATIVE SCAN RATE.
C
C SINCE DECISIONS IN THIS PROGRAM MUST BE MADE IN REAL-TIME,
C EXECUTION TIME IS CRITICAL. SUBROUTINES ARE NOT USED
C EXCEPT FOR DATA ACQUISITION AND CONTROL. THIS IS DONE IN
C ORDER TO ELIMINATE THE TIME REQUIRED TO MAKE THE SUBROUTINE
C LINKAGE.
  REAL INTRVL, HEAD(18,2), N, CURNT(10)
  REAL CHARG(4096)
  LOGICAL*1 NAME(10)
  DATA YES /'YES'/
  DATA CHARG/4096*0./
  M=10
  M1=M-1
  N=M
C GET OUTPUT FILE, HEADING, AND SCAN PARAMETERS
C RUN NUMBERS ARE ASSIGNED AUTOMATICALLY
  CALL ASSIGN(2, 'RUNNUM.RSH/C')
  DEFINE FILE 2 (100,1,U,I)
  READ (2'1) INUM
990  ENCODE (10,990,NAME) INUM
  FORMAT('RUN',I3, '.RSH')
  CALL ASSIGN(1,NAME,10)
  TYPE 995,NAME
995  FORMAT (' ',10A1)
  INUM=INUM+1
  WRITE(2'1) INUM
  WRITE(7,1000)
1000  FORMAT(' ENTER A HEADING (TWO LINES)')
  READ(5,1010) (HEAD(I,1),I=1,18)
  READ(5,1010) (HEAD(I,2),I=1,18)
1010  FORMAT(18A4)
  WRITE(7,1020)
1020  FORMAT(' ENTER INITIAL AND FINAL POTENTIALS (MV), '
  1 'SCAN RATE, (V/MIN)'/, ' VOLUME (MLS), '
  2 'AND INSTRUMENT SCALE (MA)')
  READ(5,1030) IN,IF,SRATE,V,CSCALE
1030  FORMAT(2I8,3F12.0)
  IBEG=IN+2048
  IEND=IF+2048
  IPOT=IBEG
  CALL CNTRL(IPOT)
  WRITE(7,1040)
1040  FORMAT(' IS THE CELL READY ?'$)
  READ(5,1050) ANSR
1050  FORMAT(A3)
  IF(ANSR.NE.YES) GO TO 1
  ISCAN=ISIGN(1,IF-IN)
  CALL RATE(10,3)
  WRITE(1) HEAD
  IF (SRATE.LE.0.) GO TO 10
C IF SRATE IS > 0 THEN GENERATE A LINEAR SCAN
  INTRVL=1./((SRATE/60.)
  ICOUNT=INTRVL/10.+5
  SRATE= 60./INTRVL
  WRITE(1) IN,IF,SRATE,V,CSCALE
  CALL INPUT2(ICHARG)

```

```

2      DO 4 IPOT=IBEG, IEND, ISCAN
      DO 3 I=1, ICOUNT
      CALL CNTRL(IPOT)
      CALL INPUT2(ICHARG)
3      CHARG(IPOT)=CHARG(IPOT)+ICHARG
4      CONTINUE
      GO TO 50
C DO A NONLINEAR SCAN
10     WRITE(1) IN, IF, SRATE, V, CSCALE
      CALL RATE(10, 3)
C CALCULATE X SUMS SINCE THEY WILL NOT CHANGE DURING SCAN
      SUMX=0.
      SUMX2=0.
      DO 11 I=1, M
11     SUMX = SUMX + I
      SUMX2 = SUMX2 + I*I
      DELTA = N*SUMX2-SUMX**2
      CALL INPUT2(ICHARG)
      DO 30 IPOT=IBEG, IEND, ISCAN
C CALCULATE Y SUMS
12     SUMY = 0.
      SUMY2 = 0.
      DO 14 I=1, M
      CALL CNTRL(IPOT)
      CALL INPUT2(ICHARG)
      CURNT(I) = ICHARG
      SUMY = SUMY + CURNT(I)
14     SUMY2 = SUMY2 + CURNT(I)**2
      CHARG(IPOT) = CHARG(IPOT) + CURNT(I)
      CNT=N
C OLDEST VALUE IS DELETED, ALL OTHER VALUES ARE SLID DOWN
C AND NEW VALUES ARE ADDED.
C CALCULATE SLOPE
16     SUMY = SUMY - CURNT(1)
      SUMY2 = SUMY2 - CURNT(1)**2
      SUMXY = 0.
      DO 20 I=1, M1
20     CURNT(I) = CURNT(I+1)
      SUMXY = SUMXY + I*CURNT(I)
      CALL CNTRL(IPOT)
      CALL INPUT2(ICHARG)
      CURNT(M)=ICHARG
      CHARG(IPOT) = CHARG(IPOT) + CURNT(M)
      SUMY = SUMY + CURNT(M)
      SUMY2 = SUMY2 + CURNT(M)**2
      SUMXY = SUMXY + N*CURNT(M)
      CNT = CNT + 1.
      SLOPE = (N*SUMXY - SUMX*SUMY)/DELTA
C SLOPE MUST GO NEGATIVE OR THE DOUBLE LAYER IS STILL CHARGING.
      IF (SLOPE.GT.0.) GO TO 16
C MAJORITY OF CHARGE IS FROM ELECTROLYSIS
C CHECK FOR SLOPE GREATER THAN SCAN
22     SUMY = SUMY - CURNT(1)
      SUMY2 = SUMY2 - CURNT(1)**2
      SUMXY = 0.
      DO 25 I=1, M1
25     CURNT(I) = CURNT(I+1)
      SUMXY = SUMXY + I*CURNT(I)

```

```

CALL CNTRL(IPOT)
CALL INPUT2(ICHARG)
CURNT(M)=ICHARG
CHARG(IPOT) = CHARG(IPOT) + CURNT(M)
SUMY = SUMY + CURNT(M)
SUMY2 = SUMY2 + CURNT(M)**2
SUMXY = SUMXY + N*CURNT(M)
CNT = CNT +1.
SLOPE = (N*SUMXY - SUMX*SUMY)/DELTA
IF (SLOPE.LT.SRATE) GO TO 22
C NOW AT BACKGROUND
OFFSET = (SUMX2*SUMY - SUMX*SUMXY)/DELTA
CHARG(IPOT) = CHARG(IPOT) - SUMY
30 CONTINUE
C WRITE DATA TO DISC AND ALSO PLOT DATA
50 YSCALE=0.
DO 55 I=IBEG,IEND,ISCAN
IF (YSCALE.LT.CHARG(I)) YSCALE=CHARG(I)
55 WRITE(1) CHARG(I)
CALL ERASE
ENDFILE 1
YSCALE=700./YSCALE
XSCALE = 1000./IABS(IEND-IBEG)
IBEG1=IBEG
IF (IBEG.GT.IEND) IBEG1=IEND
IY=CHARG(IBEG)*YSCALE
IX=XSCALE*(IBEG-IBEG1)
CALL MOVE (IX,IY)
DO 60 I=IBEG,IEND,ISCAN
IX=XSCALE*(I-IBEG1)
IY=CHARG(I)*YSCALE
60 CALL DRAW (IX,IY)
CALL MOVE (0,780)
CALL EXIT
END

```

```

.TITLE  INTRFC
.GLOBL  ENABLE,DISABL,RATE,MPX,GAIN,CNTRL,INPUT1,INPUT2
.CSECT

.MCALL  ..V2...GTJB,.INTEN,.SYNCH,.RSUM,.SPND
.MCALL  .PROTECT,.PRINT,.EXIT
;
;
;..V2..
;
;THE FOLLOWING ROUTINES CONTROL AND READ REGISTERS FROM THE PDP-11
;INTERFACE. THE ROUTINES ARE FORTRAN CALLABLE ACCORDING TO
;THE SUBPROGRAM LINKAGE SECTION OF THE RT-11/RSTS/E FORTRAN IV
;USER'S GUIDE.
;DEFINE REGISTERS
;
;R0=%0
;R1=%1
;R2=%2
;R3=%3
;R4=%4
;R5=%5
;SP=%6
;PC=%7
;
;DEFINE INTERFACE REGISTERS
;
;CNTRO=177520
;CNTR1=CNTR0+2
;CNTR2=CNTR0+4
;CNTR3=CNTR0+6
;
;ENABLE SETS UP INTERRUPT VECTOR FOR CNTRL ROUTINE
;
;ENABLE: MOV      #170,R5
;        RTS      PC
;ERR:    .PRINT   #NOVEC
;        .EXIT
;NOVEC:  .ASCIZ   /INTERRUPT VECTORS ALREADY IN USE/
;
;LIST:   .BLKW    2           ;ARGUMENTS FOR EMT
;JOBARG: .BLKW    8.         ;JOB PARAMETERS
;
;DISABL  DISABLES INTERRUPT
;
;DISABL: BIC      #060000,INTR1
;        MOV      INTR1,CNTR1 ;DISABLE INTERRUPT
;        RTS      PC

```

```

;RATE SETS SAMPLE INTERVAL
;
RATE:  MOV      (R5)+,RO      ;GET # OF ARGUMENTS
      MOV      @(R5)+,RO     ;GET MANTISSA
      BIC      #177760,RO    ;CLEAR UNWANTED BITS
      BIC      #177,INTR3    ;MAKE ROOM FOR SAMPLE INTERVAL
      BIS      RO,INTR3      ;SET MANTISSA
      MOV      @(R5)+,RO     ;GET EXPONENT
      BIC      #177770,RO    ;CLEAR UNWANTED BITS
      ASL      RO           ;SHIFT TO PROPER LOCATION
      ASL      RO
      ASL      RO
      ASL      RO
      BIS      RO,INTR3      ;SET EXPONENT
      MOV      INTR3,CNTR3   ;SEND CONTROL WORD
      RTS      PC           ;RETURN TO PROGRAM

;MPX SETS RANDOM ACCESS MULTIPLEXER CHANNEL
;
MPX:   MOV      (R5)+,RO      ;GET # OF ARGUMENTS
      MOV      @(R5)+,RO     ;GET MULTIPLEX CHANNEL
      BIC      #177770,RO    ;CLEAR UNWANTED BITS
      BIC      #160000,INTR3 ;CLEAR MPX AREA
      MOV      #13.,R2       ;SET UP SHIFT COUNT
      JSR      PC,SHIFT      ;SHIFT TO PROPER LOCATION
      BIS      RO,INTR3      ;SET MPX CHANNEL
      MOV      INTR3,CNTR3   ;SEND CONTROL WORD
      RTS      PC           ;RETURN TO PROGRAM

;GAIN SET THE GAIN OF THE PROGRAMMABLE AMPLIFIER
;
GAIN:  MOV      (R5)+,RO      ;GET # OF ARGUMENTS
      MOV      @(R5)+,RO     ;GET GAIN
      BIC      #177770,RO    ;CLEAR UNWANTED BITS
      BIC      #1600,INTR3   ;CLEAR GAIN AREA
      MOV      #7,R2         ;SET UP SHIFT COUNT
      JSR      PC,SHIFT      ;SHIFT TO PROPER LOCATION
      BIS      RO,INTR3      ;SET AMPLIFIER GAIN
      MOV      INTR3,CNTR3   ;SEND CONTROL WORD
      RTS      PC           ;RETURN TO PROGRAM

;CNTRL CHECKS TO SEE IF INTERFACE IS READY FOR NEW CONTROLS AND IF
; IT IS CNTRL SENDS THE INTERFACE THE EXPERIMENT CONTROL WORD. IF
; NOT CNTRL WAITS UNTILL INTERFACE IS READY.
;
CNTRL: MOV      (R5)+,RO      ;GET # OF ARGUMENTS
      MOV      @(R5)+,INTRO  ;SAVE CONTROL WORD
CNTRL1: TSTB   CNTR1
      BPL     CNTRL1
      MOV     INTRO,CNTR0    ;SEND CONTROL WORD
      RTS    PC             ;RETURN TO SUBROUTINE

;INPUT1 READS ANALOG-DIGITAL CONVERTER REGISTER
;
INPUT1: MOV      (R5)+,RO      ;GET # OF ARGUMENTS
      MOV      CNTR0,@(R5)+  ;READ AND STORE REGISTER
      RTS      PC           ;RETURN TO PROGRAM

```

```

;
;INPUT2 READS REGISTER 2 AND THEN CLEARS IT
;
INPUT2: MOV      (R5)+,R0      ;GET # OF ARGUMENTS
        MOV      CNTR2,@(R5)+ ;READ AND STORE REGISTER
        RTS      PC          ;RETURN TO PROGRAM
;
;SHIFT WIL SHIFT R0 LEFT BY THE COUNT IN R2
;
SHIFT:  ASL      R0          ;SHIFT LEFT
        DEC      R2          ;DECREMENT COUNTER
        TST      R2          ;ARE WE DONE
        BNE      SHIFT      ;NO - DO IT AGAIN
        RTS      PC          ;YES- RETURN
;
;
INTR0:  0          ;INTERFACE WORD 0 SAVE REGISTER
INTR1:  0          ;INTERFACE WORD 1 SAVE REGISTER
INTR2:  0          ;INTERFACE WORD 2 SAVE REGISTER
INTR3:  0          ;INTERFACE WORD 3 SAVE REGISTER
;
        .END

```


APPENDIX B

The Data Analysis Program

This program does the data analysis for computer controlled scanning potential coulometry. Non-linear least squares curve fitting is used to resolve overlapping peaks and background. Equation (27) in this dissertation is used to fit the charge contributions made by constituents with two soluble species and also the charge contribution made by constituents that form an insoluble deposit on a partially covered inert electrode. Equation (19) in this dissertation is used to fit the charge contribution of constituents that form an insoluble deposit on a completely covered electrode. The complement of the error function used by this equation is approximated by a Taylor series (68).

This program allows either a selected portion of the curve or the entire curve to be analyzed. After the curve portion is selected and the initial parameters are entered the program is completely automatic. The parameters which will give the best fit to the data are calculated by this program. When these parameters have been calculated, the data, the calculated fit to the data, the contribution due to each individual constituent, and the background are plotted on a Tektronix 4662 plotter and the numerical results are printed on a GE Terminet terminal. The routines to plot the

results automatically scale the plots and label both x and y axes. The Tektronix Plot-10 Terminal Control System release 1.0 was modified to use the assembly language routines in Appendix C and was used in conjunction with routines listed here to generate all plots.

```

C THIS PROGRAM DOES THE DATA ANALYSIS FOR COMPUTER CONTROLLED
C SCANNING POTENTIAL COULOMETRY. NON-LINEAR LEAST SQUARES
C CURVE FITTING IS USED TO RESOLVE OVERLAPPING PEAKS AND
C BACKGROUND.
C THIS PROGRAM FINDS THE BEST PARAMETERS TO FIT THE DATA.
  DOUBLE PRECISION ARRAY(20,20)
  LOGICAL*1 LIST(200)
  REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
  1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
  COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
  1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
  2 EINIT,EFINL,HEAD,IPLTON
  COMMON/PARAM/ C,NPEAK
  COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
  EXTERNAL ECALC
C INITILIZE PLOTTER
  IPLTON=0
  CALL PLOTON
  CALL PLTSET
  CALL PLOTOF
C ENTER THE DATA FILE
  TYPE 100
100  FORMAT(' ENTER THE NAME OF THE FILE TO BE ANALIZED '$)
  CALL ASSIGN(11,NAME,-1)
  FLAMDA=.001
  FDIVRT=23060./(R*T)
  READ(11) HEAD
  READ(11) IN,IF,SRATE,V,CSCALE
  ISCAN=ISIGN(1,IF-IN)
  NPNTS=IABS(IF-IN)
  YSCALE=0.
  DO 1 I=1,NPNTS
  READ(11) Y(I)
  Y(I)=1E-5*CSCALE*Y(I)/V
  1  YSCALE=AMAX1(YSCALE,Y(I))
  YSCALE=1.1*YSCALE
  ENDFILE 11
  CALL CLOSE(11)
C SET UP PARAMETERS TO PLOT DATA
  CALL INITT(960)
  IFINL=NPNTS
  IINIT=IN
  IF (IINIT.GT.IF) IINIT=IF
  EINIT=.001*IINIT
  EFINL=EINIT+.001*NPNTS
  EIN=EINIT
  EFI=EFINL
  IINIT=1
  CALL VWINDO(EINIT,.001*NPNTS,0,YSCALE)
  CALL SWINDO(110,885,50,620)
  CALL PLTSCL(SCALE)
C ENTER PARAMETER FILE
  TYPE 102
102  FORMAT(' ENTER THE NAME OF THE PARAMETER FILE '$)
  CALL ASSIGN(11,NAME,-1)
  TYPE 103
103  FORMAT(' ENTER NUMBER OF PEAKS '$)
  READ(11,104) NPEAK
104  FORMAT(I)

```

```

TYPE 106
106  FORMAT(' ENTER TYPE, N, ENOT, B, DELTA B, SYMBOL')
      DO 11 I=1,NPEAK
      READ(11,108) TYPE(I),N(I),ENOT(I),C(I+2*NPEAK+2),
11    1 C(I+3*NPEAK+2),CONSTI(I)
      CONTINUE
108  FORMAT(5F10.0,A4)
      TYPE 110
110  FORMAT(' ENTER A 1 IF YOU WANT FIRST FIT PLOTED')
      ACCEPT 104,IPLT1
C ONLY ANALYZE PORTION OF THE CURVE DESIRED
13  CALL VCURSR(ICHR,EINIT,SCALE)
      CALL VCURSR(ICHR,EFINL,SCALE)
      IF (EINIT.LE.EFINL) GO TO 3
      TEMP=EINIT
      EINIT=EFINL
      EFINL=TEMP
3    IF (EFINL.GT.EFI) EFINL=EFI
      IF (EINIT.LT.EIN) EINIT=EIN
      IINIT=ICALC(EINIT)
      IFINL=ICALC(EFINL)
      IF (IFINL.GT.IINIT) GO TO 5
      I=IFINL
      IFINL=IINIT
      IINIT=I
      IF (IINIT.LE.0) IINIT=1
      IF (IFINL.GT.NPNTS) IFINL=NPNTS
5    CALL PLTSCL(SCALE)
C FIT WITH BACKGROUND
      YSCALE=1.1*SCALE
      CALL VWINDO(EINIT,EFINL-EINIT,0.,YSCALE)
      NTERMS=NPEAK+2
      CALL PLTSCL(SCALE)
7    CALL CURFIT(CHISQ,FLAMDA)
      IF (IPLT1.NE.0) CALL PLTON
      CALL RESULT
C FIT ALL TERMS
      NTERMS=4*NPEAK+2
      DO 10 I=1,4
      CHISQ1=CHISQ
      CALL CURFIT(CHISQ,FLAMDA)
      IF ((CHISQ1-CHISQ)/CHISQ1.LE..001) GO TO 20
10   CONTINUE
20   IF (CHISQ.LT.CHISQ1) GO TO 30
C IF LAST FIT WAS BETTER THAN THIS FIT KEEP LAST.
      DO 25 J=1,NTERMS
25   C(J)=CL(J)
30   CALL PLTON
      CALL RESULT
      CALL MOVABS(0,780)
      CALL EXIT
      END

```

```
BLOCK DATA
COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
DATA LIST/200*0/
DATA R/1.987/
DATA T/298.15/
DATA F/96487./
DATA C/20*0./,CL/20*0./
END
```

```

SUBROUTINE RESULT
C TYPES AND PLOTS RESULTS
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
C PLOT DATA AND SCALE MARKINGS
CALL PLTSCL(D)
101 FORMAT(36A4)
C PLOT EACH INDEPENDENT PEAK
DO 30 J=1,NPEAK
ENOTT=ENOT(J)+C(J+2+NPEAK)
E=C(J+2+2*NPEAK)
EFFN=N(J)*AMIN1(B,B+C(J+2*3*NPEAK))
IF (TYPE(J).NE.0.) ENOTT=ENOTT+TYPE(J)*(ALOG(C(J)))/
1 (EFFN*FDIVRT) -.15/EFFN)
IBEG=ICALC(ENOTT-.19/EFFN)
IF (IBEG.LT.IINIT) IBEG=IINIT
IEND=ICALC(ENOTT+.19/EFFN)
IF (IEND.GT.IFINL) IEND=IFINL
E=ECALC(IBEG)
CALL MOVEA(E,CURNT(E,ENOT(J),C(J),N(J),J,TYPE(J)))
Q=0.
Q1=0.
DO 25 I=IBEG,IEND,ISCAN
E=ECALC(I)
YFIT=CURNT(E,ENOT(J),C(J),N(J),J,TYPE(J))
Q=Q+YFIT
Q1=Q1 + Y(I) + YFIT - CURNT(E,ENOT,C,N,0,TYPE)
25 CALL DASHA(E,YFIT,12)
BETA(J)=Q/F
SIGMAC(J)=Q1/F
30 CONTINUE
C PLOT FITTED FUNCTION
CALL MOVEA(ECALC(IINIT),Y(IINIT))
DO 40 I=IINIT,IFINL,2
YFIT=CURNT(ECALC(I),ENOT,C,N,0,TYPE)
40 CALL DASHA(ECALC(I),YFIT,34)
C PLOT BACKGROUND
CALL MOVEA(ECALC(IINIT),Y(IINIT))
DO 50 I=IINIT,IFINL,2
E=ECALC(I)
50 CALL DASHA(E,BCKGND(E),3212)
CALL ANMODE
CALL PLOTON
CALL PLOTOF
C WRITE OUT RESULTS
CALL CRLF
ENCODE(150,101,LIST)HEAD
LIST(71) = 13
LIST(72) = 10
CALL KBOUT(150)

```

```
CALL CRLF
ENCODE(74,110,LIST)
CALL KBOUT(74)
CALL CRLF
110  FORMAT('      N ENOT      C      C INTG      C DATA',
      1 5X,'E OFF      B      DELTA B')
DO 60 I=1,NPEAK
ENCODE(75,200,LIST) CONSTI(I),N(I),ENOT(I),C(I),PETA(I),
1 SIGMAC(I),C(I+NPEAK+2),C(I+2*NPEAK+2),C(I+3*NPEAK+2)
CALL KBOUT(75)
60  CALL CRLF
200  FORMAT(A4,F2.0,F6.3,3(1PE11.4),3(E10.3))
ENCODE(68,300,LIST) C(NPEAK+1),C(NPEAK+2),V
CALL KBOUT(68)
CALL CRLF
300  FORMAT(' BACKGROUND OFFSET =',1PE11.4,' SLOPE =',E11.4,
1 ' VOLUME =',OPF7.3)
RETURN
END
```

```

SUBROUTINE PLTSCL(SCALE)
C PLOTS BORDER, SCALE MARKINGS, AND DATA. ALSO LABELS PLOT
C AND SCALE MARKINGS.
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
CALL NEWPAG
C DRAW BORDER AND SCALE MARKINGS
CALL MOVEA(EINIT,0.)
DO 1 I=1,4
CALL DRAWA(EFINL,0.)
CALL DRAWA(EFINL,YSCALE)
CALL DRAWA(EINIT,YSCALE)
1 C DRAW X SCALE MARKINGS AND LABELS
CALL DRAWA(EINIT,0.)
IENIT=INT(EINIT*20+.99)
IF (EINIT.LT.0.) IENIT=INT(EINIT*20.)
IEFIN=INT(EFINL*20.)
DO 60 I=IENIT,IEFIN
E=.05*I
CALL MOVEA(E,0.)
IF (MOD(I,2).EQ.0) GO TO 55
CALL DRWREL(0,6)
GO TO 60
55 CALL DRWREL(0,10)
CALL MOVREL(-32,-33)
CALL ANMODE
ENCODE(4,400,LIST)E
CALL STRING(4)
60 CONTINUE
C DRAW Y SCALE MARKINGS AND LABELS
IENIT=INT(ALOG10(YSCALE)-1.7482)
E=10.**IENIT
IEFIN=YSCALE/E
ISTEP=1
IF (IEFIN.GT.11) ISTEP=2
IF (IEFIN.GT.21) ISTEP=5
DO 70 I=ISTEP,IEFIN,ISTEP
CALL MOVEA(EINIT,I*E)
CALL DRWREL(10,0)
CALL MOVREL(-84,-8)
CALL ANMODE
ENCODE (5,500,LIST) I,IENIT
CALL STRING(5)
70 CONTINUE
IENIT=INT(EINIT*10.)+1
400 FORMAT(F4.1)
500 FORMAT(I2,'E',I2)
C PLOT DATA
SCALE=0.
CALL MOVEA(ECALC(IINIT),Y(IINIT))
DO 90 I=IINIT,IFINL
SCALE=AMAX1(SCALE,Y(I))
90 CALL DRAWA(ECALC(I),Y(I))

```



```

C LABEL PLOT
  CALL MOVABS(440,5)
  CALL ANMODE
  ENCODE(17,600,LIST)
  CALL STRING(17)
  IF (IPLTON.EQ.0) GO TO 100
  CALL MOVABS(25,130)
  CALL PROT90
  CALL ANMODE
  ENCODE(33,700,LIST)
  CALL KBOUT(33)
  CALL PLTSET
600  FORMAT('POTENTIAL (VOLTS)')
700  FORMAT('CHARGE/MILLIVOLT/LITER (COULOMBS)')
100  IPLTON=0
  CALL MOVABS(0,780)
  CALL ANMODE
  RETURN
  END

```

```

SUBROUTINE PLTON
C TURNS ON PLOTTER AND SETS IPLTON TO 1
  DOUBLE PRECISION ARRAY(20,20)
  LOGICAL*1 LIST(200)
  REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
  1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
  COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
  1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
  2 EINIT,EFINL,HEAD,IPLTON
  IPLTON=1
  CALL PLOTON
  RETURN
  END

```

```

SUBROUTINE STRING(NCHR)
C SENDS AN OUTPUT STRING TO THE TEKTRONIX TERMINAL, AND ALSO TO
C THE TEKTRONIX PLOTTER IF THE PLOTTER IS ON.
  DOUBLE PRECISION ARRAY(20,20)
  LOGICAL*1 LIST(200)
  REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
  1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
  COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
  1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
  2 EINIT,EFINL,HEAD,IPLTON
  DO 10 I=1,NCHR
  ICHR=LIST(I)
  CALL TOUTPT(ICHR)
  RETURN
  END
10

```

```
      SUBROUTINE CRLF
C SENDS AND CARRIAGE RETURN LINE FEED SEQUENCE TO THE PLOTTER IF
C THE PLOTTER IS ON OR TO THE GE TERMINAL IF THE PLOTTER IS OFF.
      CALL PLTOUT(13)
      CALL PLTOUT(10)
      RETURN
      END
```

```
      SUBROUTINE KBOUT(NCHR)
C SENDS AN OUTPUT STRING TO THE PLOTTER IF IT IS ON, OR TO THE
C GE TERMINAL IF THE PLOTTER IS OFF.
      DOUBLE PRECISION ARRAY(20,20)
      LOGICAL*1 LIST(200)
      REAL Y(1600), C(20), SIGMAC(20), ALPHA(20,20), BETA(20)
      1, CONSTI(20), ENOT(20), N(20), CL(20), HEAD(2,18), DERIV(20)
      COMMON /RSRCH/ Y, IINIT, IFINL, ALPHA, BETA, DERIV, ARRAY, SIGMAC,
      1 CONSTI, ENOT, N, NTERMS, TYPE(20), CL, YSCALE, LIST,
      2 EINIT, EFINL, HEAD, IPLTON
      DO 10 I=1, NCHR
      ICHR=LIST(I)
      CALL PLTOUT(ICHR)
      RETURN
      END
```

10

```

SUBROUTINE CURFIT(CHISQ,FLAMDA)
C  EVALUATES PARAMETERS BY NON-LINEAR LEAST SQUARES CURVE FITTING.
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
DATA ITEST/0/
DATA ISTEP/10/
FLAG=0.
CHISQ2=0.

C
C  EVALUATE ALPHA AND BETA MATRICES
C
DO 10 J=1,NTERMS
CL(J) = C(J)
BETA(J) = 0.
DO 10 K=1,J
10 ALPHA(J,K)=0.
DO 40 I=IINIT,IFINL,ISTEP
E=ECALC(I)
CALL DERIV1(E)
DO 30 J=1,NTERMS
BETA(J) = BETA(J)+(Y(I)-CURNT(E,ENOT,C,N,0,TYPE))*DERIV(J)
DO 30 K=1,J
30 ALPHA(J,K) = ALPHA(J,K) + DERIV(J)*DERIV(K)
40 CONTINUE
DO 45 J=1,NTERMS
IF (ALPHA(J,J).EQ.0.) ALPHA(J,J)=1.
DO 45 K=1,J
45 ALPHA(K,J) = ALPHA(J,K)
IF (ITEST.NE.0) GO TO 49

C
C  EVALUATE CHI SQUARE AT STARTING POINT
C
CHISQ1 = FCHISQ(1)
ITEST=1

C
C  INVERT MODIFIED CURVATURE MATRIX TO FIND NEW PARAMETERS
C
49 DO 50 J=1,NTERMS
DO 51 K=1,NTERMS
51 ARRAY(J,K) = ALPHA(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K))
50 ARRAY(J,J) = 1. + FLAMDA
CALL INVERT
DO 60 J=1,NTERMS
DO 60 K=1,NTERMS
60 C(J) = C(J)+BETA(K)*ARRAY(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K))

C
C  ALL CONCENTRATIONS MUST BE POSITIVE
C
70 DO 70 J=1,NPEAK
C(J)=ABS(C(J))

```

```
C
C IF CHI SQUARE INCREASED, INCREASE FLAMDA AND TRY AGAIN
C
    CHISQR = FCHISQ(1)
    IF (CHISQ1.GE.CHISQR.OR.CHISQR*FLAG.GE.CHISQ2) GO TO 90
    FLAG=1.
    CHISQ2 = CHISQR
    FLAMDA = 10.*FLAMDA
    GO TO 49

C
C EVALUATE UNCERTAINTIES
C
90    FLAMDA = .1*FLAMDA
    CHISQ1=CHISQR
    DO 100 J=1,NTERMS
100   CONTINUE
    RETURN
    END
```

```

SUBROUTINE DERIV1(E)
C  CALCULATES THE DERIVATIVES OF THE FITTING FUNCTION WITH RESPECT
C  TO EACH PARAMETER
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFIML,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
REAL DELTA(3)
DATA DELTA/.005,.005,.005/
DO 20 J=1,NPEAK
IF (TYPE(J).EQ.0.) GO TO 10
CONC=C(J)
IF (CONC.NE.0.) GO TO 1
EO=ENOT(J)+TYPE(J)*ALOG(2E-6)/(N(J)*FDIVRT)
DERIV(J)=CURNT(E,EO,1.,N(J),J,0)
GO TO 20
1 Q=TYPE(J)*(E-ENOT(J))*N(J)*FDIVRT
Q1=TYPE(J)*(E-ENOT(J)+.001*ISCAN)*N(J)*FDIVRT
DERIV(J)=0.
IF (ABS(Q).GT.50..OR.ABS(Q1).GT.50.) GO TO 20
Q2=EXP(Q)
DERIV(J)=TYPE(J)*N(J)*F*(Q2-EXP(Q1))*(-EXP(-(Q2/CONC)**2))
1 *EXP(2*Q)/CONC**3
GO TO 20
10 DERIV(J)=CURNT(E,ENOT(J),1.,N(J),J,0)
20 CONTINUE
DERIV(NPEAK+1)=1.
DERIV(NPEAK+2)=E
DO 30 J=1,3
DO 30 I=1,NPEAK
K=J*NPEAK+2+I
C(K)=C(K)+DELTA(J)
YFIT=CURNT(E,ENOT,C,N,0,TYPE)
C(K)=C(K)-DELTA(J)
30 DERIV(K)=(YFIT-CURNT(E,ENOT,C,N,0,TYPE))/DELTA(J)
RETURN
END

```

```

SUBROUTINE INVERT
C  INVERT MATRIX CONTAINED IN ARRAY AND CALCULATE ITS DETERMINANT
DOUBLE PRECISION ARRAY(20,20),SAVE
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
DET = 1.
DO 120 L=1,NTERMS
SAVE = ARRAY(L,L)
IF (SAVE+1.0.EQ.1.0) SAVE=1.0
ARRAY(L,L)=1.
DET=DET*SAVE
DO 100 J=1,NTERMS
100  ARRAY(L,J)=ARRAY(L,J)/SAVE
DO 120 I=1,NTERMS
IF(I.EQ.L) GO TO 120
SAVE=ARRAY(I,L)
ARRAY(I,L)=0.
DO 110 J=1,NTERMS
110  ARRAY(I,J)=ARRAY(I,J)-SAVE*ARRAY(L,J)
120  CONTINUE
RETURN
END

```

```

FUNCTION FCHISQ(INTRVL)
DOUBLE PRECISION CHISQ,WEIGHT
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
11 CHISQ = 0.
FREE=(IFINL-IINIT)
FREE=NTERMS*FREE/INTRVL
CALL MOVEA(ECALC(IINIT),Y(IINIT))
IF (FREE.GT.0.) GO TO 20
13 FCHISQ = 0.
GO TO 40
C
C
C ACCUMULATE CHI SQUARE
20 DO 30 I=IINIT,IFINL,INTRVL
E=ECALC(I)
YFIT=CURNT(E,ENOT,C,N,0,TYPE)
CALL DASHA(E,YFIT,34)
30 CHISQ = CHISQ + (Y(I)-YFIT)**2
CALL ANMODE
C
C
C DIVIDE BY NUMBER OF DEGREES OF FREEDOM
40 FCHISQ = CHISQ/FREE
RETURN
END

```

FUNCTION CURNT(E,ENOT,CON,N,IPEAK,TYPE)

C
C
C
C
C
C
C
C
C
C
C
C
C
C
C

DESCRIPTION OF PARAMETERS

E - CELL POTENTIAL
 ENOT - ARRAY OF STANDARD POTENTIALS OF SPECIES IN SOLN.
 C - ARRAY OF CONCENTRATIONS OF VARIOUS SPECIES
 N - ARRAY OF EQUIVELENTS PER MOLE FOR SPECIES IN SOLN.
 NPEAK - NUMBER OF PEAKS
 IPEAK - PEAK NUMBER FOR SINGLE PEAK CONTRIBUTION
 F - FARADAY
 R - GAS LAW CONSTANT
 T - TEMPERATURE
 FDIVRT - $F/(R*T)$
 V - VOLUME OF SOLN.
 TYPE - ARRAY OF SPECIES TYPE (IF TYPE = 0 THEN SPECIES
 IS A REDOX COUPLE IN SOLN., IF NOT ONE OXIDATION STATE
 OF THE COUPLE IS INSOLUABLE.

REAL ENOT(1),CON(1),N(1),C(20),TYPE(1)
 COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
 COMMON/PARAM/ C,NPEAK
 CURNT=0.
 NCALC = NPEAK
 IF (IPEAK.LE.0) GO TO 1
 NCALC = 1
 J=1
 JJ=IPEAK
 GO TO 2
 1 CURNT = BCKGND(E)
 DO 10 J=1,NCALC
 JJ=J
 2 J1=NPEAK+JJ+2
 J2=J1+NPEAK
 J3=J2+NPEAK
 CHRGE=0.
 IF (CON(J).LE.0.) GO TO 10
 EODIF=ENOT(J)+C(J1)-E
 EXP1=N(J)*FDIVRT*EODIF
 B=C(J2)
 DO 3 K=1,2
 EXP2=B*EXP1
 IF (ABS(EXP2).GT.50.) GO TO 10
 3 B = C(J2) + C(J3)/(1. + EXP(EXP2))
 CR = B*N(J)*FDIVRT
 CR1 = EODIF*CR
 CR2 = (EODIF+.001*ISCAN)*CR
 IF (TYPE(J).EQ.0.) GO TO 5
 Q1 = EXP(-TYPE(J)*CR1)
 CHRGE=TYPE(J)*1.8077*ISCAN*N(J)*F*(Q1-EXP(-TYPE(J)*CR2))
 1 *ERFC(Q1/CON(J))
 GO TO 10
 5 CHRGE=ISCAN*N(J)*F*CON(J)*(1./(EXP(CR1)+1.)
 1 -1./(EXP(CR2)+1.))
 10 CURNT=CURNT+CHRGE
 RETURN
 END


```

FUNCTION BCKGND(E)
C CALCULATES BACKGROUND CHARGE (CONSTANT + SLOPE)
DOUBLE PRECISION ARRAY(20,20)
LOGICAL*1 LIST(200)
REAL Y(1600),C(20),SIGMAC(20),ALPHA(20,20),BETA(20)
1, CONSTI(20),ENOT(20),N(20),CL(20),HEAD(2,18),DERIV(20)
COMMON /RSRCH/ Y,IINIT,IFINL,ALPHA,BETA,DERIV,ARRAY,SIGMAC,
1 CONSTI,ENOT,N,NTERMS,TYPE(20),CL,YSCALE,LIST,
2 EINIT,EFINL,HEAD,IPLTON
COMMON/PARAM/ C,NPEAK
BCKGND = C(NPEAK+1) + C(NPEAK+2)*E
RETURN
END

FUNCTION ERFC(X)
C CALCULATES THE ERROR INTEGRAL COMPLEMENT
ERFC=1.
IF (X.LT.1E-8) GO TO 10
ERFC=0.
IF (X.GT.5.) GO TO 10
ERFC=1./((1+.278393*X+.230389*X*X+.000972*X**3+.078108*X**4
1 )**4
10 RETURN
END

FUNCTION ECALC(I)
C CALCULATES A POTENTIAL GIVEN A SUBSCRIPT
COMMON /CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
ECALC=.001*(IN+ISCAN*I)
RETURN
END

FUNCTION ICALC(E)
C CALCULATES A SUPSCRIPT GIVEN A POTENTIAL
COMMON/CONSTN/ R,T,V,F,FDIVRT,IN,IF,ISCAN
ICALC=(1000.*E-IN)**ISCAN+.5
RETURN
END

```

APPENDIX C

Plot Routines

The FORTRAN routines in this section are core and time efficient versions of the Absolute Graphics routines in the Tektronix Plot 10 Terminal Control System. These routines are used because they are faster and they take less core than the equivalent Plot 10 routines. The assembly language routines generate special control character sequences for both the Tektronix terminal and the Tektronix plotter. These routines are used to transmit characters and character strings to the Tektronix terminal and plotter, turn the plotter on or off, send the reset code to the plotter, and send the code to rotate the characters the plotter draws 90 degrees. These routines are used by the FORTRAN routines in this section and also by a modified version of the Tektronix Plot 10 Terminal Control System.

```

SUBROUTINE ANMODE
C ROUTINE SETS THE TERMINAL INTO THE ALPHA-NUMERIC MODE.
  CALL TOUTPT(31)
  RETURN
END

SUBROUTINE ERASE
C ROUTINE ERASES SCREEN & SETS CURSOR AT HOME POSITION
  CALL TOUTPT(27)
  CALL TOUTPT(12)
  CALL WAIT(60)
  RETURN
END

SUBROUTINE POINT(IX,IY)
C ROUTINE PUTS A POINT IN THE CORD. SPECIFIED
  CALL MOVE(IX,IY)
  CALL DRAW(IX,IY)
  RETURN
END

SUBROUTINE DRAW(IX,IY)
C ROUTINE DRAWS A LINE FROM PRESENT POS. TO CORD. SPECIFIED
  CALL XYOUT(IX,IY)
  RETURN
END

SUBROUTINE MOVE(IX,IY)
C ROUTINE MOVES BEAM TO POS. SPECIFIED
  CALL TOUTPT(29)
  CALL XYOUT(IX,IY)
  RETURN
END

SUBROUTINE XYOUT(IX,IY)
C ROUTINE CALCULATES AND OUTPUTS X-Y CORD.
  LOX=MOD(IX,32)+64
  IHOX=MOD(IX/32,32)+32
  LOY=MOD(IY,32)+96
  IHOY=MOD(IY/32,32)+32
  CALL TOUTPT(IHOY)
  CALL TOUTPT(LOY)
  CALL TOUTPT(IHOX)
  CALL TOUTPT(LOX)
  RETURN
END
```

```
      SUBROUTINE DCURSR(ICHAR, IX, IY)
C  ROUTINE SETS TERMINAL FOR GRAPHICS INPUT IN INPUTS COORDINATS
C  OUTPUT (ESC) (SUB) TO TURN ON CURSOR
      CALL TOUTPT(27)
      CALL TOUTPT(26)
      CALL TINPUT(ICHAR)
      K=0
10     CALL TINPUT(KOOR)
      KOOR=MOD(KOOR, 32)*32
      CALL TINPUT(KOOR2)
      KOOR=KOOR+MOD(KOOR2, 32)
      K=K+1
      IF(K.EQ.2)GO TO 20
      IX=KOOR
      GO TO 10
20     IY=KOOR
      RETURN
      END
```

```

;THE FOLLOWING ROUTINE CONTROL THE TEKTRONIX GRAPHICS TERMINIL AND
; THE TEKTRONIX 4662 DIGITAL PLOTTER. THE ROUTINES ARE FORTRAN
; CALLABLE ACCORDING TO THE SUBPROGRAM LINKAGE SECTION
; OF THE RT-11/RSTS/E FORTRAN IV USERS GUIDE.
;
; .TITLE IOPUT
; .MCALL ..V2..,.REGDEF,.TTYOUT,.TTYIN,.WAIT,.WAIT
;
; .GLOBL TOUTPT,TINPUT,PLOTON,PLOTOF,WAIT,PLTOUT,PLTSET,PROT90
; ..V2..
;
; .REGDEF
PLTS = 176504
PLTD = PLTS+2
PLTON: 0
PLOTSV: 0

;TOUTPT OUTPUTS A SINGLE CHARACTER TO CONSOLE AND IF PLOTON IS
; NOT ZERO THEN ALSO TO PLOTTER
;
TOUTPT: MOV (R5)+,R0
MOV @(R5),R0
BIC #177600,R0
.TTYOUT
TST PLTON
BEQ OUTEND
JSR PC,PLTOT
OUTEND: RTS PC

;TINPUT INPUTS A CHARACTER TO COMPUTER
;
TINPUT: MOV (R5)+,R0
MOV 177560,R1
CLR 177560
MOV #1,177560
IN: TSTB 177560
BPL IN
MOVB 177562,R0
BIC #177600,R0
MOV R0,@(R5)
MOV R1,177560
RTS PC

;WAIT GENERATES A DELAY FOR TERMINAL WHEN ERASED
;
WAIT: MOV (R5)+,R0
MOV @(R5),TIME+2
MOV #EMTLST,R0
.TWAIT
RTS PC

EMTLST: .BYTE 0,24
.WORD TIME
TIME: .WORD 0,60.

```

```

;THE FOLLOWING ROUTINES ARE TO BE USED WITH THE 4662 PLOTTER
;PLTOT IS NOT FORTRAN CALLABLE BUT USED BY THESE ROUTINES

```

```

;THIS ROUTINE OUTPUTS A CHARACTER TO THE PLOTTER

```

```

PLTOT:  TSTB    PLTS
        BPL     PLTOT
        MOVB   RO,PLTD
        RTS    PC

```

```

;THIS ROUTINE OUTPUTS A STRING OF CHARACTERS TO PLOTTER

```

```

PLTSTR:  MOVB   (R2)+,RO
        TSTB   RO                ;CHECK FOR LAST CHARACTER
        BEQ    STREND
        JSR    PC,PLTOT          ;OUTPUT CHARACTER
        BR     PLTSTR
STREND:  RTS    PC

```

```

;PLTOUT IS FORTRAN CALLABLE

```

```

PLTOUT:  MOV    (R5)+,RO
        MOV    @(R5),RO
        BIC   #177600,RO
        JSR   PC,PLTOT
        RTS   PC

```

```

;THIS ROUTINE ENABLES THE PLOTTER

```

```

PLTON:   MOV    #1,PLTON
        MOV    #ON,R2            ;SET UP CODE TO TURN PLOTTER ON
        JSR   PC,PLTSTR
        RTS   PC

```

```

ON:      .BYTE  33
        .ASCIZ  /AE/

```

```

;THIS ROUTINE CAUSES THE PLOTTER TO GO OFFLINE

```

```

PLOTOF:  TST    PLTON
        BEQ    PLTEND           ;ALREADY OFF
        CLR    PLTON
        MOV    #OFF,R2         ;SET UP CODE TO TURN PLOTTER OFF
        JSR   PC,PLTSTR
PLTEND:  RTS    PC

```

```

OFF:     .BYTE  33
        .ASCIZ  /AF/

```

```

;THIS ROUTINE SENDS RESET CODE TO PLOTTER

```

```

PLTSET:  MOV    #RESET,R2       ;SET UP CODE FOR PLOTTER RESET
        JSR   PC,PLTSTR
        RTS   PC

```

```

RESET:   .BYTE  33
        .ASCIZ  /AN/

```

```

;
```

;THIS ROUTINE SENDS CODE TO ROTATE PLOTTER ALPHA 90 DEGREES

PROT90: MOV #ROT90,R2
JSR PC,PLTSTR
RTS PC

;ROT90: .BYTE 33
.ASCII /AJ90/
.BYTE 15,0
.EVEN
.END

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REAL-TIME COMPUTER OPTIMIZED SCANNING POTENTIAL COULOMETRY
FOR MULTI-COMPONENT TRACE ANALYSIS

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ABSTRACT

The instrumentation and methodology for real-time computer controlled scanning potential coulometry for multi-component trace analysis is described. The sensitivity limit was determined to be 10^{-8} F for electrochemically reversible constituents. The sensitivity limit could be extended if measures were taken to compensate for the periodic signal found on the electrolysis current. Non-linear least squares curve fitting methods accurately resolved iron-platinum and silver-iron interferences to give accurate determinations for iron and silver. The resolving capability of this method was tested using theoretically generated scanning potential coulograms. The computer resolved sample constituents with a 1 to 100 concentration ratio and a formal potential separation of 10 millivolts. It also accurately resolved sample constituents with a 1 to 1000 concentration ratio, one with 1 equivalent per and the other with 2 equivalents per mole, but with no formal potential separation.