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Instrumentation for Multi-Electrode Voltammetry

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INSTRUMENTATION FOR MULTI-ELECTRODE VOLTAMMETRY

by

I-PIN HO

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TO THE OFFICE OF GRADUATE STUDIES:

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C. William Savery, Interim Vice Provost for Graduate Studies and Research developed to detect metal pollutants at very low concentration levels. However, one important factor is often ignored, i.e., rarely is species determination required. Electrochemical (EC) methods have the particular advantage of being, in principle, a species-sensitive method rather than an element-sensitive method for the study of metal speciation in natural waters.

The goal of this research was to develop an instrument using the EC technique for speciation and general voltammetric studies. It was accomplished by designing a flow-through EC cell containing multi-electrodes to which various fixed potentials over a selected range were applied. A special potentiostat was designed to supply a selected potential to each electrode in the cell. Potential control was provided by placing a combined counter-reference electrode at circuit ground and connecting each working electrode to the inverting input of a current follower which had a potential applied to its non-inverting input from two digital-to-analog converters and a resistor network. Integrating current followers were used for measuring signal currents generated by the electrolytes samples on each electrode. A multiplexing circuit, including an analog-to-digital converter, was used to fulfill data acquisition. These circuits were interfaced to a computer and the readout was a pseudo-voltammogram which is a plot of amperometric currents versus various applied fixed potentials on each electrode. Details of the instrumentation, software, and some initial results are described.

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CHAPTER I

INTRODUCTION

Life begins in water. Life forms in water exposed to numerous metals. Since the late 1960s and early 1970s metal ions and their complexes have gained great attention in environmental studies because of the wide spread occurrence and toxicological importance of metal pollutants in the aquatic environment (1).

Many metals in the aquatic environment have more than one oxidation state and species. The toxicity of this metal toward the aquatic environment is far more dependent on the activity of certain metal species than the activity of the total concentration of that metal (2). The determination of the total concentration in a sample does not clearly describe the potential risks associated with its toxicity and the resulting hazard from exposure. For example, chromium can exist in the +2, +3, +4, +5, and +6 oxidation states in aqueous solution. Among these oxidation states, the most common states are Cr(III) and Cr(VI). Whereas Cr(III) is non-toxic and may exist as anionic or cationic species, Cr(VI) complexes are highly toxic (3) and exist as anionic species (4).

Numerous sophisticated techniques and instruments have been developed to detect metal pollutants at low concentration levels. However, one important factor is often ignored. That is, rarely is species determination done. Some of the most sensitive analytical techniques, such as atomic absorption spectrophotometry, atomic emission spectrophotometry, and X-ray fluorescence, are not suitable for species studies because they determine only the total concentration of a metal. These techniques may be accompanied with some preliminary treatment and separation methods, e.g. complex formation (5), or high-performance liquid chromatography (HPLC) (6) for the determination of metal species. However, they have serious drawbacks, such as introduction of contaminants, and incomplete separation, by these preliminary procedures.

During the past decade, there has been a rapid increase in the use of the various forms of electrochemical (EC) methods for speciation. Osteryoung (7) reviewed voltammetric techniques for determining trace metals. Florence (2) reviewed the EC approaches to metal speciation in waters. There is a growing interest in EC detection with the simultaneous use of two or more working electrodes. For example, Lunte et al. (8) used dual-electrode detectors to improve selectivity, detection limits and qualitative information content relative to single-electrode detectors.

Several characteristics make EC methods attractive for metal species analysis and studies of environmentally significant metals in all types of waters. First, EC methods have the particular advantage of being, in principle, a species-sensitive method rather than an element-sensitive method since current is proportional to concentration and potential is proportional to chemical potential (free energy) of each species. Second, they also have sensitivities for simultaneous determination of various metals. Finally, EC methods have important advantages in that the sample requires much less handling and is in contact with fewer sources of contamination than when other speciation methods, such as solvent extraction, dialysis, or ultrafiltration, are used.

There has also been increasing emphasis in recent years on the need for continuous or automated monitoring in areas such as environmental monitoring and pollution control. This trend leads to the use of EC techniques in conjunction with a flow injection system for the analysis of small samples. Several factors have motivated this recent effort. The primary reason for this trend is its high sensitivity. This is due to an improved mass transfer rate that is caused by pumping the solution toward the electrode surface since most of the analyte in an unstirred cell is not located at the electrode surface. Secondly, the hydrodynamic boundary theory (9) of the diffusion layer has been well developed. Third, EC methods include a tendency to reject time-consuming methodologies of conventional voltammetric electrolysis applied to static solutions in macrocells which are usually associated with manual transfer of solutions and lengthy deaeration periods. Finally, it is relatively simple, reproducible, and economic. Furthermore, one particular advantage of the use of flow injection for EC detection is the ease of mixing reagent streams, including supporting electrolyte, with the sample stream to promote the detection process. The other intrinsic qualities of this system which are favorable include small sample volumes, minimal reagent consumption, and a high sample throughput.

EC methods have some drawbacks. One of the main limitations of EC methods is generation of charging current, which causes sensitivity decrease, due to potential scans. EC methods are dynamic systems that draw current through the solution and disturb ionic equilibria. Davison (10) found that, during the metal deposition step, the equilibrium among metal species was disturbed as a result of the electrode potential across the electrode-solution interface. The gradual fouling of the electrode surface is always a problem with EC methods. Wang (11) and DeCastro (12) found the gradual loss of electrode activity by various organic surfactants during cyclic scans. The interference due to intermetallic compounds and adsorption-desorption processes on the electrode surface is another problem (2).

The use of series and parallel combinations of working electrodes in a flow stream can avoid the need for potential scans which are often impractical due to generation of charging currents during potential scans and short duration of solute peaks. The combination of coulometric and amperometric electrode designs is a potentially powerful technique to remove interferences and improve detection limits. Extension of these ideas leads to multi-electrode voltammetry (MEV) in which an array of electrodes in a flow-through cell at different potentials provides a pseudo-voltammogram for speciation studies (13).

These ideas can be accomplished by designing a flow-through EC cell containing multi-electrodes to which various fixed potentials in a range are applied. The number of electrodes required by this system depends upon the accessible potential range of electrode material and the potential difference between the neighboring electrodes. Commercial instrumentation for electrochemical measurements of this type costs several thousand dollars and one instrument would be required for each electrode. Hence, a special inexpensive potentiostat will be needed to supply the selected potential range to this multi-electrode cell.

Potential control can be provided by placing a combined counter-reference electrode at circuit ground and connecting each working electrode to the inverting input of a current follower which has a control potential applied to its non-inverting input from a resistor network. Current followers are used for integrating signal currents generated by the analytes on each electrode, respectively. The dynamic range of the current follower can be extended by placing a capacitor and a parallel switch instead of a resistor in the feedback loop. The output of each integrating current follower, corresponding to total faradaic charge, can be converted to digital values for easy handling, processing, and storing. Hence a custom designed and built circuitry will be needed to fulfill data acquisition since no commercial instruments of this type are available.

Finally, all of the circuits can be controllable by a personal computer through a computer interface and software programs. With a large, but reasonable number of electrodes at tens of millivolt intervals, a current-potential curve of adequate resolution can be constructed in a fraction of a second with no degradation of signal-to-noise ratio compared to single electrode detection. The qualitative and quantitative results of speciation can be obtained through a pseudo-voltammogram which is a plot of currents (charge per time interval) versus selected, applied potentials on each electrode. This pseudo-voltammogram may have the classical voltammogram shape.

The main advantages of this system will be that (i) the double layer charging current will not enter the measurement and therefore the sensitivity and accuracy will increased; (ii) the rate of mass transfer at the electrode surface will be larger than that of diffusion alone and therefore the signal will be increased and the detection limit will be lowered; (iii) minimum sample handling will be required to avoid contamination; (iv) the instrument can be used for routine analysis like other EC techniques and reliably differentiate metal species; and (v) the system can also be used as a detector for HPLC and ion chromatography. Furthermore, the EC cell in a flow system linked with this data acquisition system will make this technique even more attractive.

CHAPTER II

FLOW INJECTION ANALYSIS SYSTEM AND INSTRUMENTATION

The entire system consists of a flow injection analysis (FIA) system, a potential source, an integrating current follower unit, and a data acquisition system, all interfaced with a Commodore 64 personal computer (C-64) system. The block diagram is shown in Figure 1. The C-64 sends out the signals via the control of the software to the digital-to-analog converters which then generate and deliver the required potentials to the electrodes of the FIA system via a voltage divider. The analog currents produced by electrolysis at each electrode are sent to the current follower unit to be integrated. The data acquisition system then converts these integrated analog signals, one by one, to the digital values through the selection of the multiplexers. These values are then temporarily saved in the RAM of the C-64. Finally, these values are combined according to the "resolution time", the time interval as a basic unit for current integration, in order to reduce the requirement of the RAM of the C-64. These combined values are saved on a floppy disk for further data manipulation. Details of each unit, including interface, are discussed in

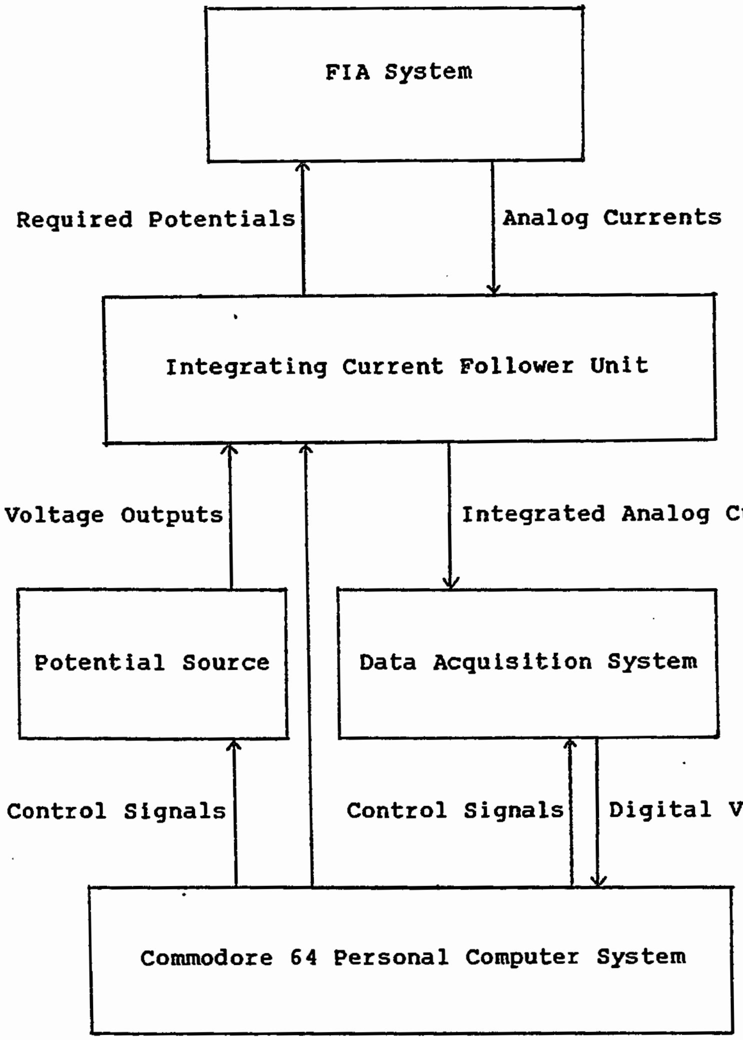


Figure 1. Block diagram of the entire instrumentation.

the following sections.

FLOW INJECTION ANALYSIS SYSTEM

The Flow Injection Analysis (FIA) system used for this research consists of a supporting electrolyte reservoir, a pump, a pulse damper and ground current isolator, a sample injection valve, and a flow-through electrochemical (EC) cell.

Electrochemical Cell Configuration

The heart of an FIA system is a flow-through EC cell. The concerns of the EC cell design for quantitative applications are the linearity of the response, the precision, and the long term stability. The concerns for qualitative applications are accurate control of electrode potential and an adequate response time for electrochemical tasks. In either case, the sensitivity and the detection limit are of concern. In order to obtain the optimum performance of this cell, certain design conditions have to be kept in mind. These include (i) high sensitivity, (ii) well-defined hydrodynamic characteristics, (iii) low effective volume, (iv) low ohmic drop, (v) ease of construction and maintenance, and (vi) a constant effective electrode area. The performance of this cell depends on the electrode material, the electrode configuration, and the cell configuration.

A variety of cell geometries, differing mainly in the flow type and the position of the electrode, has been explored over the course of two decades. Stulík and Pacáková (14) have discussed the different flow-through EC cell geometries, including the tubular, planar, and wall-jet type. The characteristic common to most of these configurations is that the rate of transport of electrochemically active species to the electrode surface is determined by the flow rate of solution.

However, according to theoretical comparison of the performance of these EC cells by Hanekamp and de Jong (15), the best design of flow-through EC cell is the wall-jet type. The term "wall-jet", first defined by Glauert (16), describes the phenomenon when a jet of fluid strikes a wall perpendicularly and then spreads rapidly over the surface of the wall. The electrode is mounted in the wall. The hydrodynamic theory and applications of the wall-jet electrode are fully developed. Yamada and Matsuda (17) have derived the theoretical expression of the limiting diffusion current and the experimental verification of the theoretical predictions for this type electrode. Gunasingham and Fleet (9) have derived the equation for the hydrodynamic boundary layer thickness in terms of the hydrodynamic parameters characteristic of the wall-jet type electrode. The hydrodynamic properties and mass transfer characteristics of this type of EC cell have also been investigated by Dalhuijsen et al.(18). The wall-jet type EC cell offers high sensitivity, low solution hold-up, and is thus suited for EC measurements in flowing solution. Therefore, a wall-jet type EC cell design is chosen for this research.

Since the behavior of the wall-jet type EC cell depends on whether or not the cell allows for unrestricted development of the hydrodynamic boundary layer, the cell fabricated for this research is somewhat different from that of the original wall-jet concept and is, in effect, a constricted wall-jet with the working electrodes forming a smaller cell volume compared to the earlier design of Yamada and Matsuda (17) and the original design by Fleet and Little (19).

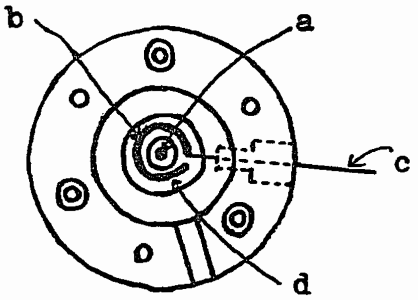
In a multi-electrode (ME) cell, the effluent from the up-stream unit will be analyzed at the down-stream working electrode. Therefore, neither Ag/AgCl nor saturated calomel electrode (SCE) can be used as a reference electrode because the chloride ion in the reference electrode compartment may leak into the flow stream and be oxidized at the down-stream working electrode. On the other hand, Zn/Zn^{2+} in 1 M sodium acetate electrode is well-known and the half-cell potential of this electrode is very stable at low current densities. Hence, the zinc/zinc acetate electrode was chosen as the reference electrode for this research.

Fabrication of Wall-Jet Type Electrochemical Cell Body

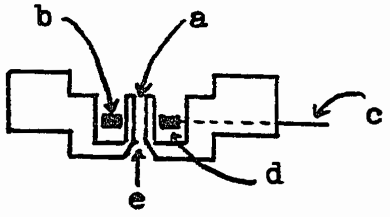
The fabrication of a single unit of the EC cell body, containing a reference electrode compartment, is described as follows. Kel-F (poly(chlorotrifluoroethylene)) (3M, USA) is used as the material to fabricate the cell body because of its wide range of desirable properties, including its being electrochemically inert and its ease of fabrication in any desired shape. Figure 2 shows a single unit of the EC cell body. In each unit a short piece, ca. 2 cm length, of zinc strip housed in an annulus compartment surrounding the inlet nozzle is soldered to a copper wire which is sealed by epoxy in a hole through the side of the cell. The inlet nozzle diameter is 0.34 mm with a funnel-shaped opening on the upstream side.

Working Electrode Material and Configuration

The heart of EC cells is the working electrode. The working electrodes in the EC cell must: (i) ideally be stable for an infinite period of time, (ii) be simple to prepare; and (iii) most importantly, have an excellent signal-to-noise (S/N) ratio. Employing electrode materials and configurations, which have a minimum amount of residual current and yet yield maximum current in response to electrochemically active species, can maximize the S/N ratio.



Top View



Side View

Figure 2. Schematic illustration of a single unit of the electrochemical cell, containing a reference electrode compartment. (a) Flow inlet with 0.34 mm diameter; (b) zinc strip; (c) lead; (d) reference electrode compartment; (e) flow direction.

The use of solid electrodes, including carbon and metal electrodes, in EC cells has gained popularity. One of the primary reasons for this is their applicability to anodic oxidations. Such electrodes thus permit important analytical applications not amenable to the mercury electrode. Secondarily, they are easy to construct and use in a flow system. The sensitivity and detection limit are thus increased by placing an electrode in the flow system. However, metal electrodes such as platinum and gold have not been as widely used as carbon electrodes because they tend to exhibit higher detection limits when used at positive potentials. This is because higher anodic residual currents arise from the oxygen evolution at lower positive potentials (20).

A variety of carbon electrodes has been used in EC cells for a long time mainly because they produce better S/N ratio in response to electrochemically-active species in contrast to other electrode materials. Furthermore, several different forms of the carbon used as electrode materials are also readily available. However, most of the carbon used as electrode material has drawbacks. Pure graphite has had limited use as an electrode material because it exhibits high porosity which leads to high residual or background currents (21). Glassy carbon (22) has been popular because of its relatively reproducible performance. It can also be used at both positive and negative potentials in aqueous solution with a range of ca. 2 V. However, glassy carbon electrodes have residual currents that are higher and tend not to give such a favorable S/N ratio compared with carbon paste or composite electrodes (23). Carbon paste electrodes (20) have been extensively used for anodic oxidation reactions due to their low residual current and wide positive potential range. However, these electrodes also have several drawbacks. First, from preparation to preparation, carbon paste electrodes have variations. Second, the dissolution of binder in organic solution restricts the use of this kind of electrode. Third, the binder may restrict the potential range of the electrode.

Electrochemists noted that composite electrodes such as Kel-Graf, which consist of Kel-F and graphite, showed improved S/N ratio (24). These electrodes also exhibit less dependence on flow-dependent noise. These improvements are attributed to the existence of small graphite particles. When the surface of the electrode is examined under the microscope, the small graphite particles existing on the surface of the electrodes are isolated from each other and act as a multiple array of microelectrodes. Anderson et al. (25) have found that small diameter electrodes are easier to use at high potential, have less noise at all potentials, and have higher sensitivity than ordinary homogeneous electrodes.

Two theories have been derived to explain these results. First is the edge effect (26). At large electrodes, the majority of the steady current arises mainly from the diffusion of the analyte in a region of solution perpendicular to the electrode surface. The amount of current due to the analyte arriving from the lateral part of this volume is negligible. If the electrode surface has a large perimeter-to-area (P/A) ratio such as graphite particles, lateral diffusion will become more important. Therefore, an increase of the P/A ratio of an electrode can increase the sensitivity and lower the detection limit.

The second effect is the noise dependency on surface area. There is an identified noise source, i.e., incomplete wetting of the electrode surface (27). It causes variations in the path of solution flow and fluctuations in the applied potential. Since these two variations are proportional to the electrode surface areas, a reduction in the electrode surface area will reduce this noise level. Therefore, using microelectrodes can capture the advantages of both the edge effect and the less noise dependency on electrode diameter. The S/N ratio can be increased with these microelectrodes.

At present, carbon fibers have been shown to be the most promising electrode materials and are used as microelectrodes due to their possession of characteristics of small electrodes that overcome many of the imperfections of carbon paste electrodes and other carbon electrodes. For example, although the carbon fiber microelectrode has a sensitivity similar to the glassy carbon electrode, the detection limits improve relative to glassy carbon electrode at more positive potentials because the background signal of the carbon fiber microelectrodes is less dependent on fluctuations in the velocity of the mobile phase (27). Schulze and Frenzel (28) have shown that carbon fiber microelectrodes give a very low background current, good peak resolution, and good reproducibility.

Several electrochemists have demonstrated that the carbon fiber array electrode (CFAE) (24), i.e., multiple carbon fiber microelectrodes connected in parallel, yield much higher currents which have the same desirable features of single carbon fiber microelectrodes. In addition to the current amplification effect, a number of other advantages have recently been reported (27). These are an improved S/N ratio, flow independence, and higher sensitivity in flow-through EC cells. Furthermore, the EC response of this kind of electrode has also been shown to be relatively constant with time. Hence, carbon fibers were chosen as the electrode material to fabricate CFAEs.

Carbon fibers are microscopic carbon materials formed from the pyrolysis of pitch or polyacrylonitrile. These fibers bonded with polymer can be formed in a variety of shapes and can also be machined to optimum dimensions. The documented morphology (29) and manufacture of carbon fibers suggests that the surface of the fiber perpendicular to the fiber axis is ideal for electrochemical applications. Therefore, the electrodes are fabricated with the electrode surface perpendicular to the fiber axis.

Fabrication of the Carbon Fiber Array Electrode

The carbon fiber array electrode (CFAE) is fabricated by inserting a bundle of 10-cm long carbon fibers of 8 μm nominal diameter (Panex 30, Stackpole Fibers Co., Mass), ca. 0.0015 g, into a short piece of thin-walled Teflon tube of 0.30 mm inner diameter so that ca. 8-9 cm of the fiber bundle protrudes. This protruded portion of the fiber bundle is thoroughly coated with an excess of an epoxy mixture consisting of 5 parts ISOCHEMREZ 1312 LV resin mixed with 1 part 15AX hardener (Isochem Resins Co., Lincoln, R.I.). Then, the fiber bundle is pulled into the Teflon tube. The fiber bundle is then cured overnight at 60°C to form a solid rod. The rod containing epoxy-embedded carbon fibers is cut into 0.8 cm lengths to make several CFAEs. Then, electrical contact to the electrode is made by using electrically conducting silver-loaded paint (Silver Print, GC Electronics, Rockford, IL) to connect a copper lead to one end of a CFAE.

Fabrication of the Working Electrode Disk Containing 4 CFAEs

Four CFAEs and four 2-cm long pieces of Teflon tube of 0.76 mm outer diameter are carefully arranged to ensure that all electrical contacts of CFAEs are completely buried in the epoxy mixture and all electrodes and Teflon tubes are also centered in the mold, shown in Figure 3. The same composition epoxy mixture is injected into the mold by means of a plastic syringe, then cured for 24 hours at 60°C to form a Working Electrode Disk (WED). After the WED is released from the mold, four Teflon tubes are removed. Both sides of the disk are polished with 600 grit emery paper perpendicular to the carbon fiber axis until the surface is flat. The surface with exposed CFAEs is then successively polished on a felt polishing cloth (Buehler Ltd., Evanston, IL) with 5.0, 1.0, 0.3, and 0.05 μm diameter alumina mixed with distilled water until a mirror finish is obtained. Residual polishing material is removed from the surface by sonication in a water bath for five minutes after each polishing process. In all polishing steps, a figure-8 pattern is employed to prevent uneven polishing of the WED surface. CFAEs contained in a WED and prepared by these procedures require electrochemical activation before use.

The fabricated WED was designed to be used in the wall-jet type EC cell. Examination of the disk surface under a low-power microscope (of power 35X) revealed an array of carbon fibers whose ends are exposed in the plane of the WED.

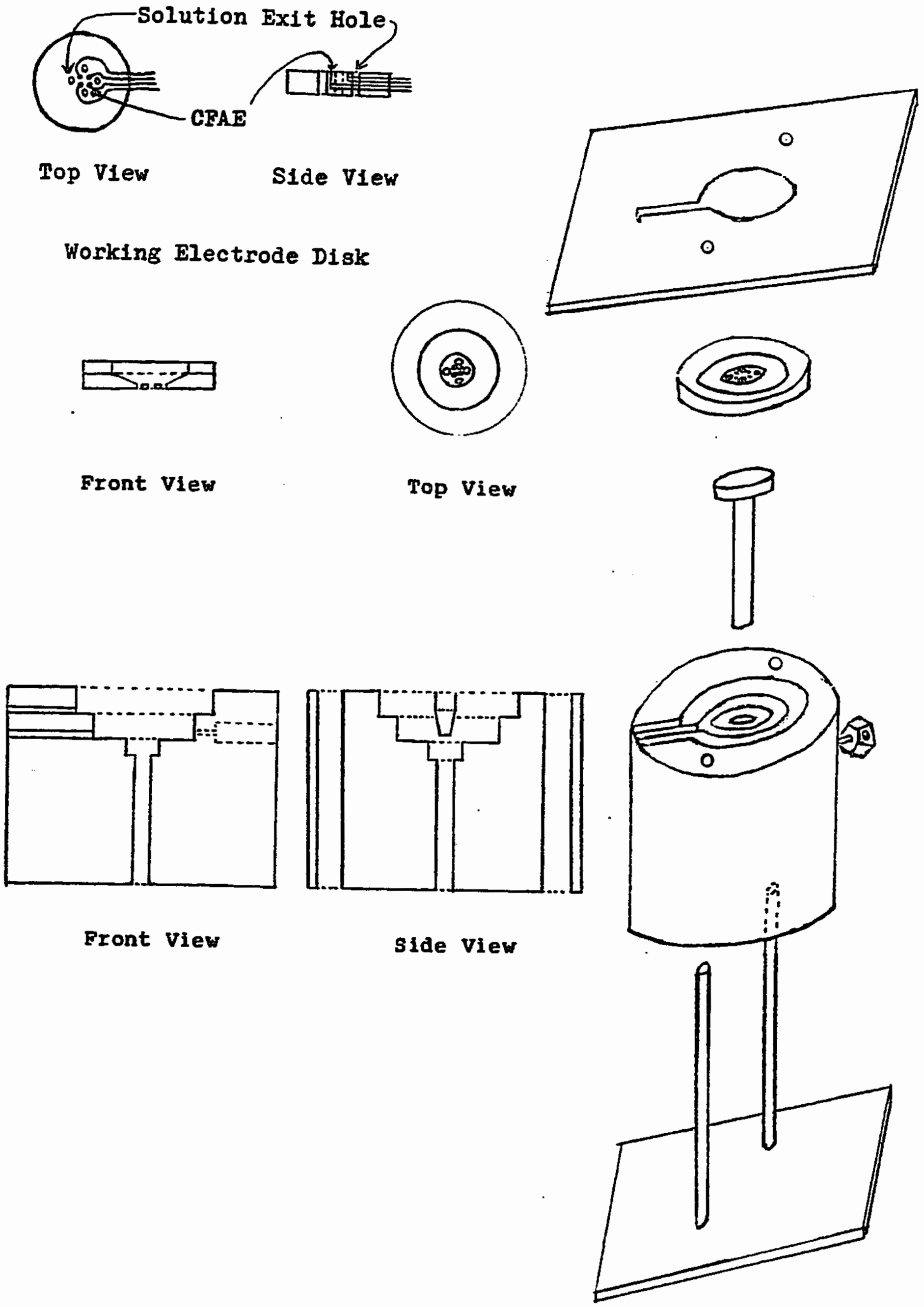


Figure 3. Schematic illustrations of the working electrode disk fabrication mold and a working electrode disk. (a,e) Mold holder; (b) positioner of CFAE and solution exit hole; (c) stainless plug; (d) mold body.

Wall-Jet Type Electrochemical Cell Assembly

A single unit assembly of the EC cell is schematically illustrated in Figure 4. A zinc/zinc acetate reference electrode is made by completely filling the annulus compartment surrounding the inlet nozzle with 1 M sodium acetate solution. The potential of this zinc/zinc acetate reference electrode measured versus a SCE is -1.055 V. This reference electrode makes contact with the cell cavity via a piece of annulus-shaped Nafion-12 film (E.I. duPont de Nemours & Co.(Inc.), DE). The Nafion-12 film contains a centered hole, which is large enough to just uncover the nozzle but completely covers the reference electrode compartment. A WED sandwiched by two gaskets is incased into the upper compartment of the cell body. Gaskets which contain a centered hole large enough to expose the central area of the WED are made from Kalrez sheet (#K05011, E.I. duPont de Nemours & Co.(Inc.), DE). The solution introduced through the inlet nozzle hits the center of the WED, spreads radially, exits through the four holes in that disk, and then enters into the nozzle of the next unit of the EC cell.

Each single unit is connected on-line by three screws, which compress both Kalrez gaskets when tightened to prevent solution leaks. The inlet-electrode separation can be varied by tightening the three bolts on the cell. Four single units are then stacked together to form a wall-jet type ME cell. However, any number of single units may be

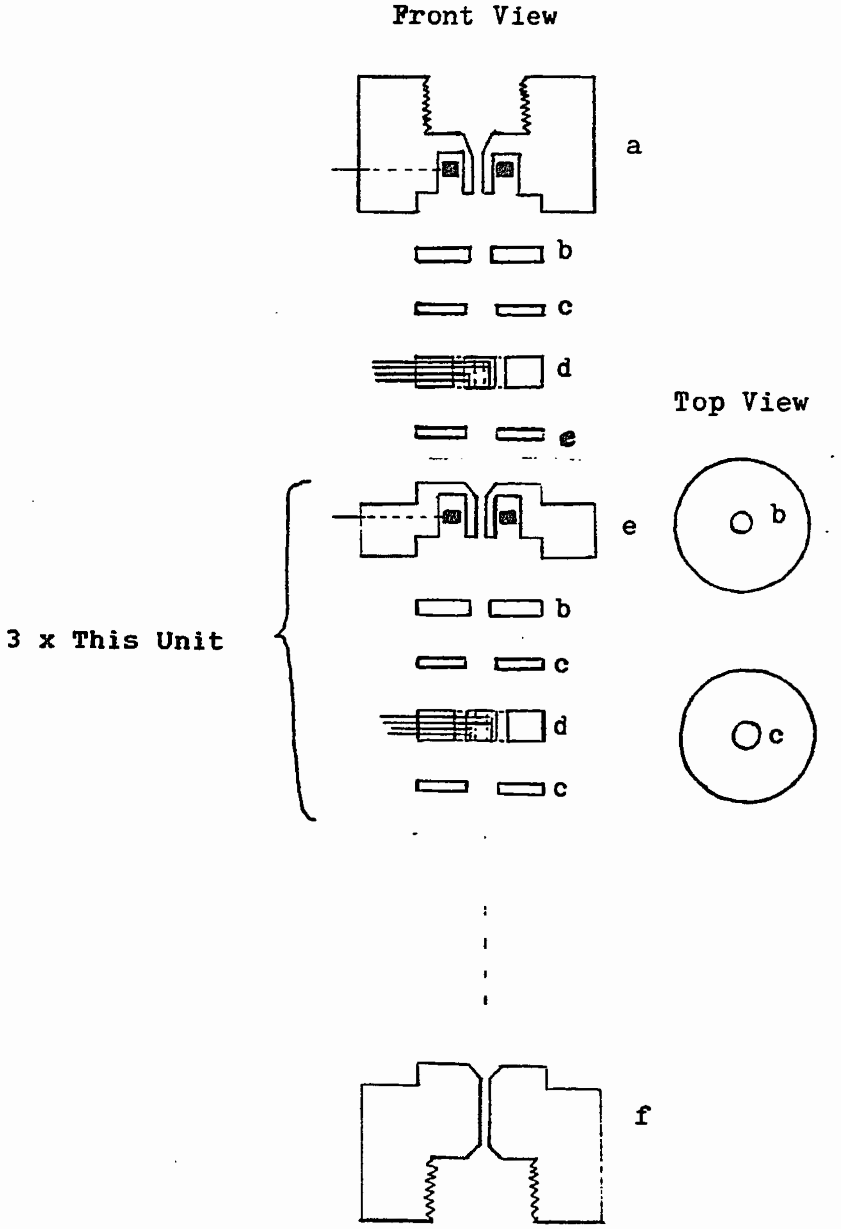


Figure 4. Schematic illustration of the wall-jet type multi-electrode cell. (a) Top piece; (b) Nafion film; (c) Kalrez spacer; (d) working electrode disk; (e) reference electrode holder; (f) bottom piece.

stacked together to form an ME cell. The cell is simple to construct, and the cell components are demountable for ease of maintenance.

Flow Injection Analysis System Assembly

The schematic diagram of the assembled FIA system is shown in Figure 5. Teflon tubing with 1.59 mm outer diameter and polyethylene fittings are used for all flow lines and connections between units except where specified. A graduated cylinder serves as a reservoir (a) to store the supporting electrolyte solution. A 0.45 μm filter (b), connected to the suction side of a minipump (d) (LDC/Milton Roy, Model 396-57, Reviera Beach, FL) through a piece of 3.18 mm outer diameter Teflon tube, is submerged in the supporting electrolyte solution. At the discharge side of the pump, a pressure gauge (e) is connected to the outlet of the pump and a plastic tube (g), ca. 70 ml capacity. The plastic tube acts as a flow pulse damper and ground-current insulator. At the down stream of the plastic tube, a sample injection valve (Hamilton, Model HV LX6-6, Reno, NV) with a sample loop (h) of 1 ml is connected on-line just ahead of the multi-electrode (ME) cell containing sixteen CFAEs and four zinc/zinc acetate reference electrodes. The connection tube between the sample injection valve and the ME cell is made as short as possible. The outlet of this ME cell is put into a waste solution container.

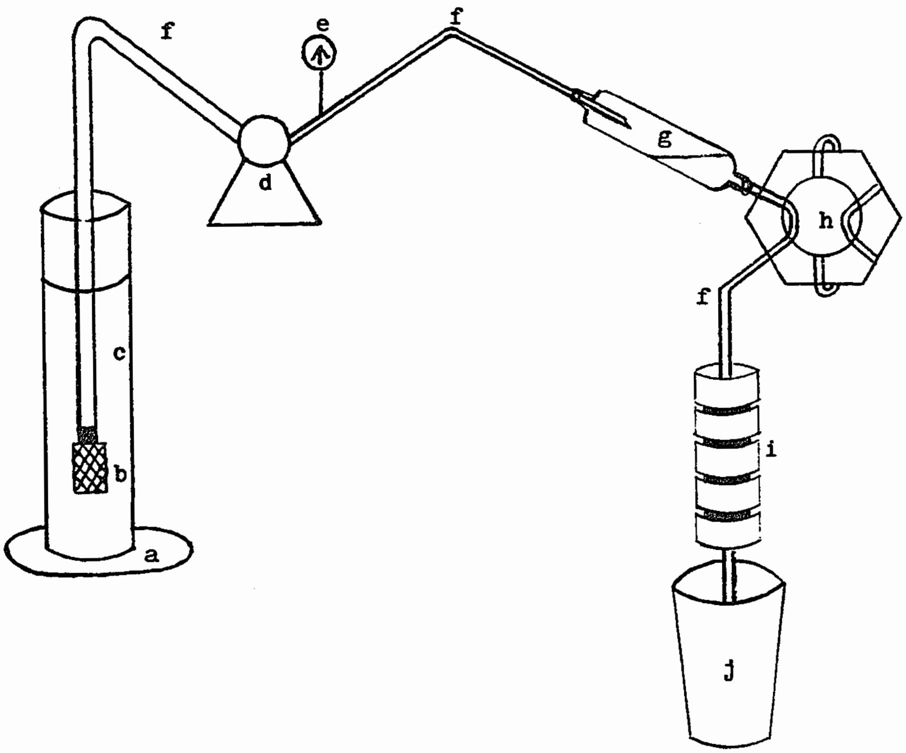


Figure 5. Flow injection analysis system setup. (a) Supporting electrolyte reservoir; (b) filter; (c) supporting electrolyte; (d) minipump; (e) pressure gauge; (f) Teflon tube; (g) pulse damper and ground current insulator; (h) sample injection valve with a sample loop; (i) multi-electrode cell; (j) waste solution container.

INSTRUMENTATION

The circuits, including two digital-to-analog converters (DACs), an integrating current follower unit, a data acquisition system, and an interface, are contained on two circuit boards. These two circuit boards are connected together by two ribbon cables. An external power supply of +/-15 volt and +5 volt is also required. A block diagram of the entire instrumentation is shown in Figure 6. The details of these units, including the interface, are discussed in the following sections. A complete schematic diagram of the circuitry with the component identification is shown in Appendix A.

Computer System

A Commodore 64 personal computer (C-64) based on a 6510 microprocessor is used for data control. It is connected to (i) a Commodore 1541 floppy disk drive; (ii) a Philco TV monitor; and (iii) a Fujitsu DX 2100 printer to handle command executions for the control of the potentiostat, data acquisition, data storage, and data management. The block diagram of the computer system is shown in Figure 7. The signal lines, including the address bus and the data bus, of the expansion port of the C-64 are buffered by two tristate buffers (LS 245 & LS 244) because they have limited drive capacity.

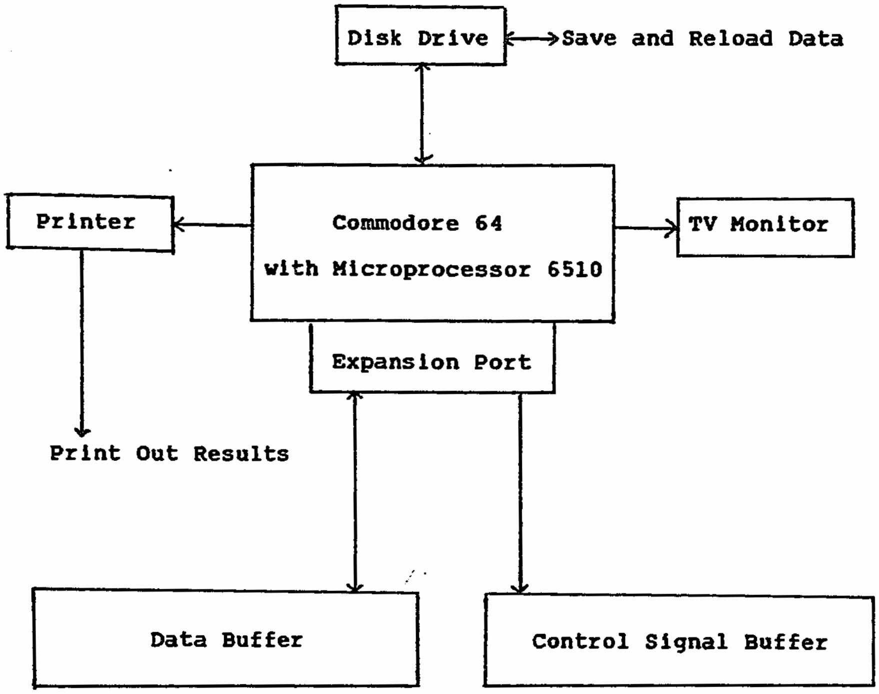


Figure 6. Block diagram of the electronic instrumentation.

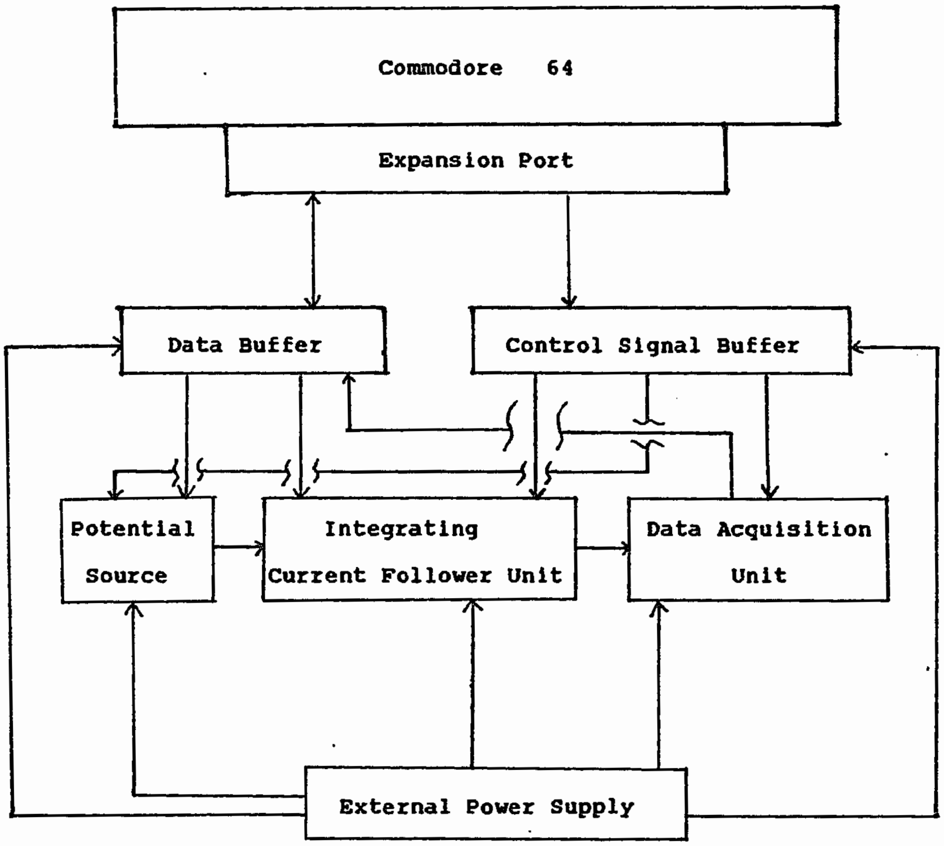


Figure 7. Block diagram of the computer system.

Potential Source

The block diagram of the potential source, which supplies the required potentials to the working electrodes relative to the reference electrode (i.e., circuit ground), is shown in Figure 8. A short BASIC program as shown in Appendix B and a digital voltmeter are used to set up the voltage outputs.

The input signals are obtained from two 12-bit DACs. The two constant current outputs from these two DACs are set, respectively, via the control of the software. These two current outputs are then converted into two voltages by two operational amplifiers. Both voltage outputs are connected to a voltage divider consisting of fifteen 1-K ohm resistors (R2) in series. These voltage outputs can be changed via the control of the same software.

Integrating Current Follower Unit

A block diagram of the integrating current follower unit is shown in Figure 9. It consists of sixteen integrating current followers with sixteen reset switches, respectively, and switch-controlling circuitry. The inverting input of each current follower is connected to one electrode in the multi-electrode cell. The noninverting inputs are connected to the voltage divider, described in the previous section. The analog signals generated by the electrodes are fed to the integrating current followers and

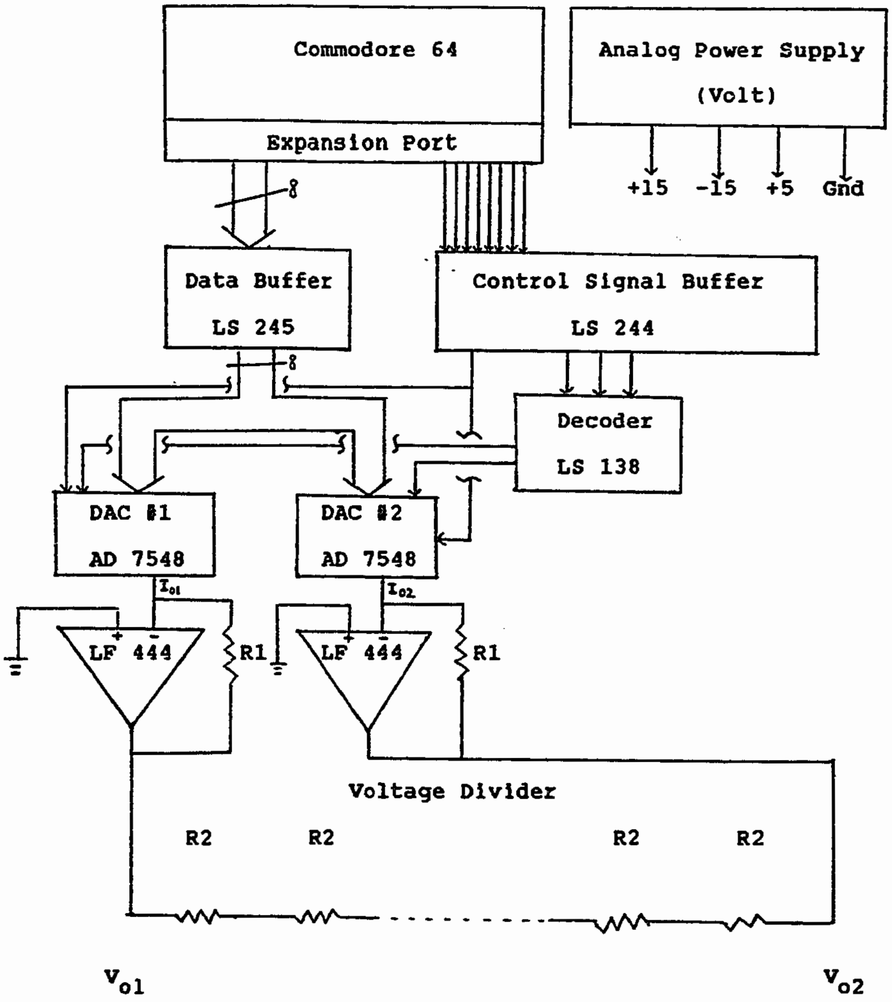


Figure 8. Block diagram of the potential source.

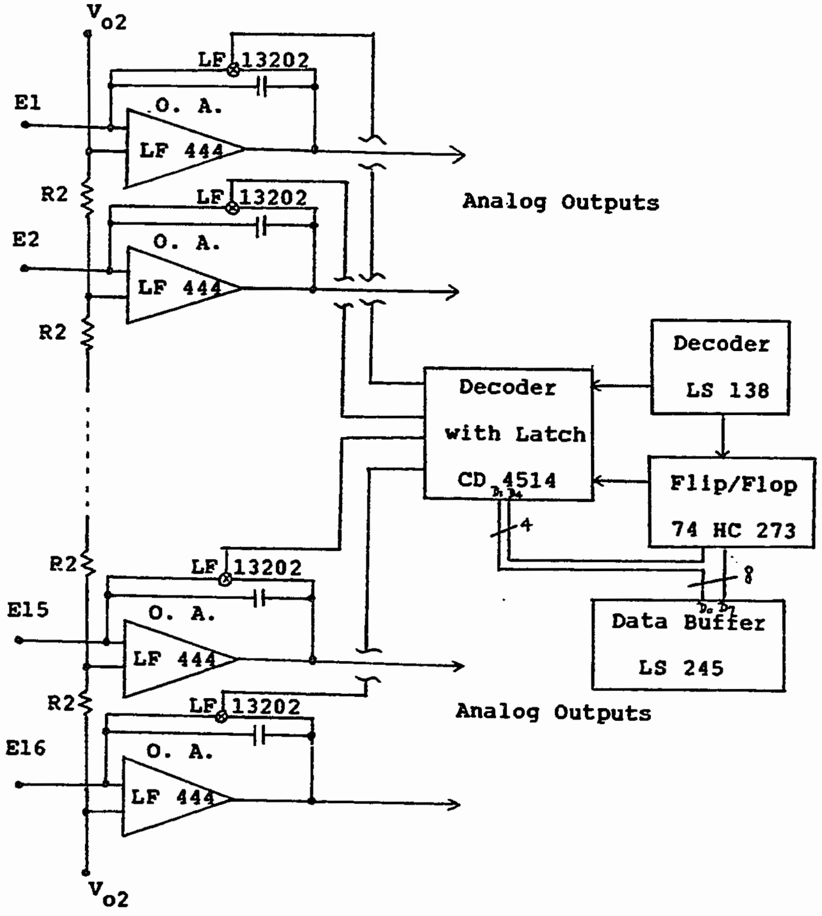


Figure 9. Block diagram of the integrating current follower unit.

continuously integrated. All integrators can be reset, one by one, via the control of an assembly language subroutine as described in Appendix D.

Data Acquisition System

Figure 10 shows a block diagram of the microprocessor-based data acquisition system. It is comprised of the following components: (i) A sample and hold (S/H) amplifier, including an S/H chip (LF 298, National Semiconductor), to perform the "hold" state for the conversion of analog signals which are generated by the electrolytes to the digital values; (ii) A peripheral interface adapter (PIA) circuitry, including a PIA chip (MC 68B21P, Motorola) which contains two 8-bit bi-directional data buses and four interrupt/control lines for interfacing the C-64 with the peripheral devices; (iii) A 12-bit analog-to-digital converter (ADC) (AD574A, Analog Devices) for converting electrical signals from the analog domain to the digital domain. This 12-bit ADC resolves the full-scale voltage range into 4096 units. (iv) A multiplexer circuitry, including three multiplexers (DG 508 & LF 13508), forming a two-level structure for sequentially allowing only one output of the current followers to reach the S/H chip (LF 298)at a time. (v) A decoder circuitry, including a decoder chip (LS 138) that is used to address and control several chips.

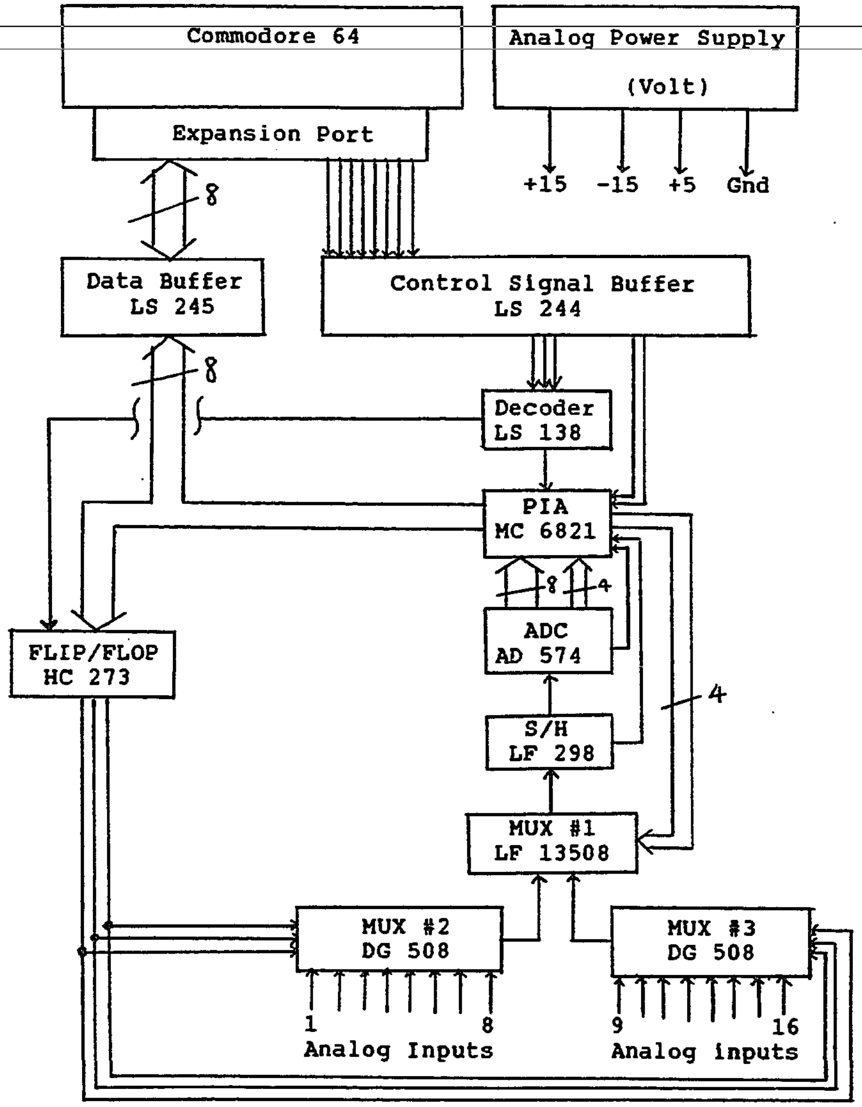


Figure 10. Block diagram of the data acquisition system.

Under the control of the software, only one output of the current followers is selected and reaches the S/H chip via the multiplexers. Then the A/D conversion circuitry converts this analog signal from the output of the current follower to a 12-bit parallel digital signal. The output of the 12-bit A/D conversion is read in as two bytes and is addressed in the memory space to be stored to accommodate the 6510 microprocessor's 8-bit data bus. After the signal is stored, the output of next current follower is sent to the S/H chip via a different combination of the opened channels of the multiplexers. Then the cycle is repeated again and again until the preset time period is over.

The A/D conversion cycle is timed under the control of a cycle-counting subroutine in an assembly language subroutine. The C-64 itself provides two presettable 16-bit down counters (30) which can be either independently programed as two separated timers or jointly programed to form a clock. The data acquisition frequency is controlled by these two presettable 16-bit down-counter timers. Timer #1 is used to set a time interval for each integrating current collected. It is set as a multiple of 1/60 sec (60 Hz) in order to get rid of the noises generated by 60 Hz power lines. Timer #2 is set so that the time of a cycle is one second longer than that of Timer #1 in order to acquire the integrating time of current signals. The parameters to set up these two timers are interrelated. They also depended on the sample size, the sample concentration, and the RAM capacity of the C-64. The combination of Timer #2 and a cycle counter is used to record the real time at each data acquisition and the total covered time period for each on-line analysis.

Software

Several software programs are used in conjunction with this multi-electrode voltammetric instrumentation. All of them are written in BASIC language except one, named "DATACQ", which is written in assembly language. The main program, named "COLLECT.DATA", is used to control the entire instrumentation, to obtain coulometric data, and to save data onto a disk. "DATACQ" software is a subroutine called up by this main program to convert analog signals generated at the electrodes to digital values and to store them in the RAM of the C-64. Two more software programs are used for further data management. The first one, named "NORMALIZE", is used for the surface area normalization factors of 16 CFAEs in the ME cell. The second one, named "RESULT", is used to get amperometric data for plotting pseudo-voltammograms after the data have been normalized. All software programs are discussed and attached in Appendices C, D, E, and F.

CHAPTER III

MATERIALS AND APPARATUS

MATERIALS

All the materials used are analytical grade and are used without any further purification. The water used to prepare all solutions is triply distilled in a quartz still (Q-water) and stored in 1-liter polyethylene bottles.

1 M Acetate Buffer Stock Solution

82.03 g of anhydrous sodium acetate and 17.2 ml of glacial acetic acid are dissolved and diluted with Q-water to equal 1 liter. The solution is then filtered through 0.45 micrometer Millipore filters (Millipore, Type HA). This solution is prepared weekly.

Argon Gas

Argon gas (AIRCO Inc., Montvale, N.J.) without any further purification is used.

0.1 M Acetate Buffer Solution

0.1 M acetate buffer solution is prepared by dilution of 1 M acetate stock solution with Q-water.

Millimolar Hydroquinone Sample Solution

Hydroquinone solutions are prepared daily by dissolving the appropriate amount of hydroquinone in 0.1 M acetate buffer solution, followed by deoxygenation with argon gas for 1 hour prior to use.

1 M Sodium Acetate Solution

8.20 g of anhydrous sodium acetate is dissolved and diluted by Q-water to 100 ml.

APPARATUS

Apparatus for Cyclic Voltammetry

A 25-mL beaker is employed as an electrochemical (EC) cell body. A carbon fiber array electrode (CFAE) contained in a working electrode disk (WED) is used as a working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a platinum wire as an auxiliary electrode. All three electrodes are joined to the beaker through holes in its plastic cover to form a conventional EC cell. This cell in conjunction with a potentiostat (HEKA, Type PG28, West Germany) and an X-Y recorder (Linear Instruments Corporation, Model 8036, Irvine, CA) is used to perform cyclic voltammetry. A square wave function generator (EXACT Electronics, Inc., Model 120, Hillsboro, OR) is used in conjunction with the potentiostat to reactivate the CFAEs. Potentials are monitored with a digital multimeter (John Fluke Co. Inc., Model FLUKE 75, Everett, WA). All potentials measured and reported for this 3-electrode cell are referred to the SCE.

Apparatus for Pseudo-Voltammetry

The previously discussed multi-electrode (ME) cell and instrumentation are used to perform the measurements. In the ME cell, 16 CFAEs contained in 4 WEDs are deployed as working electrodes. For each 4 CFAEs on the same WED, a zinc strip in 1 M sodium acetate solution is used as a reference electrode. The potential of these reference electrodes measured versus a SCE is -1.055 V. The potentials applied on the CFAEs are generated by the potentiostat via the control of the software. The whole flow injection analysis system is as described in the previous chapter.

CHAPTER IV

EXPERIMENTAL PROCEDURES

EXPERIMENTS WITH A CONVENTIONAL ELECTROCHEMICAL CELL

Since the electrochemical (EC) behavior of electrodes can be evaluated by cyclic voltammetry, cyclic voltammograms were used to examine the performance of carbon fiber array electrodes (CFAEs) on the working electrode disk (WED). All preliminary experiments were performed in an unstirred solution with a conventional EC cell. This conventional EC cell is described in the previous chapter. All potentials were measured and reported versus a saturated calomel electrode (SCE) for this conventional cell.

All cyclic scans, which were performed with the same CFAE on a WED in a solution containing approximately 1 mM HQ in 0.1 M acetate buffer (AB) solution at a scan rate of 20 mV/sec, started at +0.0 V with automatic scan reversal at +0.9 V and then scanned back to +0.0 V except where specified. The cyclic voltammograms obtained were recorded on the X-Y recorder.

Square Wave Parameter Optimization

To evaluate the results of CFAE reactivation, the same conventional EC cell was used to perform cyclic voltammetry.

The electrode reactivation process involves cycling a square wave, generated by a function generator, on a CFAE dipped in a 20 ml 0.1 M AB solution for a period of time. The different combinations of the square wave parameters, including the upper and lower potential limits, frequencies, and duration, were studied in order to find the optimized parameters of a square wave for CFAE reactivation.

After potential cycling, the electrode was moved to a hydroquinone (HQ) solution which had been purged by argon gas and held at the initial potential (+0.0 V) of a cyclic scan for a time delay period until the current generated by the electrode reactivation process on the CFAE subsided. Different time delay periods were also investigated. Finally, a cyclic scan with a scan rate of 20 mV/s was performed as described in the previous section.

EXPERIMENTS WITH THE MULTI-ELECTRODE CELL

Before WEDs were deployed in the flow cell, every CFAE on WEDs was individually examined for noise level and current leakage by cyclic voltammetry with a conventional cell. After the assembly of the ME cell, CFAEs were never polished again. All the potentials measured and reported for this ME cell referred to the zinc/zinc acetate reference electrode.

The experimental procedures are the same for both CFAE normalization factors and pseudo-voltammetry. A complete experimental cycle involves three steps: connection of the ME cell on-line, reactivation of CFAEs in the cell (including time delay for subsidence of the currents generated by the reactivation process), and coulometric data collection.

Multi-Electrode Cell On-Line

The 0.1 M AB solution was first pumped through the flow system at a constant flow rate produced by a minipump without connection of the ME cell to the circuits. This avoids supplying an unpredictable voltage to CFAEs in the cell, which may cause damage to the CFAEs. The flow rate was measured with a graduated cylinder and a stop watch. The ME cell was then pumped several times by using a plastic syringe (which was temporarily connected with the outlet of the cell via a connector) in order to avoid air bubbles being trapped in the cell.

Prior to performing the experiments, the potentials required at all CFAEs in the cell for either CFAE normalization factors or pseudo-voltammetry were determined by the cyclic voltammograms obtained from the preliminary experiments. For normalization factors of CFAE surface areas in the ME cell, a constant potential of +1.95 V was applied to all CFAEs. In contrast, the potentials in the range between +1.05 V and +1.95 V, equally divided, were applied to CFAEs, respectively, in ME cell for pseudo-voltammetry. This potential range started before the oxidation of HQ occurs and ended at where maximum steady-state current is reached, i.e., the concentration of HQ at the electrode surface approaches zero.

The software program "COLLECT.DATA", loaded in the RAM of the C-64, was activated first. Then, the experimental conditions were input through the keyboard. After the instrument warmed up, the required potentials for CFAEs, generated by the digital-to-analog converter (DAC) units on the circuit board, were ready. The zinc/zinc acetate reference electrodes in the ME cell were connected to the circuit ground. The CFAEs in the cell were connected, in order, to the inverting input of the current follower, respectively.

Reactivation of CFAEs in the ME Cell

During working with CFAEs, inconsistent performance and high background current with noise were always observed after they were in contact with the supporting electrolyte solution for a long period of time. The sensitivity of CFAEs was also diminished during the successive scans without the electrode reactivation. Therefore, reactivation of CFAEs was performed just prior to data collection.

The reactivation process of the CFAEs in the ME cell was performed by using a square wave which was generated by the DACs via the control of the same program. The parameters of this square wave were as follows: frequency, ca. 5 Hz; upper potential limit, +2.05 V; lower potential limit, +1.05 V; and duration, 5 seconds. After the CFAEs were reactivated, each CFAE was held at the required potential 4 minutes to allow the residual current generated by this electrode surface reactivation process to subside.

Collection of Coulometric Data

During the wait for the subsidence of the residual currents, a sample was loaded into the sample injection loop. After the time delay period was over, data acquisition was performed as described in Appendix D. During the first 20 seconds the data collected represented the integrated background currents. After that, the sample injection loop was manually switched into the flow stream. The data collected after this point corresponded to the composition of the sample solution.

When either the setup of the sampling time was over or the RAM of the C-64 was filled up with the data, data collection was stopped. Then the data were combined according to the resolution time, followed by saving combined data onto a floppy disk along with all experimental information for either the normalization factors of CFAEs or the construction of pseudo-voltammograms.

CHAPTER V

RESULTS AND DISCUSSION

For voltammetric studies in water, the supporting electrolyte selected must be very inert and also have high overvoltages associated with the formation of hydrogen and oxygen. That was why 0.1 M acetate buffer (AB) was chosen as the supporting electrolyte for this study.

The accessible potential range of 0.1 M AB solution was determined by cyclic voltammetry in a conventional electrochemical (EC) cell with a carbon fiber array electrode (CFAE) contained in a working electrode disk (WED). As shown in Figure 11, the cyclic voltammograms (CVs) were obtained in the AB solution either without or with deoxygenation, respectively. Compared with each other, a reduction wave, caused by the reduction of O_2 to hydrogen peroxide (31), is observed at potential ca. -0.6 V in Figure 11a. However, in both CVs the currents increased notably with potentials either more positive than +1.5 V or more negative than -1.4 V, which was due to the evolution of oxygen and hydrogen from water, respectively. Hence, the accessible potential range of 0.1 M AB solution at CFAEs is between -1.4 V and +1.5 V with deoxygenation; otherwise, between -0.3 V and +1.5 V.

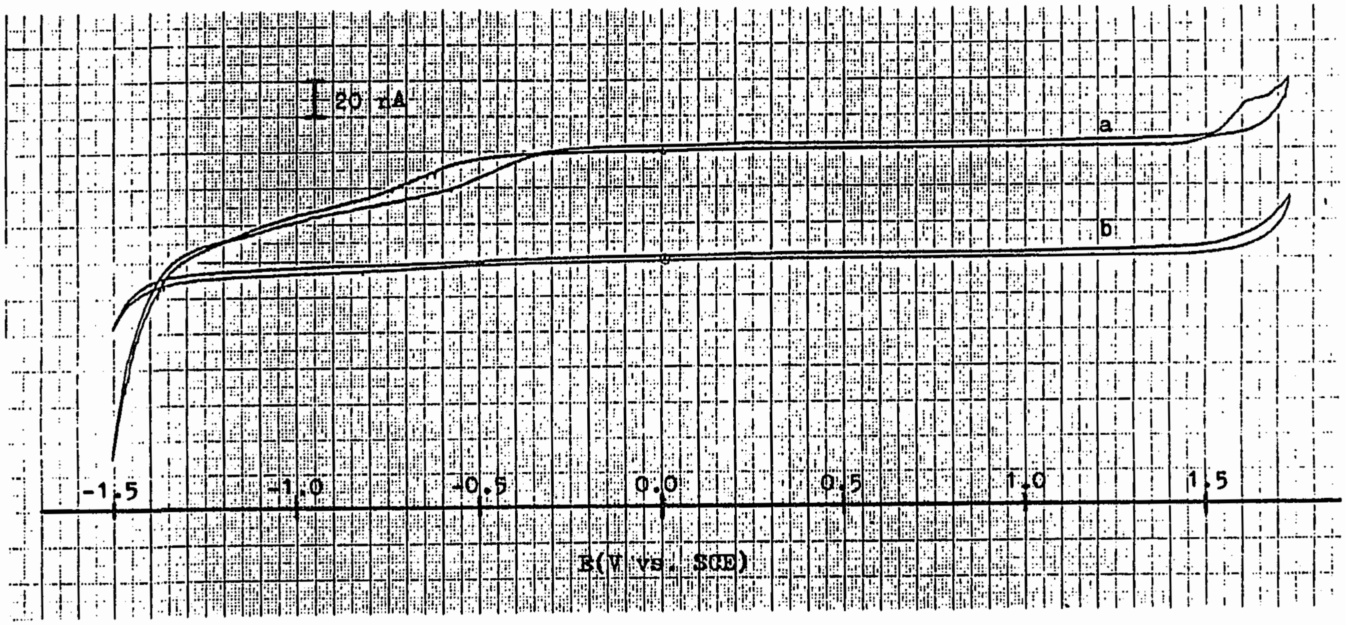


Figure 11. Cyclic voltammograms of 0.1 M acetate buffer at a carbon fiber array electrode. Scan rate, 50 mV/sec; (a) without deoxygenation; (b) with deoxygenation.

With consideration of the accessible range of the AB solution without deoxygenation, hydroquinone (HQ) was chosen as the probe to evaluate the results obtained from all experiments because its EC behavior is well-defined and it is also very sensitive to the surface state of the electrode. Furthermore, its oxidation wave falls in the potential range of 0.1 M AB solution where no other redox wave is produced.

Surface preparation is crucial for optimal performance of the CFAEs. Figure 12 shows the results of cyclic scans obtained after different polishing methods were performed. A freshly emery-polished CFAE without any other treatment showed good sensitivity, as shown in Figure 12a. However, the observed background current, noise levels, and half-wave potentials ($E_{1/2}$'s) of HQ obtained after each polishing of a CFAE were different; even though identical polishing procedures were employed. Kamau (22) has found that a variety of surface functional groups created by polishing causes the variation of the background current and noise level. The $E_{1/2}$ shift may be caused by anodization of the electrode surface. The background current and noise level were decreased dramatically by using a freshly alumina-polished CFAE, as shown in Figure 12b. The $E_{1/2}$, compared with Figure 12a, shifts to a more anodic value. If the alumina-polished CFAE was cleaned either by sonic waves or a cyclic scan, the noise level and background current

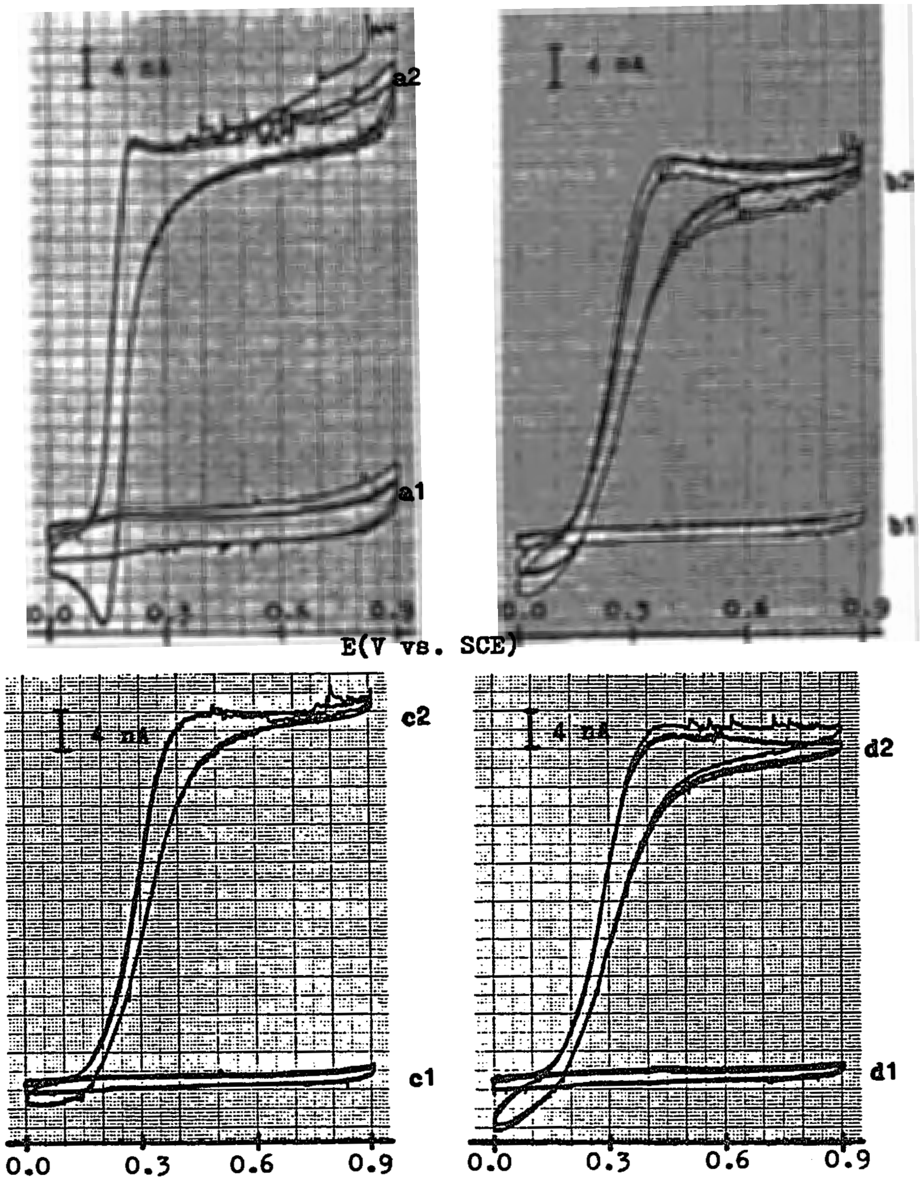


Figure 12. Effects of carbon fiber array electrode surface preparation upon the cyclic voltammogram. Scan rate, 20 mV/sec; (1) 0.1 M AB; (2) 1 mM HQ; (a) freshly emery-polished CFAE; (b) freshly alumina-polished CFAE; (c) freshly sonic wave-cleaned CFAE; (d) freshly cyclic scan-cleaned CFAE.

decreased a small amount as shown in Figure 12c and 12d. The $E_{1/2}$ shifts slightly in the anodic direction.

REACTIVATION OF CARBON FIBER ARRAY ELECTRODES

Electrochemists have observed that the performance of electrodes is always hampered by a gradually fouling of the surface during exposure of an electrode to solutions (31, 32). This leads to a gradual decrease in detection limit and sensitivity of the electrode. Such loss of electrode surface activity is usually attributed to the adsorption of analyte itself, reaction products, or impurities on the electrode surface (32).

The occurrence of analyte adsorption on the CFAE surface is demonstrated in Figure 13. Figure 13b shows a small bump at ca. +0.3 V (vs. SCE) after leaving a CFAE in HQ solution with 0.0 V applied on it for 1 hour. However, Figure 13a does not have any bump after leaving the same electrode in AB solution for the same time. This indicates that slow impurities adsorption on the CFAE surface was taking place during CFAE exposure to HQ solution. It also indicates that the adsorbent on the CFAE surface is HQ. Furthermore, the amount of HQ adsorbed on the electrode surface is proportional to time, as shown in Figure 13c, d, and e. However, this small bump disappeared and a reproducible CV was obtained after several successive scans, as shown in Figure 13c. It indicates that the adsorbent on

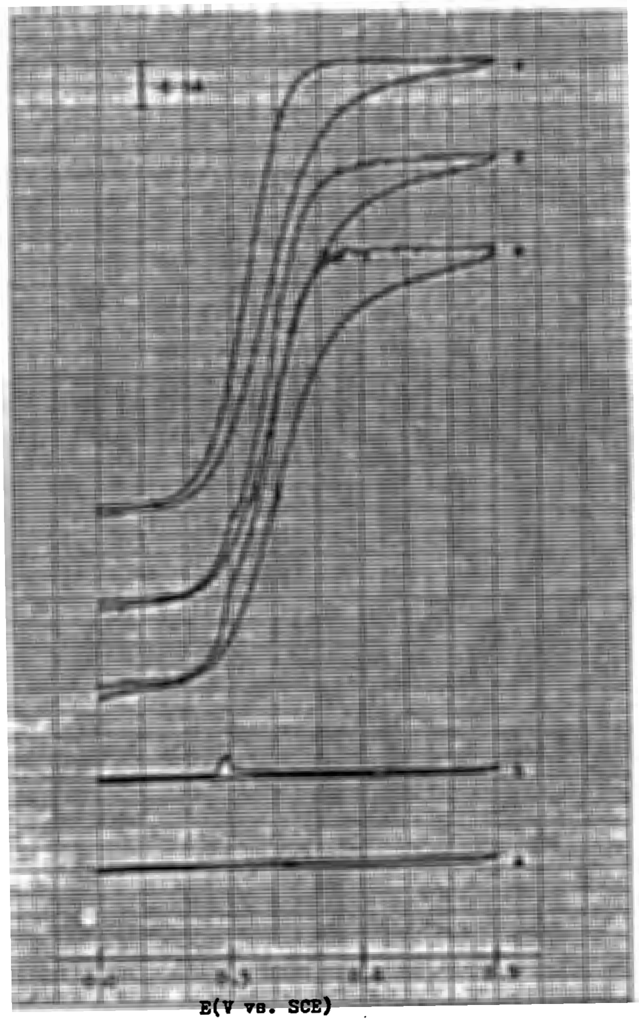


Figure 13. Time effects upon the cyclic voltammogram. Scan rate, 20 mV/sec; (a) after leaving a CFAE in AB for 1 hour with 0 volt applied at it; (b,d) after leaving a CFAE in HQ solution for 1 hour; (e) after leaving it in HQ solution for 3 hours; (c) after successive cyclic scans. Voltammograms are obtained with (a,b) 0.1 M AB; (c,d,e) 1 mM HQ.

the electrode surface can be removed by cyclic scans. It also indicates that CFAEs can reach a reproducible condition.

After leaving this activated CFAE in AB solution overnight and without potential applied at it, the $E_{1/2}$ shift in the cathodic direction by up to 200 mV and the decreased separation E_p-$E_{p/2}$ were observed, as shown in Figure 14a, compared with the values obtained in Figure 13c. It indicates that the electrode reverted to a typical condition after leaving it in the AB solution overnight without a potential applied on it. Fortunately, during successive cyclic scans between +0.0 V and +0.9 V in HQ solution, the $E_{1/2}$ gradually shifted back. And a reproducible CV was obtained eventually, as shown in Figure 14b. It indicates that the electrode surface is in a reproducible condition. This process can also be hastened by applying a positive potential at the CFAE, depending on how positive the potential is and how long it is applied. Therefore, CFAEs must be reactivated in order to get a reproducible result. A simple and rapid electrode reactivation method for the CFAEs in a multi-electrode (ME) cell needs to be found to produce a reproducible surface condition.

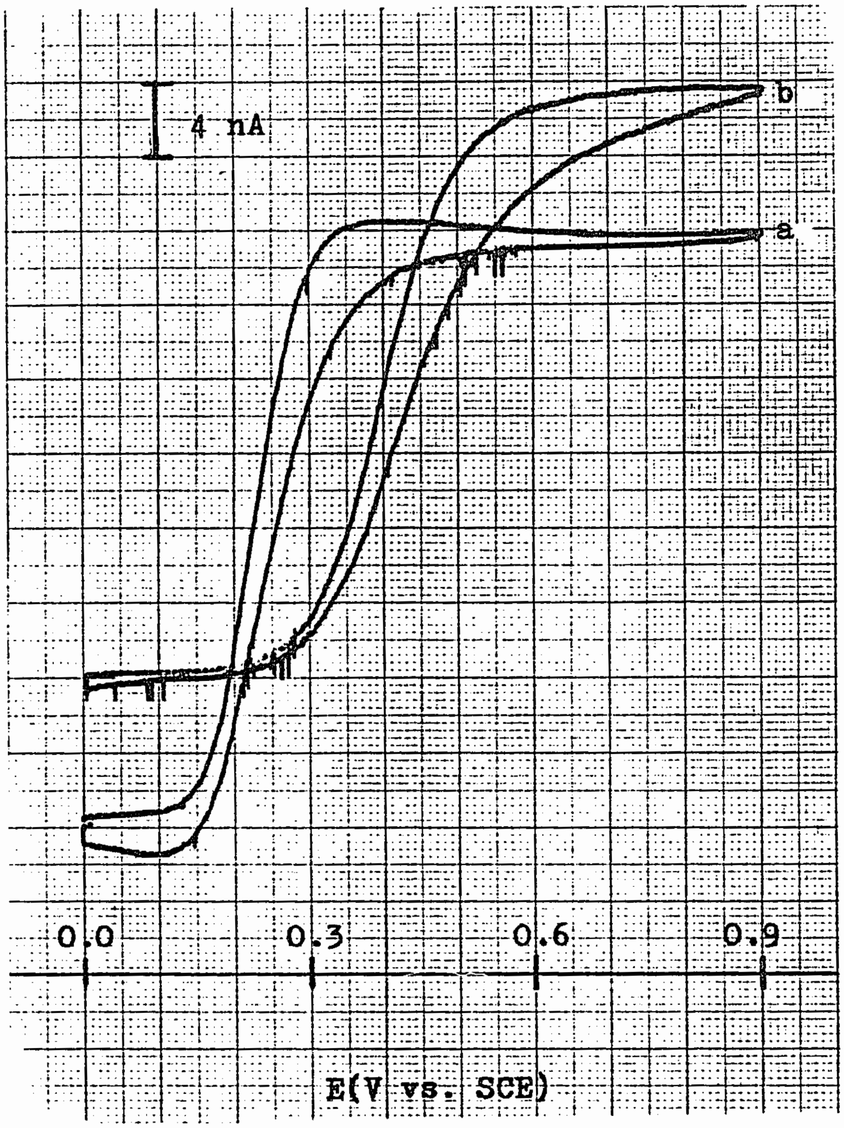


Figure 14. Effects of an applied potential at a carbon fiber array electrode upon the cyclic voltammogram. Solution, 0.9 mM HQ; scan rate, 20 mV/sec; (a) after leaving a CFAE in 0.1 M AB overnight and without potential applied at it; (b) after the reproducible result obtained with cyclic scans in 0.1 M AB.

In Situ Carbon Fiber Array Electrode Reactivation

Many methods used to reactivate electrode surfaces have been reported (33), such as a surface polished with an abrasive material, treated with radio frequency plasmas, heated at low pressures, irradiated with a laser, and treated with potential cycling. With the consideration of the configuration and instrumentation of multi-electrode voltammetry (MEV), the electrode surface reactivation with a square wave appears to be the most convenient means of achieving in situ surface activation to improve the performance of graphite electrodes in the cell. The primary reason is because a square wave is very easy to generate with software. The CFAEs placed in the ME cell are intended to be used for a considerable time without cell disassembly. When CFAEs become fouled, they can be reactivated by this method without the need of cell disassembly.

The work discussed herein is to determine the parameters of the square wave used for CFAE reactivation and to improve the sensitivity and reproducibility of CFAEs. The parameters include the upper and lower potential limits, frequency, and duration. A CFAE known to exhibit good performance was used to test the different combinations of experimental conditions and to determine all the parameters of the square wave. The apparatus and experimental procedures were described in Chapter III and IV. All potentials measured and reported in this section are versus the saturated calomel reference electrode (SCE) except where specified. The effect of CFAE surface reactivation using a square wave is evaluated by potential shifts and limiting current variations of cyclic voltammograms generated by the HQ solution.

Applying a very positive potential on the CFAE is not advisable because this may cause the destruction of the electrode (20). According to the preliminary experiments, a dramatic loss of sensitivity was observed if the upper potential limit of the square wave supplied at a CFAE was over +2.0 V and lasted a period of several minutes. The sensitivity lost under this condition can not be recovered by EC reactivation except by repolishing the electrode. Also, the accessible range of AB solution is between -1.4 V and +1.5 V (vs. SCE). Beyond that range, gas bubbles due to the formation of H_2 and O_2 by the decomposition of H_2O may be trapped on the electrode surface and cause a change of electrode activity. Therefore, the potential limits for the square wave need to be between -1.4 V and +1.5 V.

Figure 15 shows the CVs of HQ obtained after a CFAE reactivated by a square wave at frequency of 0.5 HZ, duration of 30 sec, upper potential limit of +0.9 V, but with different lower potential limits. Comparison of all CVs in Figure 15, $E_{1/2}$ as well as the limiting currents on the plateau shows that they are the same. The results obtained are independent of the lower potential limit of the

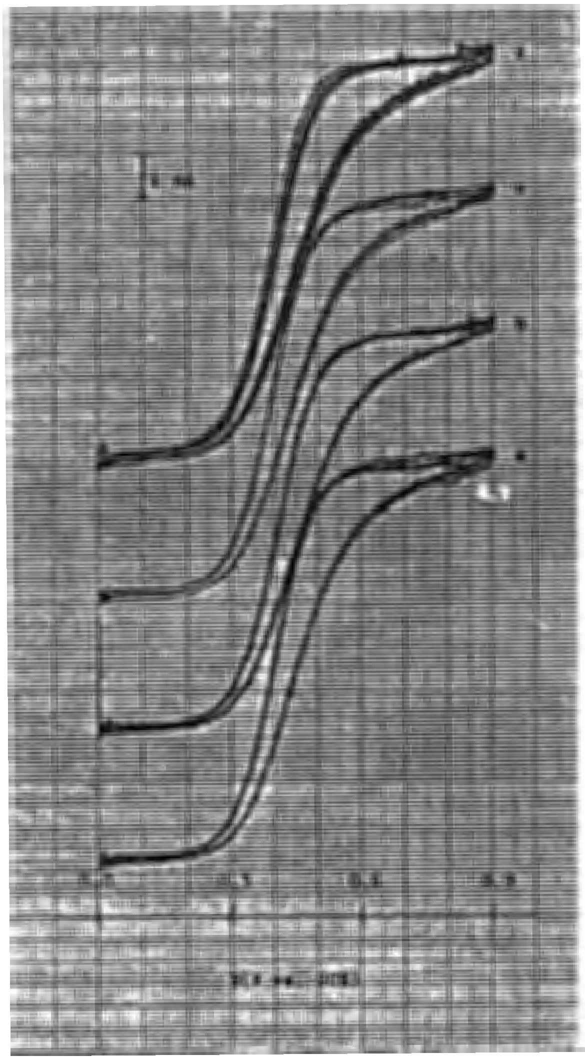


Figure 15. Effects of lower potential limit of a square wave upon the cyclic voltammogram. Solution, 1 mM HQ; scan rate, 50 mV/sec; (a) a cyclic scan-reactivated CFAE; a square wave-reactivated CFAE with parameters: upper potential limit, +0.9 V; lower potential limit, (b) -0.2 V, (c) -0.6 V, (d) -1.6 V; frequency, 0.5 Hz; duration, 30 sec; delay, 4 min.

square wave.

The correlation between the upper potential limit of the square wave and the EC behavior of the reactivated CFAE is shown in Figure 16. The experimental conditions were the same as in Figure 15 except the lower potential limit is 0 V and with different upper potential limits, respectively. Comparison of all CVs in Figure 16 shows that the $E_{1/2}$'s are constant when the upper potential limits of the square wave are not greater than +1.4 V. The shape of curves and the limiting currents on the plateau are the same. However, as the upper potential limit of the square wave is made more positive than +1.4 V, remarkable effects on the curve shape are observed, i.e., a poorly-defined wave and $E_{1/2}$ shift toward more anodic direction, as shown in Figure 16d. Therefore, the upper potential limit of the square wave chosen must be not greater than +1.4 V.

The correlation between the frequency of the square wave and the EC behavior of the reactivated CFAE is shown in Figure 17. The experimental conditions were the same as in Figure 16 except the upper and lower potential limits of the square wave were +1.0 V and -0.1 V, respectively, and with different frequencies. Comparison of these curves shows that there is no significant difference when a variety of frequencies are applied. Figure 18 shows the correlation between the duration of the square wave and the EC behavior of the reactivated CFAE. The experimental conditions were

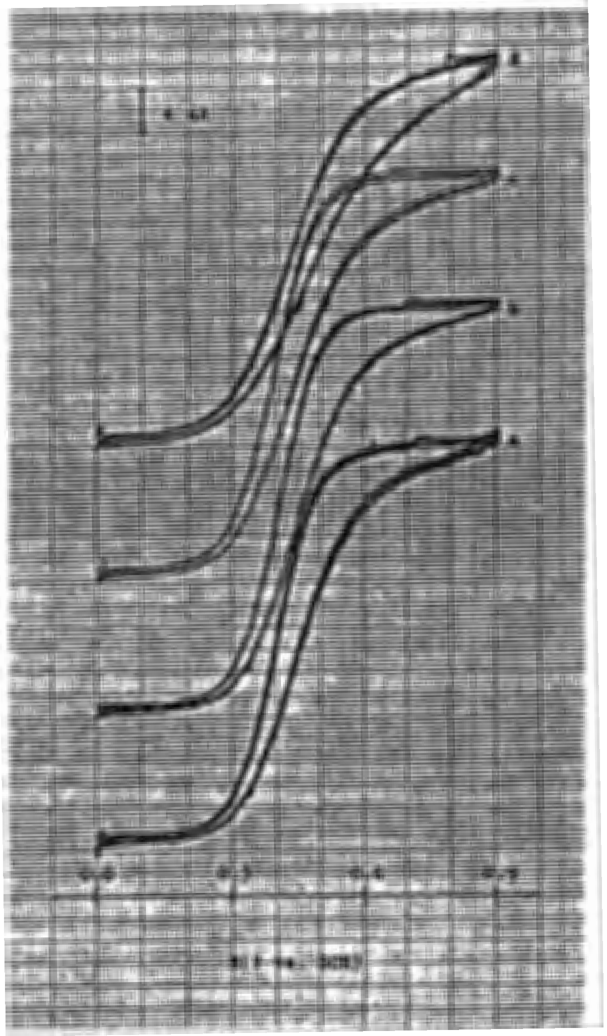


Figure 16. Effects of upper potential limit of a square wave upon the cyclic voltammogram. Solution, 1 mM HQ; scan rate, 50 mV/sec; (a) a cyclic scan-reactivated CFAE; a square wave-reactivated CFAE with parameters: upper potential limit, (b) +1.1 V, (c) +1.3 V, (d) +1.5 V; lower potential limit, 0 V; frequency, 0.5 Hz; duration, 30 sec; delay, 4 min.

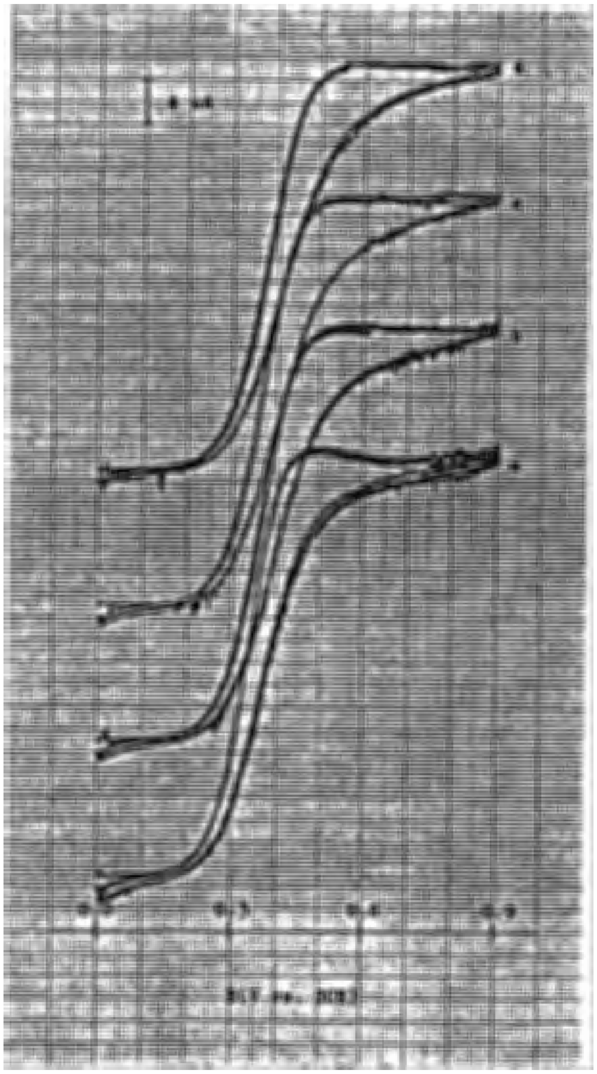


Figure 17. Effects of frequency of a square wave upon the cyclic voltammogram. Solution, 1 mM HQ; scan rate, 50 mV/sec; (a) a cyclic scan-reactivated CFAE; a square wave-reactivated CFAE with parameters: upper potential limit, +1.0 V; lower potential limit, -0.1 V; frequency, (b) 5 Hz, (c) 50 Hz, (d) 500 Hz; duration, 30 sec; delay, 4 min.

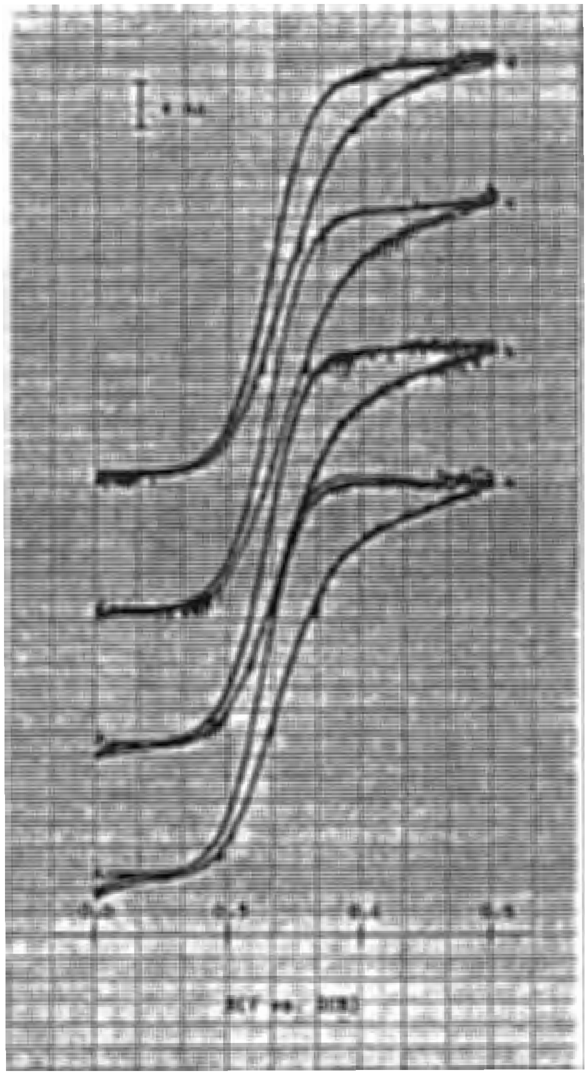


Figure 18. Effects of duration of a square wave upon the cyclic voltammogram. Solution, 1 mM HQ; scan rate, 50 mV/sec; (a) a cyclic scan-reactivated CFAE; a square wave-reactivated CFAE with parameters: upper potential limit, +1.0 V; lower potential limit, -0.1 V; frequency, 0.5 Hz; duration, (b) 5 sec, (c) 15 sec, (d) 30 sec; delay, 4 min.

the same as in Figure 17 except the frequency was 0.5 Hz and with different durations. Comparison of all CVs also shows that the EC behaviors of the CFAE shows no significant changes when different duration square waves are applied. Therefore, EC behavior of the reactivated CFAE are independent of the frequency and the duration of the square wave.

Subsidence of the Charging Current

After the CFAE reactivation process stopped, the switch of the potential at CFAEs to the required potentials for data collection generates a current spike which is due to double-layer charging. Figure 19 shows the decay of this current versus time immediately after a CFAE was reactivated with a square wave, which had the upper potential limit, +1.0 V; the lower potential limit, -0.1 V; duration, 30 sec; and frequency, 0.5 HZ. This current decayed very rapidly during the first two minutes, then gradually decreased at a constant rate. Prior to performing a cyclic scan, a four-minute delay was used to allow decay of the current generated by the electrode reactivation; this procedure was adopted for all the following experiments. During this time of delay, the potential at a CFAE was held at the required value for data collection. Therefore, a square wave having an upper potential limit, +1.0 V; a lower potential limit, -0.1 V; a frequency, 1.1 HZ; and duration, 30 sec; with delay

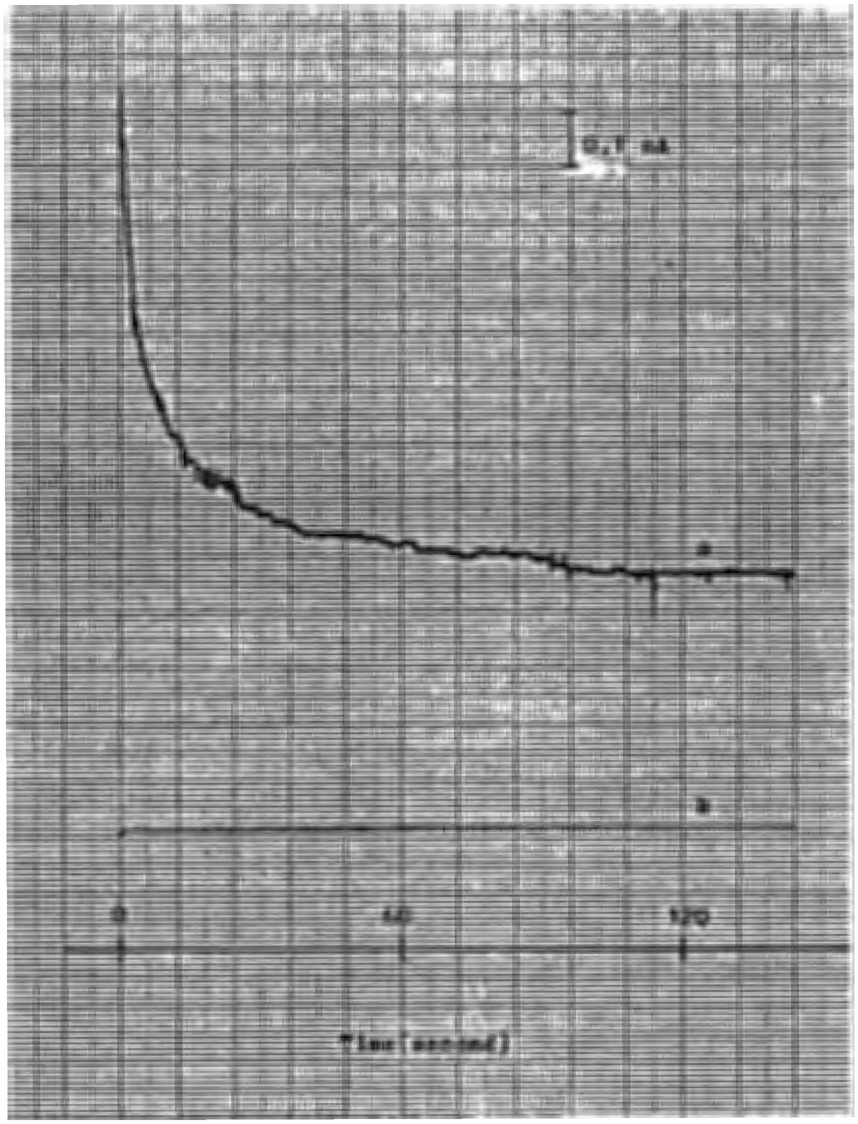


Figure 19. Decay of a charging current after the applied potential at a carbon fiber array electrode was switched to 0 V.

time, 4 min; was chosen for the CFAE reactivation. And the CVs obtained were reproducible if the CFAEs were reactivated with these optimized parameters.

Surface Morphology of the Reactivated CFAE

After a CFAE was reactivated by a square wave, the electrode surface was examined by scanning electron microscopy (SEM) and X-ray photoelectron spectrum (XPS) with the assistance of Dr. John Dash (34). The SEM of the CFAE surface showed, as in Figure 20, that carbon fibers are parallel-aligned and the ends of carbon fibers extended out of the epoxy surface. Most carbon fibers are partially isolated from each other. This arrangement of carbon fibers in a CFAE will give good sensitivity and low detection limit due to the edge effect. The XPS of the CAFE surface is shown in Figure 21. The surface is not completely cleaned and still have trace amounts of different metals, such as Al and Si. The dispersed alumina and emery particles are present on the electrode surface even after cleaning by sonic waves and square waves.

CYCLIC VOLTAMMETRY IN A FLOW CELL

In order to compare the performance of CFAEs in the designed ME cell with that in a conventional cell, a ME cell having a single electrode disk was assembled, as described in Chapter II. The experimental procedures were the same as

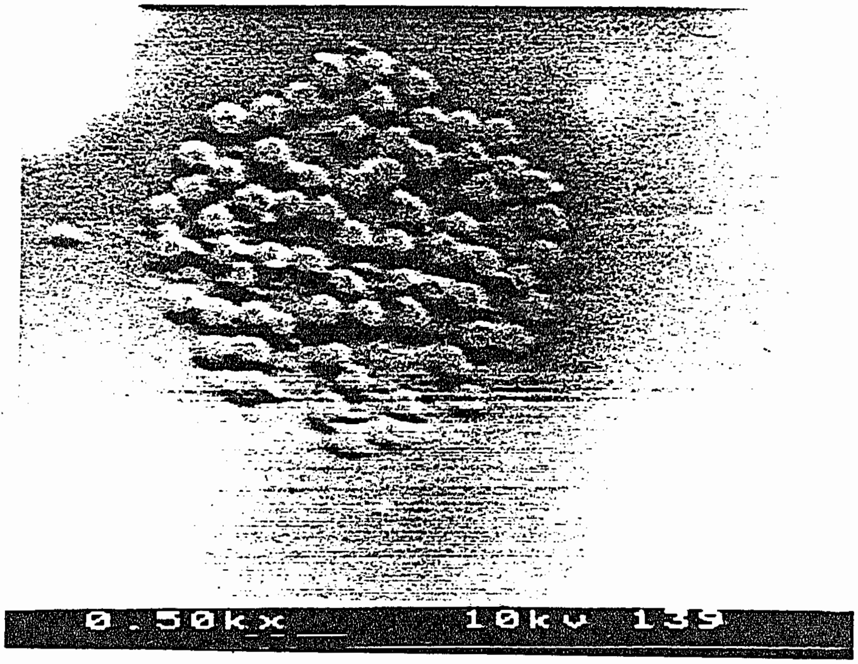


Figure 20. Scanning electron micrograph of a carbon fiber array electrode. Magnification is 500 X.

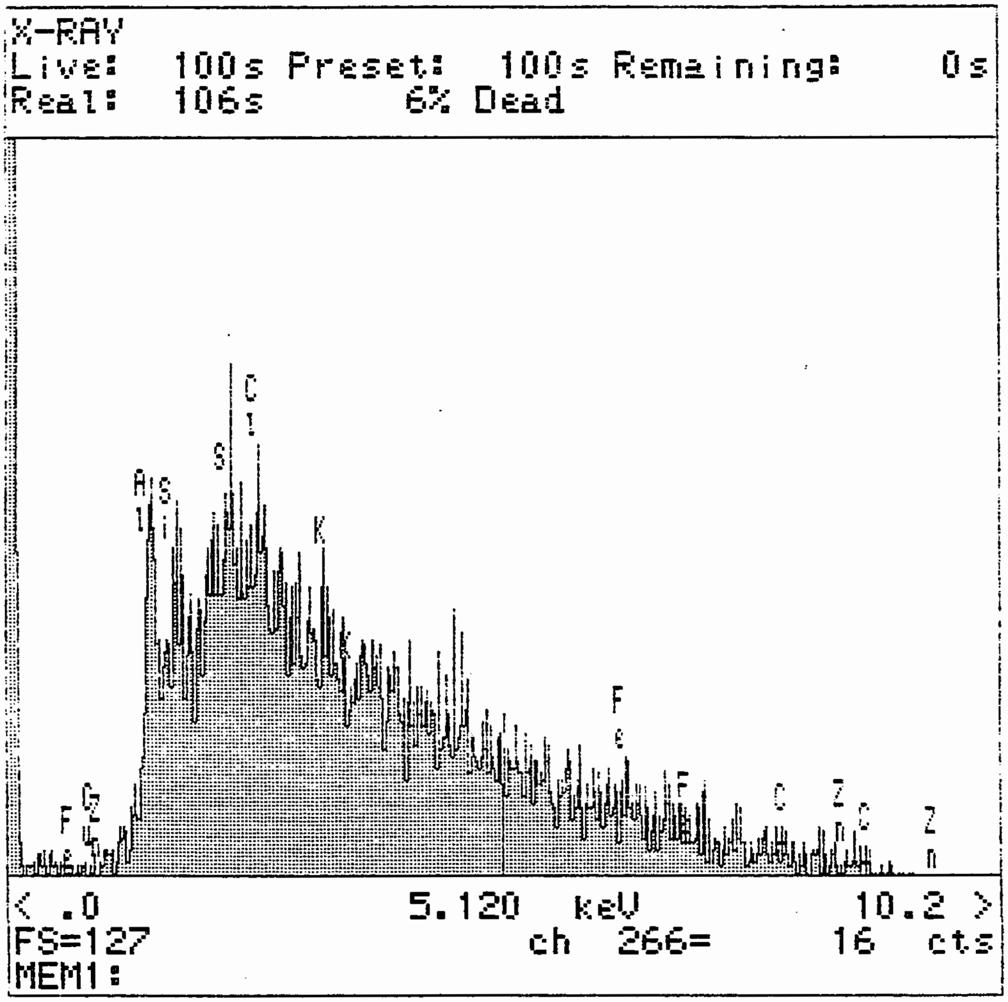


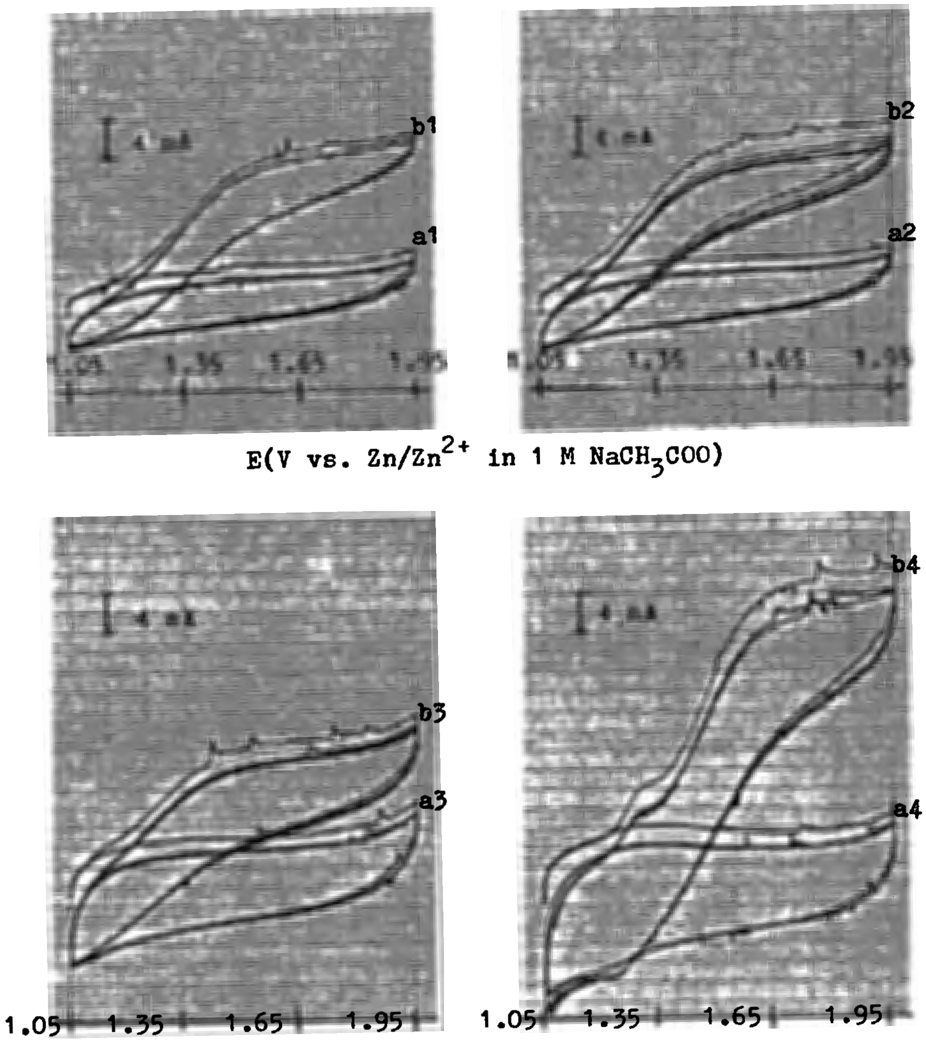
Figure 21. X-ray photoelectron spectrum of a carbon fiber array electrode.

described in Chapter IV except the pump was stopped after the HQ solution was injected into the EC cell. The potential held at the CFAE was +1.05 V (vs. the zinc/zinc acetate electrode) during the subsidence of the charging current. After that, cyclic scans were performed at a scan rate of 50 mV/s. The shape of voltammograms, as shown in Figure 22, is strongly dependent upon the tightness of the screws. The residual currents increased as the screws of the flow cell were tightened up, as shown in Figure 22a. This change in residual current was believed to be caused by the severe distortion of the CFAE disk in the flow cell due to the unevenly tightened screws. Also, the shape of the cyclic voltammogram of HQ became not well-defined, as shown in Figure 22b. A small bump was also shown at ca. +1.3 V, which might be caused by the trapped HQ in the crack adsorbing on the electrode surface. If the screws were not completely tightened, air bubbles trapped in the flow cell were not able to be removed by applying vacuum. The zinc acetate solution encapsulated in the reference electrode compartment could leak out. This problem was not correctable without changing the design of the cell body and the fabrication method of WED.

CHARACTERISTICS OF FLOW INJECTION ANALYSIS SYSTEM

Minimization of the Potential Drop in the ME Cell

One of the primary concerns of designing an EC cell is



<u>Figure 22</u>. Effects of tightness of the cell screws upon the cyclic voltammogram. (a) 0.1 M AB; (b) 1 mM HQ; tightness of the screws: (1) very loose, (2) loose, (3) tight, (4) very tight.

to minimize the potential drop across a solution. This concern is especially important for designing a ME cell. A flow cell generally has an advantage of high mass-transport rate of analytes, which increases sensitivity due to current increase. However, this current increase may also lead to an increased potential drop and consequent impairment of efficient potential control at the working electrode. In a ME cell, the current response at one electrode which causes a potential drop across the solution may also affect the potentials across all electrode-solution interfaces. This resulting "cross-talk" can render a ME cell useless if the potential drop is too large. Both can be minimized by decreasing either the cell impedance or the current.

The minimization of current response at CFAEs was accomplished by making the electrode surface area small. The minimization of the cell impedance was achieved by using the supporting electrolyte combined with positioning the reference electrode as close as possible to the working electrode, i.e., by placing a zinc/zinc acetate reference electrode in a compartment directly across a thin layer from the CFAEs with the separation of a Nafion film, as shown in Figure 4.

Nozzle-Electrode Surface Separation

For the flow cell, although the equation for the limiting current derived by Yammada and Matsuda (17) does not contain any term relating to the inlet-electrode surface separation, it has been well-known that, according to the theory (35), the jet nozzle must be located outside the hydrodynamic boundary layer for the maximum efficiency obtained from the electrode; otherwise, interference of the flow in the boundary layer would result in a loss of current efficiency. Also, the jet nozzle-electrode surface separation must not be too far; otherwise the jet may spread out and cause loss of resolution as the distance from the nozzle increased.

With these considerations in mind, the jet nozzle must be designed to remain outside the hydrodynamic boundary layer even at high flow rate. The hydrodynamic boundary layer thickness (δ_{bl}) has been calculated with the following equation by Gunasingham and Fleet (9).

$$\delta_{bl} = 5.8\ \pi^{3/4}\ a^{1/2}\ v^{3/4}\ x^{5/4}\ V^{-3/4}$$

where a : diameter of the nozzle (cm).

V : a volume flow rate (cm^3/s).

v : the kinematic viscosity (10^{-2} cm^2/s for aqueous system).

x : the distance from the electrode surface (cm).

Substituting representative values for this flow system into the above equation, where $v = 10^{-2}$ cm^2/s, inlet diameter of 0.343 mm, an electrode with a radius of ca. 1 mm at flow rate between 1.1 - 3.3 cm^3/min, the boundary layer thickness is between 0.4 and 0.8 mm. The jet nozzle-electrode separation of this ME cell was ca. 0.8 mm, i.e., a thickness of a Nafion film and a Kalrez film, which is just adequate to keep the nozzle of the inlet outside the hydrodynamic boundary. This separation can be slightly adjusted by tightening the screws. The diameters of the centered hole on the Nafion film and the Kalrez spacer are large enough to avoid disturbing the hydrodynamic boundary layer of the jet flow. The inlet diameter of the jet was 0.343 mm because the cross section of an ideal wall-jet need to be as small as possible, compared to the electrode surface area.

Geometric and Effective ME Cell Volumes

One of the characteristic features of the wall-jet cell, not present in other designs, is that the effective cell volume is only the order of the hydrodynamic boundary layer and not the geometric cell volume. Since the effective cell volume at each CFAE is very small, as seen from the previous section, the detection process does not produce appreciable change of sample concentration down stream. Although the larger geometric cell volume does not effect the hydrodynamic boundary layer, it may cause broadening of the sample band. The cell volume needs to be as small as possible.

The geometric cell volume is calculated as follows:

In each single unit,

Volume of the inlet = $\pi r^2 l$
= 5.28×10^{-4} cm^3
where the inlet diameter (r) is 0.343 mm;
the inlet length (l) is 5.72 mm

Volume on the electrode disk
= $(\pi r^2 l) \times 4 = 9.69 \times 10^{-3}$ cm^3
where the tube diameter in hole is 3.18 mm;
the inlet length is 0.305 mm

Volume of the center hole in the Nafion film
= $\pi r^2 l = 9.88 \times 10^{-4}$ cm^3
where the center hole diameter is 1.78 mm;
the thickness of Nafion film is 0.397 mm

Volume of the center hole in two Kalrez films
= $(\pi r^2 l) \times 2 = 1.30 \times 10^{-2}$ cm^3
where the center hole diameter is 4.56 mm
the thickness of Kalrez film is 0.397 mm

There are four units in the ME cell. The total geometric volume is ca. 9.7×10^{-2} cm^3. Since the geometric cell volume is small, compared with the sample in the sample injection loop (ca. 0.8 ml), and the distance between the sample injection valve and the cell was made very short, the sample band broadening by diffusion was insignificant through the whole cell.

The Pulse Damper and Ground Current Insulator

The minipump used to pump solutions through the flow system is a synchronous reciprocating pump which has advantages of having reproducible flow and a small internal volume. The relationship between pump scale and flow rate is shown in Table I. Figure 23 shows that the flow rate is proportional to the pump scale, but not linear. This pump also produces a pulsating flow in the flow system and conducts a small ground current through the system from the AC power line. Since the mass-transport rate of analytes or impurities in the solution is proportional to the flow rate, this flow fluctuation caused by the minipump was a noise source for MEV. The unwanted ground current conducted by the pump was imposed on the measured current and caused the sensitivity to be decreased. A simple device was made to overcome both drawbacks. It is made from two pieces of plastic syringe tube connected with a piece of glass tube, then placed between the minipump and the sample injection valve. This tube was only partially filled with solution. The empty part of the capacity served as both the pulse damper and the ground current isolator. With the use of this device flow fluctuation was decreased dramatically and so was noise. The ground current was also insulated from the ME cell.

THE TRUE CAPACITANCE AND LEAKAGE CURRENT OF THE INTEGRATOR

Although the nominal values of the capacitance of the integrators are known from the specifications, the true values can be different. The leakage current may be generated by the offset voltage between positive input and negative input of the amplifier. A set of dummy resistors

TABLE I

RELATIONSHIP OF PUMP SCALE AND FLOW RATE

Pump Scale	Time for 10 mL (sec)
20.0	540
30.0	352
40.0	265
50.0	210
60.0	180

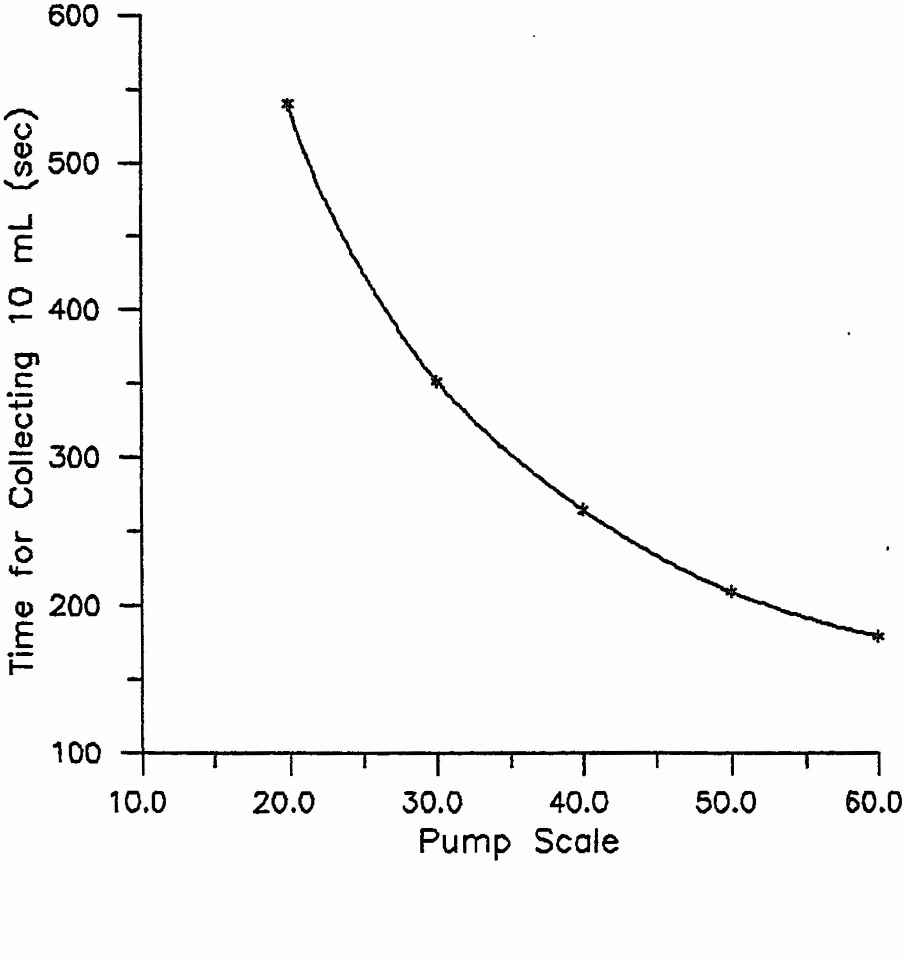


Figure 23. Correlation between the flow rate and the pump scale.

and a voltage source were used to simulate the current generation by the electroactive species at each capacitor and the current leakage generated by the offset voltage of the amplifier. One side of the resistor was connected with the negative input of the amplifier. The other side was connected with a potential source. Two potentials which were symmetrical to the circuit ground were used to obtain the currents which was generated by the voltage drop across the resistor in order to solve the combined equations for two unknown values of every integrator. The equation used is as follows:

$$E_{out} = \frac{1}{C} \int \frac{V}{R} dt + \frac{1}{C} \int i_{leak}\, dt$$

where E_{out}: output voltage of an amplifier;

C: capacitance in Coulomb;

V: potential applied at electrode;

R: measured resistance in ohm;

t: time in sec;

i_{leak}: leakage current of current follower;

10 MΩ resistors were chosen in order to lessen the chance of too large a signal entering the current integrating circuits, whose maximum limit is +/-12 V. The true resistance of each resistor was measured by a digital multimeter. The calculated capacitance of each capacitor and

leakage current of each integrator are shown in Table II. The calculated leakage currents were all very small, compared with the resolution ability of the analog-to-digital converter. They were insignificant and were ignored during the data handling for MEV.

TABLE II

RESISTANCE, LEAKAGE CURRENT, AND CAPACITANCE OF THE INTEGRATOR

Integrator	Resistance* (MΩ)	Capacitance** (nF)	Leakage Current** (nA)
# 1	10.10	0.901	0.225
# 2	9.97	0.863	0.276
# 3	10.07	0.898	0.340
# 4	10.13	0.841	0.262
# 5	9.93	0.839	0.369
# 6	10.09	0.902	0.315
# 7	9.98	0.895	0.240
# 8	9.95	0.867	0.474
# 9	10.13	0.924	-0.040
# 10	10.24	0.892	-0.083
# 11	10.14	0.897	-0.306
# 12	10.12	0.897	-0.016
# 13	9.98	0.913	0.258
# 14	9.95	0.892	0.020
# 15	10.08	0.824	0.099
# 16	9.87	0.856	0.047

* Measured by a multi-digital meter.
** Based on 4 sets of data.

NORMALIZATION FACTORS OF CARBON FIBER ARRAY ELECTRODES IN THE MULTI-ELECTRODE CELL

In the ME cell, 16 CFAEs are employed. Careful procedures have been taken to assure that reproducible results were obtained at each electrode, such as electrode reactivation procedures. The pseudo-voltammograms constructed are based on the data collected at all 16 CFAEs. The signals generated at each CFAE under the same experimental condition may differ because the electrode surface areas are not always the same, which might be caused by some carbon fibers being broken during the fabricating process, even though all CFAEs were fabricated the same way. Depending on the way the ME cell was assembled, the flow patterns at each CFAE in the cell may also differ. It has also been shown CFAEs foul gradually due to the adsorption of impurities on the surface. Hence, the surface areas of CFAEs in the ME cell need to be calibrated just prior to the collection of data for MEV in order to obtain the active electrode surface.

The experimental procedures of electrode surface area normalization were described in Chapter IV. The manipulation of amperometric data for CFAE normalization factors were described in Appendix E. All potentials measured and reported in this section are relative to the zinc/zinc acetate reference electrode. Prior to data collection for normalization factors of the CFAEs in the ME cell, a potential sufficient to spontaneously oxidize HQ and also to provide the maximum sensitivity at CFAEs needs to be determined. The potential meeting this requirement is in the limiting-current plateau of the CV. However, when the applied potential at CFAEs is at the positive end of the CV plateau, the increases of the background current generated by the oxidation of H_2O and of the noise level caused by the evolution of O_2 become limiting factors. Hence, the best sensitivity can be obtained by choosing a potential which is near the middle of the CV plateau. A potential of +1.95 V was chosen as a compromise between maximizing the analyte current response and minimizing the background current for CFAE surface area normalization. 0.5 mM HQ solution was used for optimum S/N ratio and system performance.

Flow Rate Dependency

A disadvantage of amperometric electrodes in flow cells is the noticeable effect of flow rate on the analytical signal since mass transfer in the flow system is proportional to flow rate. The flow rate dependence of the current is substantially reduced when microelectrodes are used in flow cells (27, 36). The dependency of the flow rates for normalization factors of CFAEs in the ME cell was therefore studied.

During preliminary experiments, sudden disappearance of signals at some electrodes and the expulsion of small gas bubbles from the ME cell into its outlet occurred more often when the flow was slower. It indicates that small gas bubbles generated by the fluctuation of pressure in the cell are adsorbed on the electrode surface more often when the flow is slow. Inhomogeneity of the sample solution caused by dispersion of sample was observed. Low flow rates were excluded from the study. When the flow rate is too high, the pulse damper becomes ineffective because cyclicly fluctuating data due to pulsating flow have been observed. Hence, a range of flow rate from 1.67 to 3.33 ml/min was studied, i.e., the pump scale set between 30.0 and 60.0.

To evaluate the performance of the ME cell, the residual currents and the net currents obtained at an applied potential of +1.95 V (vs. Zinc/Zinc Acetate electrode) in 5.45 x 10^{-4} HQ solution with different flow rates are compared. Table III shows the residual currents and the net currents obtained at different flow rates. Both the residual and the net currents show only a small dependence on flow rate as is expected for ultra-microelectrodes.

The currents are different at each electrode because the effective areas are different. A normalizing factor can be obtained from the data of Table III by calculation the ratio of the current at each electrode to the current at one electrode. Table IV shows the normalized factors of CFAEs relative to electrode #2 at different flow rates. The relative standard deviations are between 0.5 % and 3.6 %.

Repeatability and Reproducibility

Insufficient stability and reproducibility are often drawbacks of EC flow cells. Since air bubbles were much easier to be formed at the low flow rate, both stability and

TABLE III

INFLUENCE OF THE FLOW RATE ON THE CARBON FIBER ARRAY ELECTRODE RESPONSE CURRENT

	Current (Amp) at Flow Rate of			
	1.67 mL/Min		2.22 mL/min	
Electrode	Residual	Net	Residual	Net
# 1	5.26E-10	3.11E-8	4.96E-10	3.19E-8
# 2	4.81E-10	3.61E-8	4.77E-10	3.88E-8
# 3	5.39E-10	4.82E-8	4.90E-10	5.11E-8
# 4	2.56E-10	4.02E-8	2.44E-10	4.19E-8
# 5	1.41E-09	5.74E-8	1.17E-09	5.82E-8
# 6	1.61E-09	6.08E-8	1.35E-09	6.31E-8
# 7	1.93E-09	3.99E-8	1.69E-09	4.03E-8
# 8	9.87E-10	5.36E-8	8.95E-10	5.80E-8
# 9	1.60E-09	4.96E-8	1.31E-09	5.02E-8
# 10	1.88E-09	4.82E-8	1.62E-09	5.06E-8
# 11	2.10E-09	4.88E-8	1.71E-09	5.04E-8
# 12	1.75E-09	4.04E-8	1.43E-09	4.16E-8
# 13	7.79E-10	5.07E-8	6.90E-10	5.40E-8
# 14	1.07E-09	5.48E-8	9.98E-10	5.82E-8
# 15	2.22E-09	6.03E-8	2.10E-09	6.36E-8
# 16	4.80E-09	5.60E-8	4.07E-09	5.89E-8

	Current (Amp) at Flow Rate of			
	2.86 mL/Min		3.33 mL/min	
Electrode	Residual	Net	Residual	Net
# 1	6.12E-10	3.16E-8	6.12E-10	3.27E-8
# 2	5.89E-10	3.94E-8	5.85E-10	4.11E-8
# 3	6.81E-10	5.21E-8	6.34E-10	5.43E-8
# 4	3.06E-10	4.22E-8	3.10E-10	4.27E-8
# 5	1.85E-09	6.06E-8	1.74E-09	6.14E-8
# 6	2.20E-09	6.65E-8	2.07E-09	6.91E-8
# 7	2.37E-09	4.22E-8	2.28E-09	4.48E-8
# 8	1.33E-09	5.91E-8	1.23E-09	6.11E-8
# 9	2.23E-09	5.29E-8	2.13E-09	5.48E-8
# 10	2.65E-09	5.21E-8	2.49E-09	5.19E-8
# 11	3.12E-09	5.34E-8	2.97E-09	5.55E-8
# 12	2.73E-09	4.36E-8	2.38E-09	4.61E-8
# 13	9.96E-10	5.74E-8	9.05E-10	6.06E-8
# 14	1.42E-09	6.21E-8	1.35E-09	6.50E-8
# 15	2.63E-09	6.51E-8	2.58E-09	6.68E-8
# 16	6.49E-09	6.24E-8	6.27E-09	6.23E-8

TABLE IV

CORRELATION BETWEEN FLOW RATE AND NORMALIZATION FACTORS

Electrode	Normalization Factor at Flow Rate (mL/Min)			
	1.67	2.22	2.86	3.33
# 1	0.86	0.82	0.80	0.80
# 2	1.00	1.00	1.00	1.00
# 3	1.33	1.31	1.32	1.32
# 4	1.11	1.08	1.07	1.04
# 5	1.59	1.50	1.54	1.50
# 6	1.68	1.62	1.69	1.68
# 7	1.11	1.04	1.07	1.09
# 8	1.48	1.49	1.50	1.49
# 9	1.37	1.29	1.34	1.33
# 10	1.34	1.30	1.32	1.26
# 11	1.35	1.30	1.36	1.35
# 12	1.12	1.07	1.11	1.12
# 13	1.40	1.39	1.46	1.48
# 14	1.52	1.50	1.58	1.58
# 15	1.67	1.64	1.65	1.63
# 16	1.55	1.52	1.59	1.52

	Normalization Factor		
Electrode	Mean	Std. Dev.	Rel. Std. Dev.(%)
# 1	0.82	0.03	3.6
# 2	1.00	0.00	0.0
# 3	1.32	0.01	0.6
# 4	1.08	0.03	2.7
# 5	1.53	0.04	2.9
# 6	1.67	0.03	1.8
# 7	1.08	0.03	2.7
# 8	1.49	0.01	0.5
# 9	1.34	0.03	2.4
# 10	1.30	0.03	2.4
# 11	1.34	0.03	2.1
# 12	1.10	0.02	2.1
# 13	1.43	0.04	2.9
# 14	1.54	0.04	2.7
# 15	1.65	0.02	1.1
# 16	1.54	0.03	2.1

reproducibility of normalization was studied at the flow rate of 3.33 mL/min. Table V shows the repeatability of a series of three injections of 5.45×10^{-4} M HQ in 0.1 M AB solution. The relative standard deviations of the net limiting current for 16 CFAEs in the ME cell scatters between 0.5 % and 5.4 %. Table VI shows the reproducibility of three injections of the same HQ solution in a 6 hour period. For these injections, the relative standard deviations ranges between 2.2 % and 6.9 %.

Normalization Factor

The average of the net currents obtained at the flow rate of 3.33 mL/min for repeatability studies, as shown in Table V, were used to calculate the normalization factors of CFAEs in the ME cell. The procedures are described in Appendix E. The normalization factors, as shown in Table VII, were used to normalize all amperometric data for construction of pseudo-voltammograms.

MULTI-ELECTRODE VOLTAMMETRY

The analytical responses of MEV were examined with HQ solutions at a flow rate of 3.33 mL/min. The experimental procedures were described in Chapter IV. The pseudo-voltammograms are constructed by plotting the normalized amperometric data vs. the applied potentials at each CFAE. All potentials reported in this section are relative to the

TABLE V

REPEATABILITY OF CARBON FIBER ARRAY ELECTRODE RESPONSE CURRENTS AT APPLIED POTENTIAL OF +1.95 V

Electrode	Net Current (Amp) Set 1	 Set 2	 Set 3
# 1	3.27E-8	3.25E-8	3.11E-8
# 2	4.10E-8	4.00E-8	3.93E-8
# 3	5.43E-8	5.12E-8	5.09E-8
# 4	4.27E-8	4.10E-8	4.00E-8
# 5	6.14E-8	5.98E-8	5.53E-8
# 6	6.91E-8	6.76E-8	6.52E-8
# 7	4.48E-8	4.34E-8	4.35E-8
# 8	6.10E-8	5.95E-8	5.74E-8
# 9	5.48E-8	5.29E-8	5.07E-8
# 10	5.19E-8	5.14E-8	5.04E-8
# 11	5.55E-8	5.44E-8	5.29E-8
# 12	4.61E-8	4.32E-8	4.37E-8
# 13	6.06E-8	5.82E-8	5.78E-8
# 14	6.50E-8	6.37E-8	6.24E-8
# 15	6.68E-8	6.65E-8	6.60E-8
# 16	6.25E-8	6.01E-8	5.82E-8

Electrode	Mean	Net Current (Amp) Std. Dev.	Rel. STd. Dev. (%)
# 1	3.21E-8	8.36E-10	2.6
# 2	4.01E-8	8.64E-10	2.1
# 3	5.21E-8	1.88E-09	3.6
# 4	4.12E-8	1.36E-09	3.2
# 5	5.88E-8	3.20E-09	5.4
# 6	6.73E-8	1.95E-09	2.9
# 7	4.39E-8	7.72E-10	1.7
# 8	5.93E-8	1.81E-09	3.0
# 9	5.28E-8	2.02E-09	3.8
# 10	5.12E-8	7.57E-10	1.4
# 11	5.43E-8	1.33E-09	2.4
# 12	4.43E-8	1.56E-09	3.5
# 13	5.89E-8	1.50E-09	2.5
# 14	6.37E-8	1.30E-09	2.0
# 15	6.64E-8	3.79E-10	0.5
# 16	6.03E-8	2.18E-09	3.6

TABLE VI

REPRODUCIBILITY OF CARBON FIBER ARRAY ELECTRODE RESPONSE CURRENTS AT THE APPLIED POTENTIAL OF +1.95 V

	Net Current (Amp)		
Electrode	Set 1	Set 2	Set 3
# 1	3.27E-8	3.42E-8	3.16E-8
# 2	4.11E-8	4.17E-8	3.99E-8
# 3	5.43E-8	5.36E-8	5.16E-8
# 4	4.27E-8	4.77E-8	4.21E-8
# 5	6.14E-8	6.61E-8	6.15E-8
# 6	6.91E-8	7.19E-8	6.56E-8
# 7	4.48E-8	4.63E-8	4.42E-8
# 8	6.11E-8	6.21E-8	5.90E-8
# 9	5.48E-8	5.52E-8	5.22E-8
# 10	5.19E-8	5.28E-8	4.93E-8
# 11	5.55E-8	5.75E-8	5.33E-8
# 12	4.61E-8	4.63E-8	4.44E-8
# 13	6.06E-8	6.56E-8	6.25E-8
# 14	6.50E-8	6.92E-8	6.30E-8
# 15	6.68E-8	7.16E-8	6.97E-8
# 16	6.23E-8	6.42E-8	6.88E-8

	Net Current (Amp)		
Electrode	Mean	Std. Dev.	Rel. STd. Dev. (%)
# 1	3.28E-8	1.28E-09	3.9
# 2	4.09E-8	9.09E-10	2.2
# 3	5.32E-8	1.40E-09	2.6
# 4	4.42E-8	3.07E-09	6.9
# 5	6.30E-8	2.69E-09	4.2
# 6	6.88E-8	3.18E-09	4.6
# 7	4.51E-8	1.05E-09	2.3
# 8	6.07E-8	1.60E-09	2.6
# 9	5.40E-8	1.66E-09	3.0
# 10	5.13E-8	1.84E-09	3.5
# 11	5.54E-8	2.13E-09	3.8
# 12	4.56E-8	1.02E-09	2.2
# 13	6.29E-8	2.52E-09	4.0
# 14	6.57E-8	3.14E-09	4.7
# 15	6.93E-8	2.42E-09	3.4
# 16	6.51E-8	3.36E-09	5.1

TABLE VII

CARBON FIBER ARRAY ELECTRODE NORMALIZATION FACTORS FOR PSEUDO-VOLTAMMOGRAMS

Electrode	Ave. Net Current (Amp)	Normalization Factor
# 1	3.21E-8	0.80
# 2	4.01E-8	1.00
# 3	5.21E-8	1.30
# 4	4.12E-8	1.03
# 5	5.88E-8	1.46
# 6	6.73E-8	1.68
# 7	4.39E-8	1.09
# 8	5.93E-8	1.48
# 9	5.28E-8	1.32
# 10	5.12E-8	1.28
# 11	5.43E-8	1.35
# 12	4.43E-8	1.10
# 13	5.89E-8	1.47
# 14	6.37E-8	1.59
# 15	6.64E-8	1.66
# 16	6.03E-8	1.50

zinc/zinc acetate reference electrode.

HQ concentrations ranging from 7.26×10^{-5} M up to 5.45×10^{-4} M were used to study the analytical response of this instrumentation. The potential range between +1.05 V and +1.95 V was applied at the CFAEs in the multi-electrode cell.

Reproducibility of Multi-Electrode Voltammetry

The reproducibility of MEV was studied by a series of three injections of a 5.45×10^{-4} M HQ solution at the flow rate of 3.33 mL/min in a 6-hour period. The normalized net currents at each CFAE are shown in Table VIII. The relative standard deviations scatter between 167% in the residual current region and 0.6 % in the limiting current region.

TABLE VIII

REPRODUCIBILITY OF MULTI-ELECTRODE VOLTAMMETRY

Electrode	Potential (V) Applied	Net Current (Amp) Set 1	Set 2	Set 3
# 1	1.05	-3.23E-11	4.45E-12	-5.67E-11
# 2	1.11	7.87E-12	3.46E-11	6.07E-11
# 3	1.17	-3.02E-11	-1.86E-12	1.08E-12
# 4	1.23	-1.22E-11	-8.87E-12	-1.44E-11
# 5	1.29	-2.72E-11	-3.88E-11	-2.33E-11
# 6	1.35	1.18E-11	1.42E-11	4.20E-11
# 7	1.41	5.23E-10	5.13E-10	5.25E-10
# 8	1.47	3.26E-09	3.20E-09	3.20E-09
# 9	1.53	2.51E-09	2.54E-09	2.64E-09
# 10	1.59	7.68E-09	7.72E-09	7.99E-09
# 11	1.65	1.13E-08	1.18E-08	1.23E-08
# 12	1.71	1.53E-08	1.74E-08	1.72E-08
# 13	1.77	2.25E-08	2.34E-08	2.58E-08
# 14	1.83	2.78E-08	2.88E-08	2.90E-08
# 15	1.89	3.27E-08	3.23E-08	3.27E-08
# 16	1.95	3.92E-08	3.75E-08	3.72E-08

Electrode	Net Current (Amp) Mean	Std. Dev.	Rel. Std. Dev. (%)
# 1	-2.82E-11	3.08E-11	-109.2
# 2	3.44E-11	2.64E-11	76.7
# 3	-1.03E-11	1.73E-11	-167.4
# 4	-1.18E-11	2.78E-12	-23.6
# 5	-2.98E-11	8.09E-12	-27.2
# 6	2.27E-11	1.68E-11	74.1
# 7	5.20E-10	6.25E-12	1.2
# 8	3.22E-09	3.33E-11	1.0
# 9	2.56E-09	7.11E-11	2.7
# 10	7.80E-09	1.66E-10	2.1
# 11	1.18E-08	4.74E-10	4.0
# 12	1.66E-08	1.16E-09	6.9
# 13	2.39E-08	1.71E-09	7.1
# 14	2.85E-08	5.95E-10	2.0
# 15	3.26E-08	2.15E-10	0.6
# 16	3.80E-08	1.10E-09	2.8

The very large relative standard deviation at low potential end of the pseudo-voltammogram is due to the small currents and the resolution of the ADC. The low relative standard deviation at high potential range indicates that MEV has very good reproducibility over this time period.

Shape of Pseudo-Voltammograms

Figure 24 shows a set of sigmoidal-shaped pseudo-voltammograms constructed from the data, shown in Table IX, obtained using different concentrations of HQ solution at the flow rate of 3.33 mL/min. The shapes of these voltammograms are similar to the cyclic voltammograms obtained at a CFAE in a stationary solution, shown in Figure 22. A small bump was also shown at ca. +1.5 V (vs. the zinc/zinc acetate electrode), which might be caused by the trapped HQ in the crack adsorbing on the electrode surface. The whole instrument package worked as designed.

Calibration Curve and Detection Limit of MEV

The normalized net currents obtained at an applied potential of +1.95 V were chosen for plotting a calibration curve because the currents generated at this potential represent the limiting current. The graph plotted with these limiting currents vs. the concentrations, respectively, is shown in Figure 25. The results of the linear regression analysis of this calibration curve had a correlation coefficient of 0.9999. Obviously, the dynamic

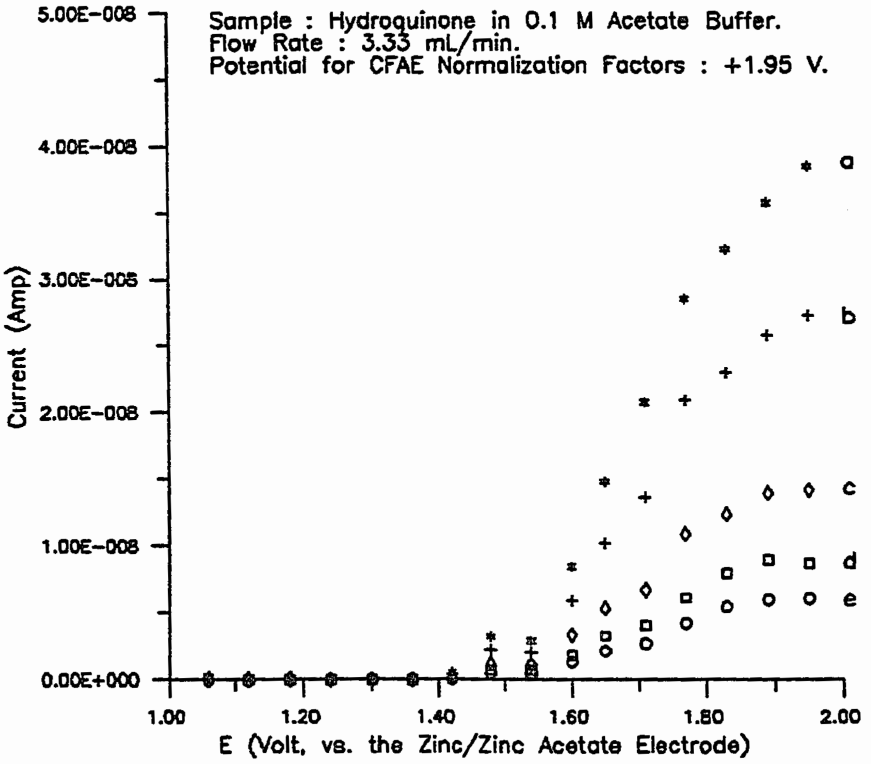


Figure 24. Pseudo-voltammograms of hydroquinone at different concentrations. Flow rate, 3.33 mL/min; (a) 5.45×10^{-4} M; (b) 3.63×10^{-4} M; (c) 1.82×10^{-4} M; (d) 1.09×10^{-4} M; (e) 7.26×10^{-5} M.

TABLE IX

DATA OBTAINED FOR PSEUDO-VOLTAMMOGRAMS AT A FLOW RATE OF 3.33 ML/MIN

Electrode	Applied Potential (V)
# 1	1.05
# 2	1.11
# 3	1.17
# 4	1.23
# 5	1.29
# 6	1.35
# 7	1.41
# 8	1.47
# 9	1.53
# 10	1.59
# 11	1.65
# 12	1.71
# 13	1.77
# 14	1.83
# 15	1.89
# 16	1.95

Electrode	Net Current (Amp) at Concentration (M) of				
	7.26E-5	1.09E-4	1.82E-4	3.63E-4	5.45E-4
# 1	-3.56E-11	3.77E-11	1.02E-11	6.28E-12	1.72E-11
# 2	-2.96E-11	-7.62E-12	-4.98E-12	3.06E-12	-1.59E-11
# 3	-4.42E-12	-1.34E-12	-1.72E-12	-1.57E-11	-3.13E-12
# 4	-5.96E-12	-1.70E-11	-2.93E-11	7.50E-12	-1.70E-11
# 5	-2.52E-11	-3.56E-11	-1.36E-11	-2.98E-11	-3.85E-11
# 6	-1.44E-11	-2.10E-11	-8.95E-12	1.28E-11	3.82E-11
# 7	3.74E-11	7.98E-11	1.59E-10	3.59E-10	5.07E-10
# 8	4.65E-10	7.00E-10	1.16E-09	2.24E-09	3.22E-09
# 9	4.45E-10	6.76E-10	1.09E-09	2.04E-09	2.88E-09
# 10	1.31E-09	1.80E-09	3.08E-09	5.96E-09	8.45E-09
# 11	2.16E-09	3.25E-09	5.34E-09	1.02E-08	1.48E-08
# 12	2.69E-09	4.08E-09	6.69E-09	1.36E-08	2.08E-08
# 13	4.20E-09	6.14E-09	1.09E-08	2.09E-08	2.85E-08
# 14	5.48E-09	7.94E-09	1.24E-08	2.30E-08	3.22E-08
# 15	5.99E-09	9.00E-09	1.40E-08	2.58E-08	3.57E-08
# 16	6.07E-09	8.66E-09	1.42E-08	2.72E-08	3.84E-08

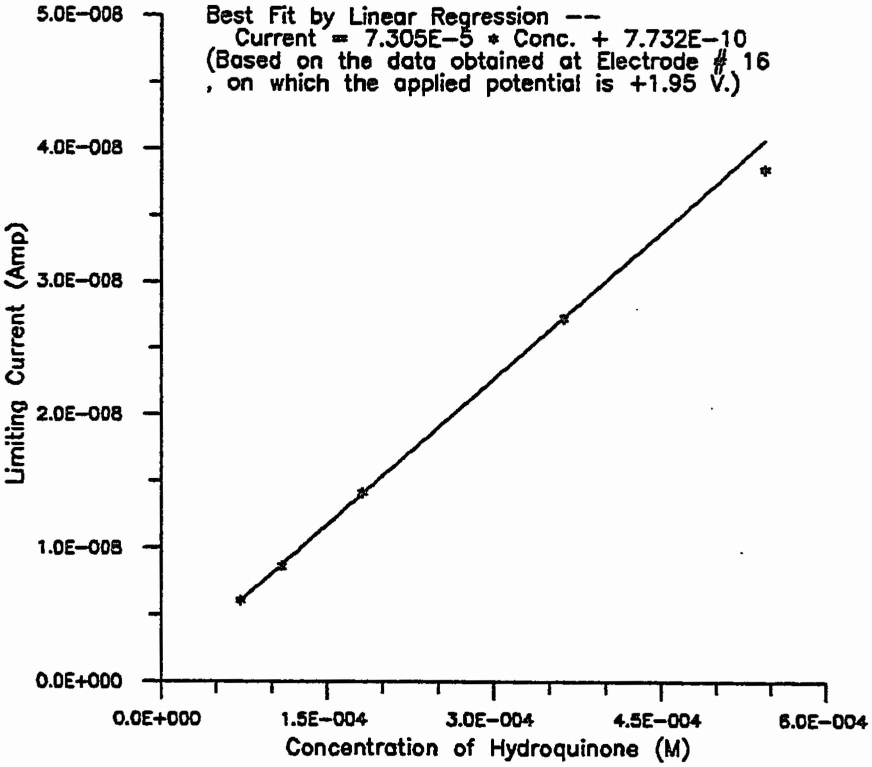


Figure 25. Calibration curve of multi-electrode voltammetry. The experimental conditions are the same as in Figure 24.

range of linear response of MEV extends over two orders of magnitude of the concentration. The detection limit based on these conditions is estimated to be 5 x 10^{-5} M HQ at 95% confidence level, ie., on the basis of a 2 times the standard deviation of the calibration curve.

CHAPTER VI

CONCLUSION

Carbon electrodes have been used in electrochemical (EC) cells for a long time. There are several reasons for using them. One of the primary reasons is the applicability to anodic oxidations of many organic and inorganic species, which are not amenable to the mercury electrode. The applicable potential range on carbon electrodes is much wider compared with electrodes made of other materials. Many forms of carbon have been used to fabricate electrodes for EC detection in the oxidative mode. Among them, carbon fiber provides an inexpensive and readily fabricated alternative to materials such as glassy carbon or pyrolytic graphite, which are expensive and difficult to fabricate. Carbon fiber overcomes many drawbacks of other types of carbon electrodes (28), such as very low background current, good peak resolution, and good reproducibility.

Based on pseudo-voltammograms obtained, multi-electrode voltammetry (MEV) is an effective method for the determination of electroactive substances. The reproducibility and stability of MEV are dependent upon the careful assembly of the flow cell, including no gas bubbles in the cell and the proper tightness of the screws. The sensitivity of MEV matches most of the EC methods, but with less expensive instrumentation and more convenient operation. This good sensitivity is obtained due to two reasons. First, capacitative charging current, one of the limiting factors in all EC techniques, is reduced to insignificant proportions because of the application of constant voltages at CFAEs. Second, the rate of mass transport to CFAEs increases due to the edge effect of CFAE. As a consequence of reduced capacitative charging currents and increased mass transport rates, CFAEs exhibit good sensitivity. Electrode surface fouling by electrochemically active species and impurities is diminished in this flow system because a very small sample solution is injected into the system so that the exposure of the electrode to the sample is relatively brief. Also, electrodes are always reactivated using a square wave prior to data collection in order to obtain a fresh surface.

Two improvements for this instrumentation need to be made in the future. First, building an interface with a computer which has larger RAM capacity is necessary. This is an important point because a lot of time was wasted waiting to record and transfer data. This diminished the speed advantage of using flow injection analysis. An unique feature of this system is the option to change the time interval according to the sample size and sample concentration in order to expand the dynamic range of the instrument. This is a very important advantage if it is used as a detector for HPLC and ion chromatography. Second, a new type of pump is needed. Gradual diminution of signal current has been occasionally observed during data collection, due to the adsorption of micro gas bubbles at CFAE surfaces. The generation of these bubbles may be caused by the combination of two factors: (1) the saturation of gas in the flow stream while the solution drips into the pulse damper in order to insulate the ground current from the AC power line and dampening the pulsating current generated by the pump; (2) the periodic pressure fluctuation in the flow cell due to the reciprocal pump.

From the constructed pseudo-voltammograms, it was shown that MEV can be used like other electrochemical techniques with minimal manipulation. It is possible that MEV can be used to determine the complexation ability between a metal ion and a ligand by the measurement of a half-wave potential shift, i.e. the stronger the binding of the complex, the larger is the shift from $E_{1/2}$ of that metal ion.

EC cells have been used as detectors for HPLC for a long time. Chemists have found that it is very unlikely that a single peak of HPLC effluent represents one and only one component of the mixture (37). The results of this study make EC detectors more important since they have the ability to determine the purity of the effluent peak. At present, EC detectors use only one or two working electrodes and can not distinguish between eluted species on the basis of redox properties. Its resolving ability can be enhanced by the use of more than one working electrode. Series and parallel combinations in a flow stream avoid the need for potential scans which is impractical due to short duration of solute peaks and slow decay of background currents of some electrode materials. Therefore, the possibility of incorporating MEV as a detector for HPLC should be investigated. With an MEV detector, additional resolving power is available and it can help in the identification of unresolved column effluent.

Anodic stripping techniques provide concentration measurements, not speciation unless additional chemical separation steps are included. There is a source of error that has been largely ignored even though it was identified many years ago (2). This error is due to intermetallic compound formation between metals during deposition. This may decrease anodic peak height or even eliminate the peak. Further, the peaks due to oxidation of the intermetallic compounds are displaced on the potential axis so that identification may be in error. MEV can easily alleviate this problem by deploying a coulometric electrode, such as porous carbon, upstream to completely remove selected metal ions in the flow so that other ions may be deposited free of interference on the electrodes used for anodic stripping. A coulometric electrode can also remove impurities in supporting electrolytes and/or certain contaminants of the sample matrix, which may interfere with species of interest. The combination of this coulometric electrode and MEV is a potentially powerful technique to improve detection limits.

At present, only 16 CFAEs have been installed in MEV. This system is ready to expand to as many as 64 electrodes. Choosing different electrode materials and expanding the number of electrodes in the flow cell may be studied to extend the domain of application.

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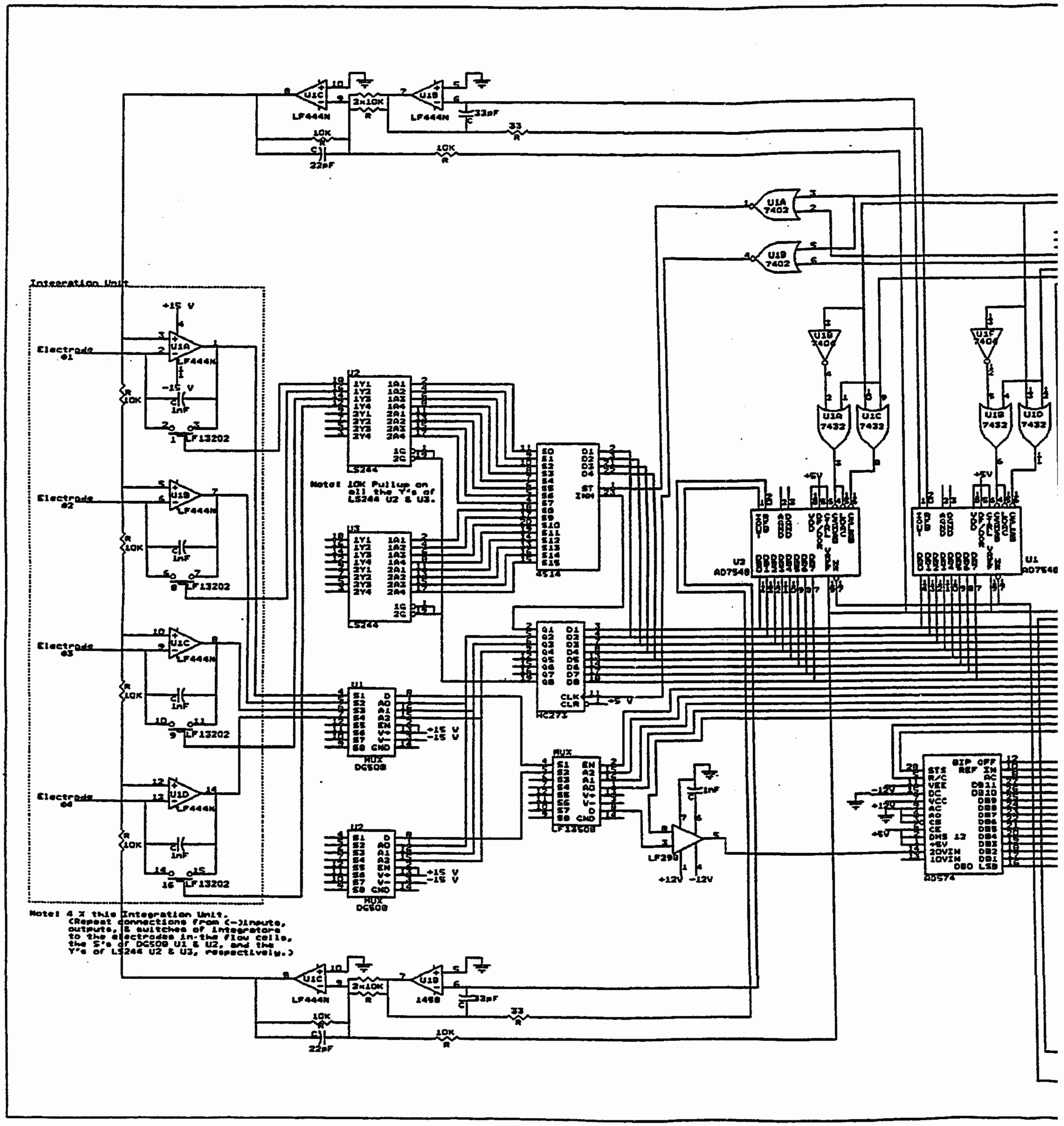
APPENDIX A

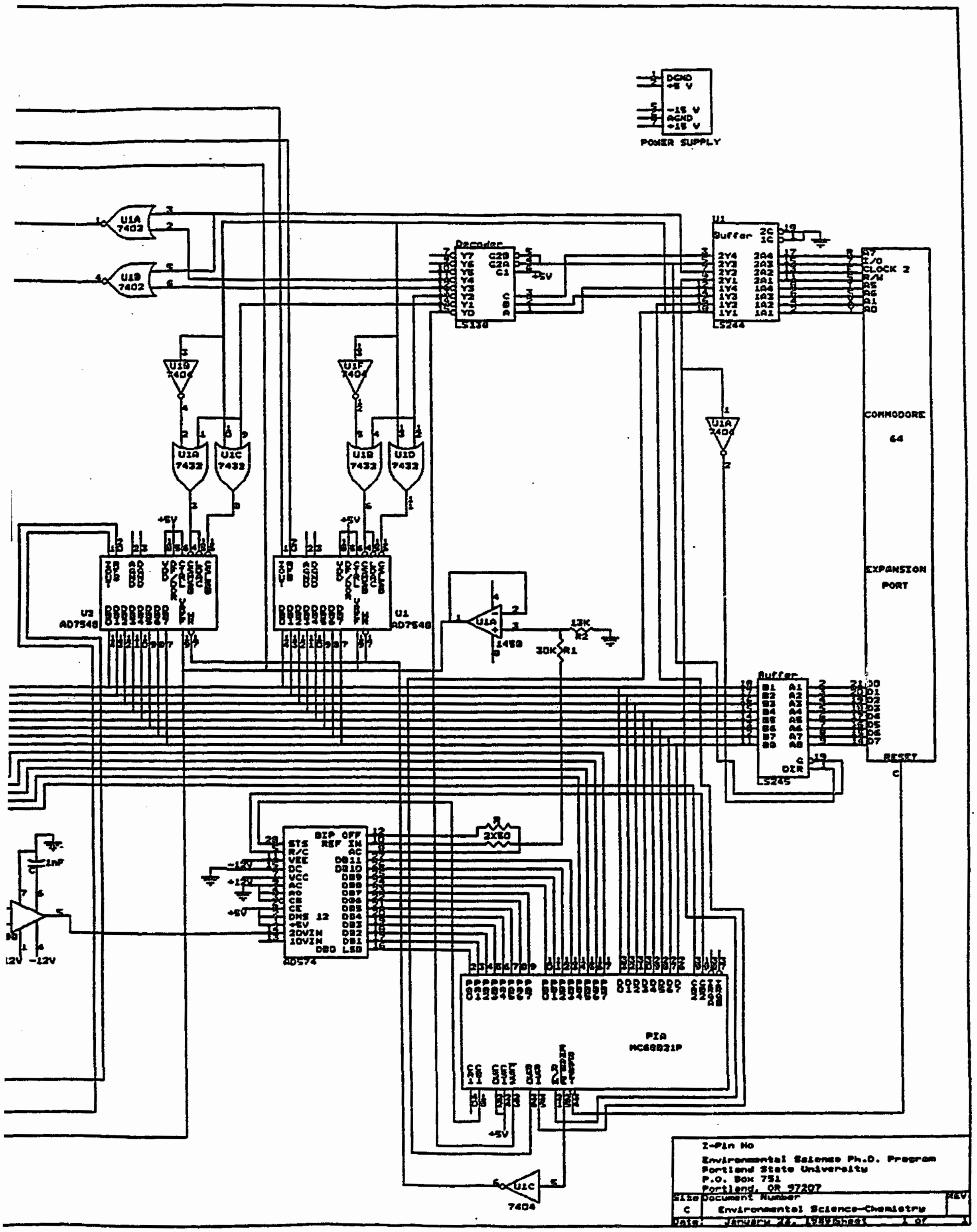
SCHEMATIC DIAGRAM OF THE CIRCUITRY WITH COMPONENT IDENTIFICATIONS



Note: 10K Pullup on all the Y's of LS244 U2 & U3.

Note: 4 X this Integration Unit. (Repeat connections from (-)inputs, outputs, & switches of integrators to the electrodes in the flow cells, the S's of DG508 U1 & U2, and the Y's of LS244 U2 & U3, respectively.)

SCHEMATIC DIAGRAM OF THE CIRCUITRY WITH COMPONENT IDENT



E CIRCUITRY WITH COMPONENT IDENTIFICATIONS

APPENDIX B

SOFTWARE
"SET.7548.OUTPUT"

```
100 REM ******************************
120 REM *        2/6/1989            *
140 REM *    "SET.7548.OUTPUT"       *
160 REM *                            *
180 REM * PROGRAM TO FIND EQUATIONS  *
200 REM * FOR DAC 7548 VOLT. OUTPUTS *
220 REM *                            *
240 REM ******************************
500 FL=56896:FH=56897:REM ADDRESS OF DAC 7548 #1
520 SL=56864:SH=56865:REM ADDRESS OF DAC 7548 #2
600 PRINT
620 PRINT
640 INPUT"HAVE FORMULA FOUND(Y/N)";DM$
660 IF DM$="Y" THEN GOTO 2000
1000 PRINT
1020 PRINT"** IF VH%<0 THEN END OF THIS PART !!
1040 PRINT
1200 INPUT"ENTER VH% & VL% FOR BOTH DACS";VH%,VL%
1240 INPUT"ARE BOTH OK(Y/N)";DM$
1260 PRINT
1280 IF DM$<>"Y" THEN 1000
1300 IF VH%<0 THEN 1700
1400 POKE FL,VL%:POKE FH,VH%
1420 POKE SL,VL%:POKE SH,VH%
1440 PRINT
1460 PRINT" MEASURE THE VOLAGE OUTPUTS ON BOTH PIN 1 AND PIN 8."
1480 PRINT" AND WRITE THEM DOWN !!"
1500 PRINT
1600 GOTO 1000
1700 PRINT"LIST 2300-2700 " :STOP
2000 PRINT
2020 PRINT"** IF VOLT LESS THAN -10 VOLT"
2040 PRINT"   THEN END OF THIS TEST !!  "
2060 PRINT
2100 INPUT"  ENTER VOLT FOR BOTH DAC";V
2140 INPUT"  IS IT OK(Y/N)";DM$
2160 PRINT
2180 IF DM$<>"Y" THEN 2100
2200 IF V=<-10 THEN 3000
2300 REM FORMULA FOR PIN 8(DAC#1)
2320 B1%=INT(V*4095/6.011+2037)
2340 LH%=INT(B1%/256)
2360 LL%=INT(B1%-LH%*256)
2380 POKE FL,LL%:POKE FH,LH%
2500 REM FORMULA FOR PIN 1(DAC#2)
2520 B2%=INT(V*4095/6.014+2047)
2540 VH%=INT(B2%/256)
2560 VL%=INT(B2%-VH%*256)
2580 POKE SL,VL%:POKE SH,VH%
2700 PRINT
2720 PRINT V;"VOLT APPLIED ON BOTH DAC"
2760 PRINT
2800 PRINT" MEASURE VOLAGE OUTPUTS ON PIN 1 & PIN 8"
2820 PRINT" OF LF444 AND COMPARE WITH INPUT VALUES !"
2840 PRINT
2900 GOTO 2000
3000 END
```

APPENDIX C

SOFTWARE
"COLLECT.DATA"

Written in BASIC language, the instruction-driven program "COLLECT.DATA" is used to instruct the experimental procedures and to perform the acquisition of coulometric data which represented the integrated analyte currents. The flow chart of this program is shown in Figure 26. The entire program is included at the end of this section.

It is first used to load the assembly language subroutine "DATACQ" into the designated area in the RAM of the C-64, followed by the input of the conditions to perform the experiment. After that, the reactivation of CFAEs in the ME cell with a square wave is performed under the direction of several parameters. These parameters of electrode reactivation are the upper and lower potential limits of the square wave, the frequency of the square wave, and the duration of the reactivation process.

The experimental conditions are applied to the CFAEs after their reactivation. These conditions included the potential applied on each electrode, the setup of timer #1 and #2, and the delay time to allow the charging currents caused by the reactivation process to subside. After the currents subside, the assembly language subroutine is activated to perform data acquisition, as described in the next section. The collected coulometric data are temporarily stored in the RAM of the C-64 until the preset time period is over.

Since the RAM capacity of the C-64 is so limited,

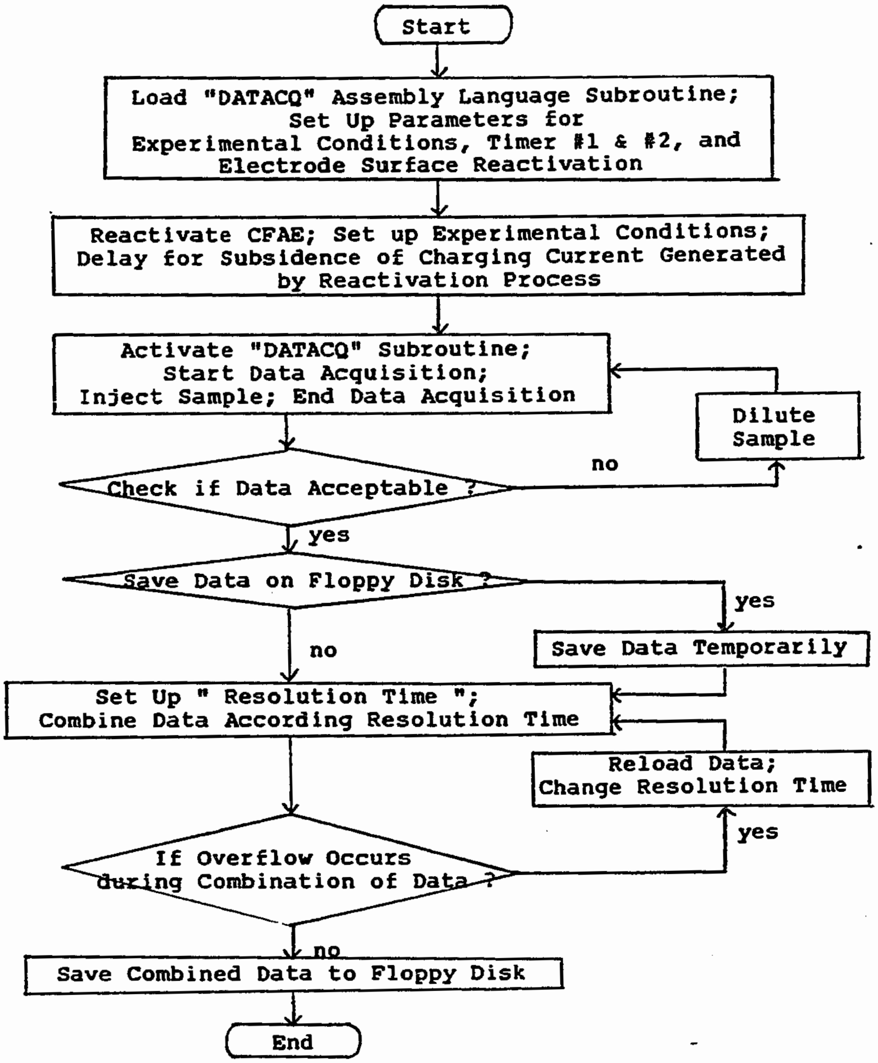


Figure 26. Flow chart of software "COLLECT.DATA".

several sets of collected data for each CFAE are then combined together in order to reduce the requirement of the RAM according to the so-called "Resolution Time". This procedure also eliminates the random errors caused by the timing of integration. Then, these combined values are stored onto a floppy disk for further data management.

If any overflow is detected during the combination of digital values, a prompt statement is printed on the monitor screen to alert the operator that the time resolution is not set appropriately. After the time resolution is changed, the data are reloaded into the matrix from the previously saved data file. Then, the combining of the digital values according to the new resolution time is performed again.

The internal clock of the C-64 is used for timing the duration of the electrode reactivation and the delay between the end of the electrode reactivation and the beginning of the data acquisition. The two internal timers of the C-64 are used for timing the frequency of the data acquisition. The parameters of these two timers were interrelated (53). Their settings are dependent on the sample size, the sample concentration, and the RAM capacity of the C-64. The use of these two timers is a unique feature of this system. Parameters for the electrode surface activation, the setup of timer #1 and #2, and experimental conditions are all input through the keyboard.

```
1 IF AA=1 THEN 100
2 IF AA=0 THEN AA=1:LOAD"DATACQ.BIN",8,1
10 REM ****************************
11 REM *        2/9/1988          *
20 REM *     "COLLECT.DATA"       *
21 REM *                          *
30 REM * DATA ARE COLLECTED BY    *
31 REM *  AN ASSEMBLY SUBROUTINE  *
32 REM *  & ALSO SAVE INTO A FILE *
40 REM ****************************
100 DIM DD%(16,700)
120 POKE 56928,128:REM KEEP ALL SWITCHES CLOSED
200 PRINT
220 PRINT"** DO NOT CONNECT CELL !!"
240 PRINT
300 INPUT"   TODAY IS(2/9)";DA$
320 INPUT"   IS DATE OK(Y/N)";DM$
340 PRINT
360 IF DM$="N" THEN 300
400 REM DD%(M,N)=DIGITAL DATA OBTAINED
410 REM TR=TIME OF RESOLUTION
420 REM U2=LEAST U2 BYTE
430 REM TT=TOTAL COVERED TIME
440 REM UL=UPPER POTENTIAL LIMIT OF SQUARE WAVE
450 REM LL=LOWER POTENTIAL LIMIT OF SQUARE WAVE
460 REM HZ=FRQUENCY OF SQUARE WAVE
470 REM DU=DURATION OF SQUARE WAVE
480 REM TD=TIME OF DELAY TO STABLE RESIDUAL CURRENT
490 REM DA$= DATE OF EXPT. RUN
500 AD=56832:AC=56833:REM DDR-A & CR-A OF PIA
510 BD=56834:BC=56835:REM DDR-B & CR-B OF PIA
520 CD=56960:REM ADDRESS OF CD4514
530 HC=56928:REM ADDRESS OF 74HC273
540 L1=56896:H1=56897:REM ADDRESS OF DAC7548 #1
550 L2=56864:H2=56865:REM ADDRESS OF DAC7548 #2
560 REM $DC06 IS THE TB-LO ADDRESS OF 6526 U1
570 REM $DD04 IS THE TA-LO ADDRESS OF 6526 U2
600 REM POKE AC,0 & POKE BC,0
610 REM POKE AD,0 & POKE BD,240
620 REM POKE AC,52 & POKE BC,60
630 REM 640 IS EQUILVANT TO 600,610,& 620
640 SYS 49152:REM $C000 TO SET UP PIA
660 ID$="'NONE'"
700 PRINT"** MAKE SURE FLOW PUMP IS ON"
720 PRINT"   & INJECTOR IS AT STANDBY"
740 PRINT"   THEN PUSH 'G' TO GO ON"
760 PRINT
780 GET A$: IF A$<>"G" THEN 780
800 PRINT"** IF BEEP IS NOT HEARD,"
820 PRINT"   TURN THE VOLUME UP !!"
840 PRINT
860 GOSUB 8000:REM TEST BEEP
1000 GOSUB 13000:REM SET STANDBY POTENTIAL
1100 GOSUB 13500:REM APPLY STANDBY POTENTIALS TO ELECTRODES
1200 PRINT"** EVACUATE FLOW SYSTEM &"
1220 PRINT"   THEN CONNECT CABLE TO IT"
1240 PRINT"   PUSH 'G' TO GO ON ! "
1260 PRINT
1280 GET A$:IF A$<>"G" THEN 1280
```

```
1300 PRINT"-- DO NOT INJECT SAMPLE & DO NOT"
1320 PRINT"   PRECONDITION ELECTRODE BECAUSE"
1340 PRINT"   THIS IS THE FIRST RUN TO CHECK"
1360 PRINT"   IF ELECTRODE LEAKS"
1380 PRINT
1400 INPUT"TIME OF DELAY(>=180 SEC)";TD
1420 INPUT"IS IT OK(Y/N)";DM$
1440 PRINT
1460 IF DM$<>"Y" THEN 1400
1500 TI$="000000"
2000 INPUT"WANT TO COLLECT DATA(Y/N)";DM$
2020 PRINT
2040 IF DM$="N" THEN 5000
2100 REM SET PARAMETERS FOR DATA COLLECTION
2120 GOSUB 15000
2200 PRINT"-- NOW, TIME IS ";TI$
2220 PRINT"   TIME MUST BE LESS THAN";TD;"SEC"
2240 PRINT
2260 PRINT"   WAIT FOR BEEP !"
2280 PRINT
2400 BT=TD:GOSUB 9200:REM LET OVERSHOOT CURRENT SUBSIDE DOWN
2500 PRINT"-- NOW, COLLECTING DATA !!"
2520 PRINT
2600 POKE 56928,0:REM PIN 1 & 19 OF 74HC244 LOW
2620 SYS 49209:REM $C039 OBTAIN DATA
2640 PRINT"-- DATA'VE BEEN COLLECTED !"
2660 PRINT
2700 POKE 56928,128:REM KEEP ALL SWITCHES CLOSED
2720 GOSUB 13500:REM APPLY STANDBY POTENTIAL
2800 PRINT"-- HANG ON, CHECKING DATA !"
2820 PRINT
2840 GOSUB 10500:REM FIND OUT HOW MANY SETS OBTAINED
2860 GOSUB 8000:REM BEEP
2880 PRINT"** MOVE FLOW OUTLET BACK TO CYLINDER !"
2900 PRINT
3000 GOSUB 9600:REM CHECK A DATA SET
3100 INPUT"PRINT OUT UNTREATED DATA(Y/N)";DM$
3120 PRINT
3140 IF DM$<>"Y" THEN 3200
3160 GOSUB 20000
3200 INPUT"SATISFY WITH DATA(Y/N)";DM$
3220 PRINT
3240 IF DM$="N" THEN 5000
3500 REM COMBINE DATA TOGETHER ACCORDING TO RESOLUTION TIME
3520 PRINT"WANT TO COMBINE DATA"
3540 INPUT" ACCORDING TO TR(Y/N)";DM$
3560 PRINT
3580 IF DM$<>"Y" THEN 5000
3600 GOSUB 11000:REM COMBINE DATA
3620 GOSUB 8000:REM BEEP
4000 GOSUB 9600:REM CHECK COMBINED RESULTS
4100 INPUT"PRINT OUT THESE DATA(Y/N)";DM$
4120 PRINT
4140 IF DM$<>"Y" THEN 4200
4160 GOSUB 20000
4200 INPUT"IS TIME RESOLUTION OK(Y/N)";DM$
4220 PRINT
4240 IF DM$<>"Y" THEN 5000
4400 INPUT"WANT TO SAVE RESULTS ON DISK(Y/N)";DM$
4420 PRINT
4440 IF DM$="N" THEN 5000
4460 GOSUB 9000:REM CHECK DISK
4480 PRINT
4500 PRINT" SAMPLE LABEL : ";LB$
4520 PRINT" FLOW RATE : ";FR$
4540 PRINT" INI. VOLT : ";IV;" VOLT"
```

```
4560 PRINT" FINAL VOLT : ";FV;" VOLT"
4580 PRINT" PREVIOUS REMARK : ";RM$
4600 PRINT
4620 PRINT"**************************************"
4640 PRINT"* FOR AREA, FILE NAME STARTS WITH A- *"
4660 PRINT"* FOR SAMP, FILE NAME STARTS WITH S- *"
4680 PRINT"**************************************"
4700 PRINT
4720 PRINT"PREVIOUS DATA FILE ID: ";ID$
4800 INPUT"NEW DATA FILE ID";ID$
4820 INPUT"REMARK (NO)";RM$
4840 INPUT"ARE THEY OK(Y/N)";DM$
4860 PRINT
4880 IF DM$<>"Y" THEN 4800
4900 PRINT"  HANG ON, RECORDING DATA !"
4920 PRINT
4940 GOSUB 6000:REM RECORD DATA
4960 GOSUB 8000:REM BEEP
5000 INPUT"ANOTHER RUN(Y/N)";DM$
5020 PRINT
5040 IF DM$="Y" THEN 5100
5060 PRINT"* YOU ARE SURE. RIGHT?":STOP
5080 GOTO 5000
5100 GOSUB 14000:REM SET UP EXPT. CONDITIONS
5120 GOSUB 13000:REM SET STANDBY POTENTIALS
5140 GOSUB 13500:REM APPLY STANDBY POTENTIALS
5200 PRINT"** MAKE SURE"
5220 PRINT"    A SAMPLE IS READY TO INJECT"
5240 PRINT"    THEN PUSH 'G' TO GO ON !"
5260 PRINT
5280 GET A$:IF A$<>"G" THEN 5280
5300 INPUT"WANT TO CLEAN ELECTRODE(Y/N)";DM$
5320 PRINT
5340 IF DM$="Y" THEN 5500
5400 PRINT"TIME OF DELAY";TD
5410 INPUT"IS IT OK(Y/N)";DM$
5420 PRINT
5440 IF DM$="Y" THEN 5600
5460 INPUT"TIME OF DELAY(>=240 SEC)";TD
5480 GOTO 5400
5500 GOSUB 7500:REM SET UP PARAMETERS OF SQUARE WAVE
5520 GOSUB 8500:REM APPLY SQUARE WAVE
5600 GOSUB 8800:REM EXPT. POTENTIAL READY
5620 TI$="000000"
5640 PRINT"-- TIMING BEGIN --"
5660 PRINT
5680 GOSUB 8000:REM BEEP
5700 INPUT"WANT TO CLEAR MATRIX(Y/N)";DM$
5720 PRINT
5740 IF DM$<>"Y" THEN 5800
5760 GOSUB 10000:REM CLEAR MATRIX
5780 GOSUB 8000:REM BEEP
5800 GOTO 2000
5900 END
6000 REM SUBROUTINE TO SAVE DATA
6100 PRINT"-- IF DRIVE LIGHT BLINKS, STOP"
6120 PRINT"    PROGRAM IMMEDIATELY.  THEN TYPE"
6140 PRINT"    'CLOSE 2', FOLLOWED BY TYPING"
6160 PRINT"    'GOTO 4000' !!"
6180 PRINT
6200 REM SAVE DATA INTO A SEQ. FILE
6220 OPEN 2,8,2,ID$+DA$+",S,W"
6240 PRINT#2,DA$
6260 PRINT#2,LB$
6280 PRINT#2,FR$
6300 PRINT#2.UL
```

```
6320 PRINT#2,LL
6340 PRINT#2,HZ
6360 PRINT#2,DU
6380 PRINT#2,TD
6400 PRINT#2,IV
6420 PRINT#2,FV
6440 PRINT#2,U1
6460 PRINT#2,TR
6480 PRINT#2,U2
6500 PRINT#2,TT
6520 PRINT#2,NC
6540 PRINT#2,RM$
6560 FOR S=0 TO NC
6580 FOR M=0 TO 16
6600 PRINT#2,DD%(M,S)
6620 NEXT M
6640 NEXT S
6660 CLOSE 2
6800 RETURN
7500 REM SET UP PARAMETERS OF SQUARE WAVE
7510 PRINT"SQUARE WAVE PARAMETERS FOR REACTIVATION --"
7520 PRINT"  UPPER POTENTIAL LIMIT :";UL;"VOLT"
7530 PRINT"  LOWER POTENTIAL LIMIT :";LL;"VOLT"
7540 PRINT"  FREQUENCY :";HZ;"HZ"
7550 PRINT"  DURATION :";DU;"SEC"
7560 PRINT
7570 PRINT"DELAY PRIOR TO COLLECT DATA :";TD;"SEC"
7580 PRINT
7590 INPUT"ARE ALL ABOVE OK(Y/N)";DM$
7600 PRINT
7610 IF DM$="Y" THEN 7800
7700 PRINT"INPUT NEW SQUARE WAVE PARAMETERS --"
7710 INPUT"  UPPER LIMIT(+2.05 V)";UL
7720 INPUT"  LOWER LIMIT(+0.95 V)";LL
7730 PRINT"  FREQ. IS CA. 5 HZ":HZ=5
7740 INPUT"  DURATION(30 SEC)";DU
7750 PRINT
7760 INPUT"DELAY(>=240 SEC)";TD
7770 PRINT
7780 GOTO 7500
7800 REM CONVERT UL TO DIGITAL
7810 DM%=INT(UL*4095/6.012+2042)
7820 OH%=INT(DM%/256)
7830 OL%=INT(DM%-OH%*256)
7840 REM CONVERT LL TO DIGITAL
7850 DM%=INT(LL*4095/6.012+2042)
7860 RH%=INT(DM%/256)
7870 RL%=INT(DM%-RH%*256)
7900 RETURN
8000 REM GENERATE A BEEPER (REF. P.185)
8020 PRINT"   PUSH 'S' TO STOP THE BEEP &"
8040 PRINT"   WATCH THE SCREEN FOR THE HINT !"
8060 PRINT
8100 GET A$: IF A$="S" THEN 8400
8200 S=54272
8220 FOR L=S TO S+24:POKE L,0:NEXT
8240 POKE S+5,9:POKE S+6,0
8260 POKE S+24,15
8280 HF=37:LF=162:DR=500
8300 POKE S+1,HF:POKE S,LF
8320 POKE S+4,33
8340 FOR T=1 TO DR:NEXT
8360 POKE S+4,32:FOR T=1 TO 50:NEXT
8380 GOTO 8100
8400 RETURN
8500 REM SUBROUTINE FOR APPLYING SQUARE WAVE
```

```
8520 PRINT"-- NOW, REACTIVATE ELECTRODES &"
8540 PRINT"   WAIT";DU;"SEC FOR ELECTRODE CLEAN !"
8560 PRINT
8600 REM FREQUENCY OF S.W. IS 5 HZ
8620 TI$="000000"
8640 REM APPLY UPPER LIMIT FIRST, THEN LOWER LIMIT
8660 POKE L1,OL%:POKE H1,OH%
8680 POKE L2,OL%:POKE H2,OH%
8700 FOR DM=1 TO 80: NEXT DM
8720 POKE L1,RL%:POKE H1,RH%
8740 POKE L2,RL%:POKE H2,RH%
8760 FOR DM=1 TO 75: NEXT DM
8780 IF TI/60<DU THEN 8660
8790 RETURN
8800 REM APPLY EXPT. POTENTIAL TO BOTH DAC
8820 POKE L1,IL%:POKE H1,IH%
8840 POKE L2,FL%:POKE H2,FH%
8860 PRINT"-- EXPT. POTENTIALS JUST APPLIED TO"
8880 PRINT"   BOTH DAC AND READY FOR ELECTRODES"
8900 PRINT
8920 RETURN
9000 PRINT"**************************"
9020 PRINT"* MAKE SURE              *"
9040 PRINT"*  A RIGHT DISK IN DRIVE *"
9060 PRINT"*  & SPACE ALSO ENOUGH   *"
9080 PRINT"**************************"
9100 PRINT
9120 INPUT"WANT TO CHECK DISK(Y/N)";DM$
9140 PRINT
9160 IF DM$="Y" THEN STOP
9180 RETURN
9200 REM LET OVERSHOOT CURRENT SUBSIDE DOWN
9210 IF TI/60<=BT-40 THEN 9250
9220 PRINT"** DO NOT INJECT THE SAMPLE !"
9230 PRINT"   TIMING IS NOT GOOD !":PRINT
9240 GOTO 9520
9250 IF TI/60<=BT-40 THEN 9250
9260 GOSUB 8000:REM BEEP
9270 PRINT"-- 20 SEC LATER, MOVE"
9280 PRINT"   FLOW OUTLET INTO THE WASTE JAR !"
9290 PRINT
9300 IF TI/60<=BT-20 THEN 9300
9320 PRINT"** PUT FLOW OUTLET INTO A WASTE JAR &"
9340 PRINT"   15 SEC LATER, QUICK INJECT SAMPLE !"
9360 PRINT
9400 IF TI/60<=BT-5 THEN 9400
9420 PRINT"** QUICK INJECT SAMPLE !"
9440 PRINT"   & NOW, TIME IS ";TI$
9460 PRINT
9500 IF TI/60<=BT THEN 9500
9520 RETURN
9600 REM CHECK PART OF RAW DATA BEFORE SAVING
9620 PRINT" --ANY DATA SHOULD NOT = 0 OR 4095"
9640 PRINT"   Z MUST <=";N
9660 PRINT"   IF Z<0 THEN END OF CHECKING DATA"
9680 INPUT"   NEW STARTING SET #";Z
9700 PRINT
9720 IF Z<0 THEN 9900
9740 PRINT" M  DD%Z DD%Z+1 DD%Z+2 DD%Z+3 DD%Z+4"
9760 FOR M=0 TO 16
9780 PRINT M;DD%(M,Z);DD%(M,Z+1);DD%(M,Z+2);DD%(M,Z+3);DD%(M,Z+4)
9800 NEXT M
9820 PRINT
9840 PRINT"STARTING SET #(Z) =";Z
9860 PRINT
9880 GOTO 9620
```

```
9900 RETURN
10000 REM CLEAR THE WHOLE MATRIX
10020 PRINT" HANG ON, EMPTY THE MATRIX !"
10040 PRINT
10060 FOR DM=0 TO NR+2
10080 FOR M=0 TO 16
10100 DD%(M,DM)=0
10120 NEXT M
10140 NEXT DM
10160 RETURN
10500 REM FIND OUT HOW MANY SETS OF RAW DATA COLLECTED
10520 NR=700
10540 IF DD%(0,NR)>0 THEN 10600
10560 NR=NR-1
10580 GOTO 10540
10600 PRINT"LAST DATA SET(NR) AT ";NR
10620 N=NR
10640 PRINT
10660 RETURN
11000 REM ROUTINE TO TREAT RAW DATA
11020 REM J REPRESENTS ORIGINAL ROW
11040 REM N REPRESENTS EACH ROW AFTER DATA COMBINATION
11060 REM DD%(0,N) REPRESENTS INTEGRATION TIME
11080 REM M REPRESENTS THE M ELECTRODE
11100 PRINT"TIME OF RESOLUTION(TR) :";TR;"SEC"
11120 INPUT"IS IT OK(Y/N)";DM$
11130 PRINT
11140 IF DM$="Y" THEN 11200
11150 INPUT"NEW TR (<=1.00 SEC)";TR
11160 PRINT
11180 GOTO 11100
11200 PRINT"WAIT (ABOUT 5 MIN.) TO COMBINE"
11220 PRINT"  DATA ACCORDING TO TR !"
11240 PRINT
11260 PRINT"  --IF PROGRAM STOPPED BY ILLEGAL"
11270 PRINT"    QUANTITY, TYPE 'GOTO 5000' !"
11280 PRINT
11300 D1=TR*(1.023E6):XX%=INT(D1/U2)
11310 IF DD%(0,1)<=DD%(0,2) THEN 12200
11320 DD%(0,1)=DD%(0,1)-DD%(0,2)
11330 FOR M=1 TO 16
11340 DD%(M,1)=DD%(M,2)-DD%(M,1)
11350 NEXT M
11360 IF DD%(0,2)>DD%(0,4) THEN 11390
11370 DD%(0,2)=DD%(0,2)+(32767-DD%(0,4))
11380 GOTO 11400
11390 DD%(0,2)=DD%(0,2)-DD%(0,4)
11400 FOR M=1 TO 16
11410 DD%(M,2)=DD%(M,4)-DD%(M,3)
11420 NEXT M
11440 J=5
11460 N=3
11500 FOR M=0 TO 16
11520 DD%(M,N)=0
11540 NEXT M
11600 IF DD%(0,J+1)=0 AND DD%(0,J+3)=0 THEN 12300
11620 IF DD%(0,J-1)>DD%(0,J+1) THEN 11700
11640 DD%(0,N)=DD%(0,J-1)+(32767-DD%(0,J+1))+DD%(0,N)
11680 GOTO 11800
11700 DD%(0,N)=DD%(0,J-1)-DD%(0,J+1)+DD%(0,N)
11800 FOR M=1 TO 16
11820 DD%(M,N)=DD%(M,J+1)-DD%(M,J)+DD%(M,N)
11840 IF DD%(M,N)>=30700 THEN 12600
11860 NEXT M
12000 IF DD%(0,N)>=XX% THEN 12100
12020 J=J+2
```

```
12040 GOTO 11600
12100 N=N+1
12120 J=J+2
12140 GOTO 11500
12200 REM PRINT OUT MESSAGE TO IMPLY RAW DATA NOT RIGHT
12220 PRINT"** SOMETHING WRONG ABOUT RAW DATA"
12240 PRINT
12260 GOSUB 8000:REM BEEP
12280 GOTO 12700
12300 REM CALCULATE THE ACTUAL TOTAL COVERED TIME
12320 NC=N-1:REM LAST SET DO NOT HAVE INT. DATA
12340 TT=0
12360 FOR Z=1 TO NC
12380 TT=TT+DD%(0,Z)
12400 NEXT Z
12420 TT=TT*U2/(1.023E6):REM IN UNIT OF SEC
12440 PRINT"** TOTAL COVERED TIME IS";TT;"SEC"
12460 PRINT"  ";NC;"SETS OF DATA ARE OBTAINED !"
12480 PRINT
12500 N=NC
12520 GOTO 12700
12600 REM TIME OF RESOLUTION NOT RIGHT
12620 PRINT"** TR IS TOO LONG & HAS TO BE SHORTER !"
12640 PRINT
12700 RETURN
13000 REM SET STANDBY POTENTIAL
13100 PRINT"STANDBY VOLT ON BOTH DAC :";SV;"VOLT"
13120 INPUT"IS IT OK(Y/N)";DM$
13140 PRINT
13160 IF DM$="Y" THEN 13300
13200 INPUT"STANDBY VOLT(+1.0)";SV
13220 PRINT
13240 GOTO 13100
13300 REM CONVERT ANALOG POTENTIALS TO DIGITAL
13320 DM%=INT(SV*4095/6.012+2042)
13340 SH%=INT(DM%/256)
13360 SL%=INT(DM%-SH%*256)
13400 RETURN
13500 REM APPLY STANDBY POTENTIAL
13600 POKE L1,SL%:POKE H1,SH%
13620 POKE L2,SL%:POKE H2,SH%
13640 PRINT"-- STANDBY POTENTIAL JUST APPLIED"
13660 PRINT"   TO BOTH DAC !!"
13680 PRINT
13800 RETURN
14000 REM SET EXPT. CONDITIONS
14100 PRINT"SAMPLE LABEL : ";LB$
14120 PRINT
14140 PRINT"!! CHECK PUMP SCALE !!"
14160 PRINT"   FLOW RATE(FR$) : ";FR$
14180 PRINT
14200 PRINT"INIT.VOLT ON DAC #1 :";IV;"VOLT"
14220 PRINT"FIN.VOLT ON DAC #2 :";FV;"VOLT"
14240 PRINT
14260 INPUT"ARE ALL ABOVE OK(Y/N)";DM$
14280 PRINT
14300 IF DM$="Y" THEN 14700
14500 INPUT"SAMPLE LABEL(CONC, SPECIES)";LB$
14520 PRINT
14540 PRINT"* CHECK PUMP SCALE(60.0)"
14560 INPUT"  FR$ (ON SCALE 60.0)";FR$
14580 PRINT
14600 INPUT"VOLT ON DAC #1(+1.05/+1.95 V)";IV
14620 INPUT"VOLT ON DAC #2(+1.95/+1.95 V)";FV
14640 PRINT
14660 GOTO 14100
```

```
14700 REM CONVERT ANALOG POTENTIALS TO DIGITAL
14720 DM%=INT(IV*4095/6.011+2037)
14740 IH%=INT(DM%/256)
14760 IL%=INT(DM%-IH%*256)
14800 DM%=INT(FV*4095/6.014+2047)
14820 FH%=INT(DM%/256)
14840 FL%=INT(DM%-FH%*256)
14900 RETURN
15000 REM SET TIME PARAMETERS FOR DATA COLLECTING
15010 PRINT"U1 CLOCK TIME = U1*(1/60) SEC"
15020 PRINT"  U1 VALUE :";U1
15030 PRINT"U2 CLOCK PERIOD(CP) =";CP;"SEC"
15040 PRINT"  LEAST U2 BYTE =";U2
15050 PRINT"SET-UP OF COVERED TIME =";CT;"SEC"
15060 PRINT"  (GREATER THAN 60 SEC BE OK)"
15070 PRINT"  COUNTER HI-BYTE(CH) =";CH
15080 PRINT"  COUNTER LO-BYTE(CL) =";CL
15090 PRINT
15100 INPUT"ARE ALL ABOVE OK(Y/N)";DM$
15120 PRINT
15140 IF DM$="Y" THEN 15700
15200 PRINT"U1 CLOCK TIME = U1*(1/60) SEC"
15220 INPUT" U1 VALUE WANTED(<=60)";U1
15240 PRINT
15300 PRINT"LEAST U2 BYTE DEPENDS ON U1 VALUE(64= 2 S)"
15320 INPUT"  LEAST U2 BYTE(>=64)";U2
15360 CP=(127*256+255)*U2/(1.023*10^6)
15380 PRINT"  CLOCK PERIOD(CP) =";CP;" SEC"
15400 PRINT
15500 PRINT"TOTAL COVERED TIME = (CH*256+CL)*CP SEC"
15520 INPUT"  COUNTER HIBYTE(=0)";CH
15540 INPUT"  COUNTER LOBYTE(=30)";CL
15580 CT=(CH*256+CL)*CP
15600 PRINT"  SET-UP TOTAL COVERED TIME =";CT;"SEC"
15610 PRINT"  (AROUND 60 SEC BE OK)"
15620 PRINT
15640 GOTO 15000
15700 POKE 49905,U1:REM $C2F1=U1BLO
15720 POKE 49906,U2:REM $C2F2=U2ALO
15740 POKE 49907,CL:REM $C2F3=CNTLO
15760 POKE 49908,CH:REM $C2F4=CNTHI
15800 RETURN
16660 GOSUB 8000:REM BEEP
20000 REM PRINT OUT ORIGINAL DATA
20100 OPEN4,4:CMD4
20200 PRINT"  SAMPLE LABEL : ";LB$
20220 PRINT
20240 PRINT"  FLOW RATE : ";FR$
20260 PRINT
20280 PRINT"  POTENTIAL ON DAC#1 :";IV;" VOLT"
20300 PRINT"  POTENTIAL ON DAC#2 :";FV;" VOLT"
20320 PRINT
20340 PRINT"  U1 VALUE :";U1
20360 PRINT"  LEAST U2 BYTE =";U2
20380 PRINT"  U2 CLOCK PERIOD(CP) =";CP;" SEC"
20400 PRINT"  SET-UP TOTAL COVERED TIME =";CT;"SEC"
20420 PRINT
20440 PRINT"  AFTER ELECTRODES REACTIVATED,"
20450 PRINT"    PROGRAM STARTED TO COLLECT DATA";TD;"SEC LATER !!"
20460 PRINT
20480 PRINT#4:CLOSE4
20500 PRINT"** Z MUST <=";N;" & = MULTIPLE OF 5"
20520 PRINT"   IF Z<0 THEN END OF PRINTING "
20540 INPUT"   NEW STARTING SET #";Z
20560 PRINT
20580 IF Z<0 THEN 21000
```

```
20600 OPEN4,4:CMD4
20700 PRINT
20720 PRINT" ** Z =";Z
20730 PRINT
20740 PRINT" M  DD%Z DD%Z+1 DD%Z+2 DD%Z+3 DD%Z+4"
20760 FOR M=0 TO 16
20780 PRINT M;DD%(M,Z);DD%(M,Z+1);DD%(M,Z+2);DD%(M,Z+3);DD%(M,Z+4)
20800 NEXT M
20820 PRINT
20840 PRINT#4:CLOSE4
20900 GOTO 20500
21000 RETURN

READY.
```

APPENDIX D

SOFTWARE
"DATACQ"

The "DATACQ" subroutine, shown at the end of this section, is used to perform data acquisition in conjunction with the 12-bit data acquisition circuitry and is written in assembly language to increase speed of data acquisition and to reduce memory requirements of the software. The flow chart of this subroutine is shown in Figure 27.

The subroutine begins with masking all of the high level interrupts of the C-64, followed by setting up the PIA, Timer #1, Timer #2, and Cycle Counter (CC) of Timer #2. Both timers are stopped prior to their setup. The initial setup on Timer #2 is recorded and stored. Then, starting with the first electrode, the applied potential on each electrode is converted to a digital value while the switch of the current follower for that electrode is closed, followed by storing the digital value in the RAM of the C-64. The same processes are applied to the next electrode and so on until all 16 electrodes are completed. Both timers are then started and the time on Timer #2 is immediately recorded and stored. Starting with the first electrode again, the switch is opened and the converted integrating current at the electrode is recorded and stored also. The same procedures continued until all 16 electrodes are processed.

The overflow bit of Timer #2 is then Checked. If the bit is set, the cycle counter is decreased by one. After that, the overflow bit of Timer #1 is checked. Otherwise,

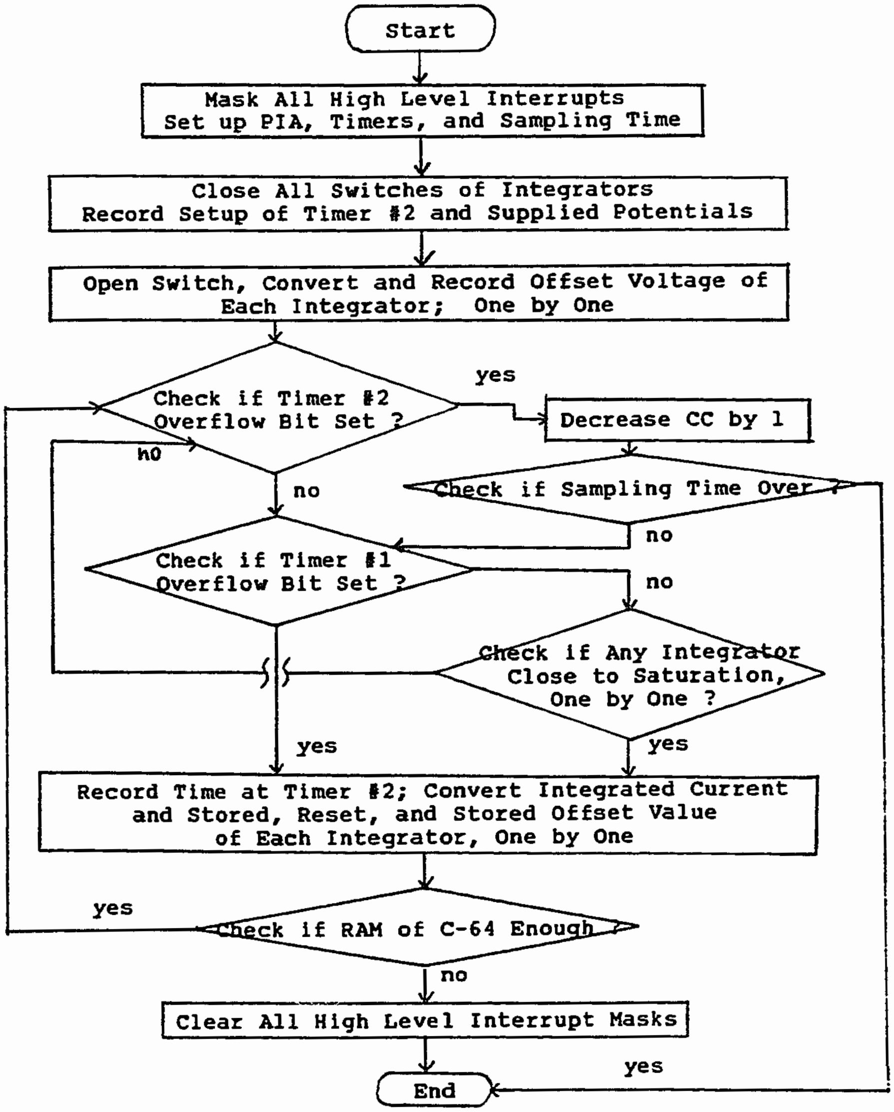


Figure 27. Flow chart of software "DATACQ".

the overflow bit of Timer #1 is checked directly. If the overflow bit of Timer #1 is set, the time on Timer #2 at that moment is stored in the RAM of the C-64, followed by the clearing of that bit and the restarting of Timer #1. Next, beginning with the first electrode, the analog signal generated by the electrode is converted to a digital value and stored in the RAM of the C-64. The reset switch is closed to discharge the capacitor of the current follower of this electrode and after 30 microseconds the switch is opened again. The offset value at this integrator is obtained after opening the switch of the integrator 30 microseconds. The same procedures are applied to the next electrode until all 16 electrodes are serviced.

If the overflow bit of Timer #1 is not set, the digital values converted from the integrating current on each electrode are checked, one by one, according to their order. If any of digital values obtained on any electrode is over the preset threshold value, i.e., close to saturation, a flag is set. Then, the time at this moment on Timer #2 is stored in the RAM. Starting with the first electrode again, the present integrated current is converted to the digital value and stored in the RAM of the C-64, followed by the immediate discharge of the capacitor of the current follower of this electrode. Then, the switch is re-opened. The offset value of each integrator is obtained as previously described. The same procedures are applied to the next electrode until all 16 electrodes are serviced. After that, the RAM of the C-64 is checked to determine whether enough memory is available. If not enough, the subroutine will stop collecting data and clear all high level interrupt mask. Otherwise, the cycle is repeated, as shown in Figure 27.

If neither the overflow bit of Timer #1 is set nor any of the digital value readouts is over the preset threshold value, the same procedures are repeated, i.e., checking whether the overflow bits of Timer #2 and #1 are set, converting the integrated analog signals to digital values, and checking whether any of the digital values was over the threshold value, etc., until the preset time period is over.

Different data acquisition rates may be accommodated by changing the setup of both timers via the "COLLECT.DATA" program. The fastest sampling rate for this data acquisition system in this subroutine is approximately 5.7 ms/datum on each electrode.

Obviously, a discontinuity of integrating analyte current is created while resetting the integrator. The reset process should be as quick as possible. However, a current surge, which decays with time, is also observed after the switch of the integrator re-opens and which almost disappears within 30 microsecond. Hence, there is a short holding time of 30 microseconds before collecting the offset value of the integrator.

```
DATACQ......PAGE 0001

LINE# LOC    CODE         LINE


00001  0000              ;ADC SUBROUTINE "DATACQ"
00002  0000              ;FOR DISSERTATION
00003  0000              ;2/21/89
00004  0000              ;
00005  0000              *=$C000
00006  C000              AD=$DE00
00007  C000              AC=$DE01
00008  C000              BD=$DE02
00009  C000              BC=$DE03
00010  C000              LATCH   = $DE60
00011  C000              SET     = $DE80
00012  C000              SAVX    = $FD
00013  C000              SAVY    = $FE
00014  C000              FLAG    = $C2F0
00015  C000              U1BLO   = $C2F1
00016  C000              U2ALO   = $C2F2
00017  C000              CNTLO   = $C2F3
00018  C000              CNTHI   = $C2F4
00019  C000              ;
00020  C000              ;SET-UP OF ADC PIA REGISTERS
00021  C000              ;FIRST, PUTS S&H IN HOLD STATE
00022  C000              ;(NOTE !! MUST BE IN SAMPLE STATE
00023  C000              ; BEFORE ENTRY)
00024  C000              ;WILL LEAVE S&H IN SAMPLE STATE
00025  C000  A9 00       ASETUP LDA #0
00026  C002  8D 01 DE           STA AC
00027  C005  8D 03 DE           STA BC
00028  C008  8D 00 DE           STA AD
00029  C00B  A9 F0              LDA #$F0
00030  C00D  8D 02 DE           STA BD
00031  C010  A9 3C              LDA #$3C
00032  C012  8D 01 DE           STA AC
00033  C015  8D 03 DE           STA BC
00034  C018  60                 RTS
00035  C019              ;
00036  C019              ;ONE ADC CONVERSION
00037  C019              ;LOW DATA IN REG-X & HI DATA IN REG-A
00038  C019  A9 34       CNVRT  LDA #$34
00039  C01B  8D 01 DE           STA AC
00040  C01E  8D 03 DE           STA BC
00041  C021  A9 3C              LDA #$3C
00042  C023  8D 03 DE           STA BC
00043  C026  A0 06              LDY #6
00044  C028  88          LPADC  DEY
00045  C029  D0 FD              BNE LPADC
00046  C02B  AD 02 DE           LDA BD
00047  C02E  29 0F              AND #$0F
00048  C030  AE 00 DE           LDX AD
00049  C033  A0 3C              LDY #$3C
00050  C035  8C 01 DE           STY AC
00051  C038  60                 RTS
00052  C039              ;
```

```
MAIN ROUTINE......PAGE 0002

LINE# LOC   CODE        LINE


00054  C039              ;
00055  C039              ;###########################
00056  C039              ;#                         #
00057  C039              ;#   MAIN DATA ACQ RTN     #
00058  C039              ;#                         #
00059  C039              ;###########################
00060  C039              ;
00061  C039              ARYTAB = $2F
00062  C039              ARPTR  = $FB
00063  C039  78                 SEI
00064  C03A  A5 2F       DATACQ LDA ARYTAB
00065  C03C  18                 CLC
00066  C03D  69 09              ADC #9
00067  C03F  85 FB              STA ARPTR
00068  C041  A5 30              LDA ARYTAB+1
00069  C043  69 00              ADC #0
00070  C045  85 FC              STA ARPTR+1
00071  C047  20 CC C0           JSR SETU2
00072  C04A  20 C0 C0           JSR SETU1; SET TIMER U1
00073  C04D  20 E2 C0           JSR STPCLK
00074  C050  20 B7 C0           JSR MSKINT
00075  C053  20 46 C1           JSR R5000
00076  C056  AD 0D DD           LDA $DD0D
00077  C059  A9 55              LDA #$55
00078  C05B  8D 0F DD           STA $DD0F
00079  C05E  8D 0E DD           STA $DD0E
00080  C061  20 F3 C0           JSR STRCLK
00081  C064  20 92 C1           JSR R6000
```

```
MAIN ROUTINE......PAGE 0003

LINE# LOC   CODE        LINE


00083  C067  A9 02       CHKU2  LDA #%00000010
00084  C069  2C 0D DD           BIT $DD0D
00085  C06C  F0 18              BEQ CHKU1
00086  C06E  38                 SEC
00087  C06F  AD F3 C2           LDA CNTLO
00088  C072  E9 01              SBC #1
00089  C074  8D F3 C2           STA CNTLO
00090  C077  AD F4 C2           LDA CNTHI
00091  C07A  E9 00              SBC #0
00092  C07C  8D F4 C2           STA CNTHI
00093  C07F  D0 05              BNE CHKU1
00094  C081  AD F3 C2           LDA CNTLO
00095  C084  F0 25              BEQ CLRMSK
00096  C086  A9 02       CHKU1  LDA #%00000010
00097  C088  2C 0D DC           BIT $DC0D
00098  C08B  D0 0F              BNE SAVRST
00099  C08D  A9 00              LDA #0
00100  C08F  8D F0 C2           STA FLAG
00101  C092  20 E3 C1           JSR R7000
00102  C095  AD F0 C2           LDA FLAG
00103  C098  C9 01              CMP #1
00104  C09A  D0 EA              BNE CHKU1
00105  C09C  20 F3 C0    SAVRST JSR STRCLK
00106  C09F  20 36 C2           JSR R9000
00107  C0A2  20 15 C1           JSR MOVPTR
00108  C0A5  A9 90              LDA #$90
00109  C0A7  C5 FC              CMP ARPTR+1
00110  C0A9  10 BC              BPL CHKU2
00111  C0AB  58          CLRMSK CLI
00112  C0AC  A9 7E              LDA #$7E
00113  C0AE  8D 0D DC           STA $DC0D
00114  C0B1  A9 7F              LDA #$7F
00115  C0B3  8D 0D DD           STA $DD0D
00116  C0B6  60                 RTS
00117  C0B7  A9 FF       MSKINT LDA #$FF
00118  C0B9  8D 0D DC           STA $DC0D
00119  C0BC  8D 0D DD           STA $DD0D
00120  C0BF  60                 RTS
00121  C0C0  A9 00       SETU1  LDA #0
00122  C0C2  8D 07 DC           STA $DC07
00123  C0C5  AD F1 C2           LDA U1BLO
00124  C0C8  8D 06 DC           STA $DC06
00125  C0CB  60                 RTS
00126  C0CC  A9 7F       SETU2  LDA #127
00127  C0CE  8D 07 DD           STA $DD07
00128  C0D1  A9 FF              LDA #255
00129  C0D3  8D 06 DD           STA $DD06
00130  C0D6  A9 00              LDA #0
00131  C0D8  8D 05 DD           STA $DD05
00132  C0DB  AD F2 C2           LDA U2ALO
00133  C0DE  8D 04 DD           STA $DD04
00134  C0E1  60                 RTS
00135  C0E2  A9 54       STPCLK LDA #$54
00136  C0E4  8D 0F DC           STA $DC0F
00137  C0E7  8D 0F DD           STA $DD0F
```

```
MAIN ROUTINE......PAGE 0004

LINE# LOC    CODE         LINE


00138  C0EA   A9 54             LDA #$54
00139  C0EC   8D 0E DC          STA $DC0E
00140  C0EF   8D 0E DD          STA $DD0E
00141  C0F2   60                RTS
00142  C0F3   AD 0D DC   STRCLK LDA $DC0D
00143  C0F6   A9 55             LDA #$55
00144  C0F8   8D 0F DC          STA $DC0F
00145  C0FB   8D 0E DC          STA $DC0E
00146  C0FE   60                RTS
00147  C0FF   A0 00      SAVINF LDY #0
00148  C101   91 FB             STA (ARPTR),Y
00149  C103   8A                TXA
00150  C104   C8                INY
00151  C105   91 FB             STA (ARPTR),Y
00152  C107   A5 FB             LDA ARPTR
00153  C109   18                CLC
00154  C10A   69 02             ADC #2
00155  C10C   85 FB             STA ARPTR
00156  C10E   A5 FC             LDA ARPTR+1
00157  C110   69 00             ADC #0
00158  C112   85 FC             STA ARPTR+1
00159  C114   60                RTS
00160  C115   A5 FB      MOVPTR LDA ARPTR
00161  C117   18                CLC
00162  C118   69 22             ADC #34
00163  C11A   85 FB             STA ARPTR
00164  C11C   A5 FC             LDA ARPTR+1
00165  C11E   69 00             ADC #0
00166  C120   85 FC             STA ARPTR+1
00167  C122   60                RTS
00168  C123   A6 FD      RSTLCH LDX SAVX
00169  C125   CA                DEX
00170  C126   8E 60 DE          STX LATCH
00171  C129   20 3C C1          JSR DELAY
00172  C12C   E8                INX
00173  C12D   8E 60 DE          STX LATCH
00174  C130   20 19 C0          JSR CNVRT
00175  C133   A0 22             LDY #34
00176  C135   91 FB             STA (ARPTR),Y
00177  C137   8A                TXA
00178  C138   C8                INY
00179  C139   91 FB             STA (ARPTR),Y
00180  C13B   60                RTS
00181  C13C   EA         DELAY  NOP
00182  C13D   EA                NOP
00183  C13E   EA                NOP
00184  C13F   EA                NOP
00185  C140   EA                NOP
00186  C141   EA                NOP
00187  C142   EA                NOP
00188  C143   EA                NOP
00189  C144   EA                NOP
00190  C145   60                RTS
```

```
R5000- GET REAL TIME......PAGE 0005

LINE# LOC    CODE         LINE


00192  C146  AD 07 DD    R5000  LDA $DD07
00193  C149  AE 06 DD           LDX $DD06
00194  C14C  20 FF C0           JSR SAVINF
00195  C14F  A9 80              LDA #$80
00196  C151  8D 02 DE           STA BD
00197  C154  A9 00              LDA #0
00198  C156  85 FD              STA SAVX
00199  C158  A9 00              LDA #0
00200  C15A  85 FE              STA SAVY
00201  C15C  20 70 C1           JSR GETPOT
00202  C15F  A9 90              LDA #$90
00203  C161  8D 02 DE           STA BD
00204  C164  A9 00              LDA #0
00205  C166  85 FD              STA SAVX
00206  C168  A9 10              LDA #$10
00207  C16A  85 FE              STA SAVY
00208  C16C  20 70 C1           JSR GETPOT
00209  C16F  60                 RTS
00210  C170  A6 FE       GETPOT LDX SAVY
00211  C172  8E 80 DE           STX SET
00212  C175  E8                 INX
00213  C176  E8                 INX
00214  C177  86 FE              STX SAVY
00215  C179  A6 FD              LDX SAVX
00216  C17B  8E 60 DE           STX LATCH
00217  C17E  20 3C C1           JSR DELAY
00218  C181  20 19 C0           JSR CNVRT
00219  C184  20 FF C0           JSR SAVINF
00220  C187  A6 FD              LDX SAVX
00221  C189  E8                 INX
00222  C18A  E8                 INX
00223  C18B  86 FD              STX SAVX
00224  C18D  E0 10              CPX #$10
00225  C18F  D0 DF              BNE GETPOT
00226  C191  60                 RTS
```

```
R6000- OPEN SWITCH &......PAGE 0006

LINE# LOC   CODE         LINE


00228  C192  AD 07 DD    R6000  LDA $DD07
00229  C195  AE 06 DD           LDX $DD06
00230  C198  20 FF C0           JSR SAVINF
00231  C19B  A9 80              LDA #$80
00232  C19D  8D 02 DE           STA BD
00233  C1A0  A9 00              LDA #0
00234  C1A2  85 FD              STA SAVX
00235  C1A4  A9 00              LDA #0
00236  C1A6  85 FE              STA SAVY
00237  C1A8  20 BC C1           JSR GETOFF
00238  C1AB  A9 90              LDA #$90
00239  C1AD  8D 02 DE           STA BD
00240  C1B0  A9 00              LDA #0
00241  C1B2  85 FD              STA SAVX
00242  C1B4  A9 10              LDA #$10
00243  C1B6  85 FE              STA SAVY
00244  C1B8  20 BC C1           JSR GETOFF
00245  C1BB  60                 RTS
00246  C1BC  A6 FE       GETOFF LDX SAVY
00247  C1BE  8E 80 DE           STX SET
00248  C1C1  E8                 INX
00249  C1C2  E8                 INX
00250  C1C3  86 FE              STX SAVY
00251  C1C5  A6 FD              LDX SAVX
00252  C1C7  8E 60 DE           STX LATCH
00253  C1CA  20 3C C1           JSR DELAY
00254  C1CD  E8                 INX
00255  C1CE  86 FD              STX SAVX
00256  C1D0  8E 60 DE           STX LATCH
00257  C1D3  20 19 C0           JSR CNVRT
00258  C1D6  20 FF C0           JSR SAVINF
00259  C1D9  A6 FD              LDX SAVX
00260  C1DB  E8                 INX
00261  C1DC  86 FD              STX SAVX
00262  C1DE  E0 10              CPX #$10
00263  C1E0  D0 DA              BNE GETOFF
00264  C1E2  60                 RTS
```

```
R7000- CHECK DATA IF......PAGE 0007

LINE# LOC   CODE        LINE


00266  C1E3  A9 80       R7000  LDA #$80
00267  C1E5  8D 02 DE           STA BD
00268  C1E8  A9 01              LDA #1
00269  C1EA  85 FD              STA SAVX
00270  C1EC  A9 00              LDA #0
00271  C1EE  85 FE              STA SAVY
00272  C1F0  20 0B C2           JSR CMPVAL
00273  C1F3  AD F0 C2           LDA FLAG
00274  C1F6  C9 01              CMP #1
00275  C1F8  F0 10              BEQ RT7000
00276  C1FA  A9 90              LDA #$90
00277  C1FC  8D 02 DE           STA BD
00278  C1FF  A9 01              LDA #$01
00279  C201  85 FD              STA SAVX
00280  C203  A9 10              LDA #$10
00281  C205  85 FE              STA SAVY
00282  C207  20 0B C2           JSR CMPVAL
00283  C20A  60          RT7000 RTS
00284  C20B  A6 FE       CMPVAL LDX SAVY
00285  C20D  8E 80 DE           STX SET
00286  C210  E8                 INX
00287  C211  E8                 INX
00288  C212  86 FE              STX SAVY
00289  C214  A6 FD              LDX SAVX
00290  C216  8E 60 DE           STX LATCH
00291  C219  20 19 C0           JSR CNVRT
00292  C21C  C9 0F       CHKHI  CMP #$0F
00293  C21E  F0 10              BEQ SETFLG
00294  C220  C9 00       CHKLO  CMP #$00
00295  C222  F0 0C              BEQ SETFLG
00296  C224  A6 FD              LDX SAVX
00297  C226  E8                 INX
00298  C227  E8                 INX
00299  C228  86 FD              STX SAVX
00300  C22A  E0 11              CPX #$11
00301  C22C  D0 DD              BNE CMPVAL
00302  C22E  F0 05              BEQ RTCMPV
00303  C230  A9 01       SETFLG LDA #1
00304  C232  8D F0 C2           STA FLAG
00305  C235  60          RTCMPV RTS
```

```
R9000- GET TIME & EN......PAGE 0008

LINE# LOC    CODE         LINE


00307  C236   AD 07 DD     R9000  LDA $DD07
00308  C239   AE 06 DD            LDX  $DD06
00309  C23C   20 FF C0            JSR SAVINF
00310  C23F   A9 80               LDA #$80
00311  C241   8D 02 DE            STA BD
00312  C244   A9 01               LDA #1
00313  C246   85 FD               STA SAVX
00314  C248   A9 00               LDA #0
00315  C24A   85 FE               STA SAVY
00316  C24C   20 60 C2            JSR SAVVAL
00317  C24F   A9 90               LDA #$90
00318  C251   8D 02 DE            STA BD
00319  C254   A9 01               LDA #$01
00320  C256   85 FD               STA SAVX
00321  C258   A9 10               LDA #$10
00322  C25A   85 FE               STA SAVY
00323  C25C   20 60 C2            JSR SAVVAL
00324  C25F   60                  RTS
00325  C260   A6 FE        SAVVAL LDX SAVY
00326  C262   8E 80 DE            STX SET
00327  C265   E8                  INX
00328  C266   E8                  INX
00329  C267   86 FE               STX SAVY
00330  C269   A6 FD               LDX SAVX
00331  C26B   8E 60 DE            STX LATCH
00332  C26E   20 19 C0            JSR CNVRT
00333  C271   A0 00               LDY #0
00334  C273   91 FB               STA (ARPTR),Y
00335  C275   8A                  TXA
00336  C276   C8                  INY
00337  C277   91 FB               STA (ARPTR),Y
00338  C279   20 23 C1            JSR RSTLCH
00339  C27C   A5 FB               LDA ARPTR
00340  C27E   18                  CLC
00341  C27F   69 02               ADC #2
00342  C281   85 FB               STA ARPTR
00343  C283   A5 FC               LDA ARPTR+1
00344  C285   69 00               ADC #0
00345  C287   85 FC               STA ARPTR+1
00346  C289   A6 FD               LDX SAVX
00347  C28B   E8                  INX
00348  C28C   E8                  INX
00349  C28D   86 FD               STX SAVX
00350  C28F   E0 11               CPX #$11
00351  C291   D0 CD               BNE SAVVAL
00352  C293   60                  RTS
00353  C294                .END

ERRORS = 00000
```

APPENDIX E

SOFTWARE
"NORMALIZE

The program "NORMALIZE", shown at the end of this section, is used to obtain the normalization factors of all CFAEs in the ME cell. The flow chart of this software is shown in Figure 28.

The program first transfers the coulometric data, which has been saved on the floppy disk for the normalization factors of CFAEs, back to the RAM of the C-64. Then the first set of digital values are converted into the potentials which represent the applied potentials on each CFAEs. The rest of data are converted into the amperometric data. After screening all amperometric data, a band of data at each CFAE obtained prior to the injection of the sample solution is chosen to represent the residual current generated by the supporting electrolyte solution. Also, a band of highest data is chosen to represent the current which is generated by the sample solution. The representative sample solution currents and the residual currents within the resolution time period at each CFAE are obtained through the average of these two band of data, respectively. The net current on each electrode, which is generated by the sample species only, is obtained by subtracting the residual current from the current generated by the sample solution. Then one averaged net current of a CFAE is chosen. All net current values are divided by this chosen value to get the normalization factors for all 16 CFAEs in the ME cell. Finally, these factors are saved onto

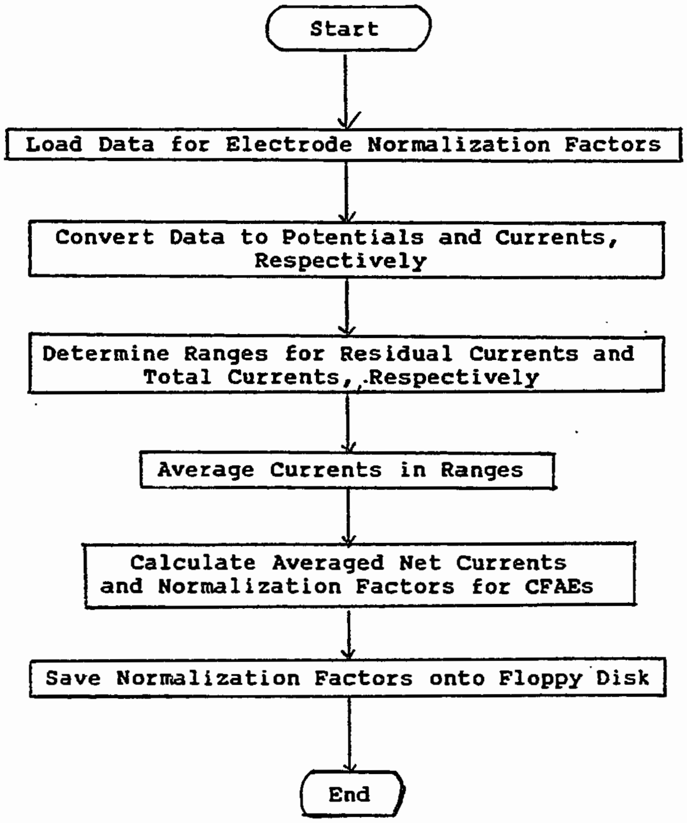


Figure 28. Flow chart of software "NORMALIZE".

a disk for normalization of the data for pseudo-voltammetry.

```
10 REM *******************************
11 REM *         2/12/1989           *
20 REM *         'NORMALIZE'         *
21 REM *                             *
30 REM * USE CALC. CAPACITANCE TO    *
31 REM *   NORM. ELECTRODE AREA BY   *
32 REM *   PEAK AREA OR HEIGHT.      *
40 REM * THEN, NORM. AREA IS SAVED   *
41 REM *   IN A FILE (N-A/H-*)       *
50 REM *******************************
60 REM DA$= DATE OF RUNNING EXPERIMENT
62 REM LB$= SAMPLE LABEL (SPECIES & CONC.)
64 REM FR$= FLOW RATE (PUMP SCALE)
66 REM IV = INITIAL VOLTAGE ON DAC 7548 #1
68 REM FV = FINAL VOLTAGE ON DAC 7548 #2
70 REM TR = TIME RESOLUTION(TR SEC)
71 REM U1 = U1BLO
72 REM U2 = U2ALO
73 REM TT = ACTUAL TOTAL COVERED TIME
74 REM NT = TOTAL DATA SET # SAVED FROM EXPT.
75 REM RM$= EXPT. REMARK
76 REM NR = RESIDUAL CURRENT SET'S #
78 REM NS = SAMPLE CURRENT SET'S #
80 REM RS(M,N)=RESULTS FROM CALCULATION
82 REM RS(0,N)=INTEGRATION TIME
84 REM RS(M,0)=REAL APPLIED VOLTAGE ON EVERY ELECTRODE
86 REM RC(M)=AVE. RESIDUAL CURRENT
88 REM SC(M,SS)=PEAK AREA/HEIGHT FOR SAMP.CURRENT
90 REM TP(N)=TIME AT WHICH DATA COLLECTED
92 REM NA(M) =NORM.AREA OF ELECTRODE M
94 REM CA(M)=CAPACITANCE OF ELECTRODE M
100 DIM RS(16,200),RC(16),SC(16,6),NA(16),TP(200)
120 DIM MN(16),SD(16),RD(16),R(16),CA(16),SF(16),SL(16)
140 ID$="'NONE'":REM DATA FILE ID
160 PRINT
200 PRINT"** MAKE SURE (1) LINE 10720 CORRECT,"
220 PRINT"   (2) RIGHT DISK IN DRIVE,"
240 PRINT"   & (3) BEEP IS HEARD !"
260 PRINT
280 GOSUB 14000:REM BEEP
300 SS=0:REM SET # FOR REPEATABILITY
400 SS=SS+1
500 INPUT"KNOW AREA DATA FILE ID(Y/N)";DM$
520 PRINT
540 IF DM$<>"N" THEN 700
560 PRINT"****************************"
580 PRINT"* TYPE '@$' & LOOK FILE    *"
600 PRINT"*   NAME STARTS WITH 'A-'  *"
620 PRINT"* THEN TYPE 'CONT'         *"
640 PRINT"****************************"
660 PRINT
680 STOP
700 PRINT"***************************"
720 PRINT"* FOR AREA DATA FILE ID,  *"
740 PRINT"*    IT STARTS WITH 'A-'  *"
760 PRINT"***************************"
780 PRINT
800 PRINT"PREVIOUS AREA DATA FILE ID : ";ID$
820 INPUT"NEW AREA DATA FILE ID(A-*)";ID$
```

```
840 INPUT"IS FILE NAME OK(Y/N)";DM$
860 PRINT
880 IF DM$<>"Y" THEN 500
900 PRINT"** IF DRIVE LIGHT BLINKS,"
910 PRINT"   STOP PROGRAM IMMEDIATELY.  THEN"
920 PRINT"   TYPE 'CLOSE 2', FOLLOWED BY TYPING"
930 PRINT"   'GOTO 500' !!"
940 PRINT
950 PRINT"   WAIT (ABOUT 5 MINUTES)"
960 PRINT"   TO LOAD & TREAT DATA !!  "
980 PRINT
1000 REM GET DATA FROM A FILE TO NORMALIZE ELECTRODE AREA
1020 OPEN 2,8,2,ID$+",S,R"
1040 INPUT#2,DA$
1060 INPUT#2,LB$
1080 INPUT#2,FR$
1100 INPUT#2,UL:REM UPPER LIMIT OF S.W.
1120 INPUT#2,LL:REM LOWER LIMIT OF S.W.
1140 INPUT#2,HZ:REM FREQ. OF S.W.
1160 INPUT#2,DU:REM DUATION OF S.W.
1180 INPUT#2,TD:REM TIME OF DELAY
1200 INPUT#2,IV
1220 INPUT#2,FV
1230 INPUT#2,U1
1240 INPUT#2,TR
1260 INPUT#2,U2
1280 INPUT#2,TT
1300 INPUT#2,NT
1310 INPUT#2,RM$
1320 IF IV=FV THEN 1500
1340 CLOSE 2
1360 PRINT"***********************************"
1380 PRINT"* PROGRAM IS TO NORMALIZE AREA    *"
1400 PRINT"*  LOAD WRONG DATA FILE           *"
1420 PRINT"***********************************"
1440 PRINT
1460 STOP
1500 REM TREAT DATA BEFORE PUT INTO A MATRIX
1520 CY=1.023E6:REM CY=FREQUENCY OF TIMER
1540 GOSUB 13000:REM LOAD CAPACITANCE FOR EACH INTEGRATOR
1560 REM ORIGINAL U2 SET-UP FOR 1 CYCLE
1580 INPUT#2,TM%
1600 RS(0,0)=TM%*U2/CY
1620 REM CALC. REAL APPLIED POTENTIAL
1640 FOR M=1 TO 16
1660 INPUT#2,TM%
1680 RS(M,0)=(TM%-2049)/204.5
1700 NEXT M
1720 TP(0)=0
1740 FOR N=1 TO NT
1760 INPUT#2,TM%
1780 RS(0,N)=TM%*U2/CY:REM INTEGRATION TIME
1800 TP(N)=RS(0,N)+TP(N-1):REM TIME SCALE
1820 FOR M=1 TO 16
1840 INPUT#2,TM%
1860 RS(M,N)=TM%/204.5*CA(M)/RS(0,N)
1880 NEXT M
1900 NEXT N
1920 CLOSE 2
1940 GOSUB 14000:REM BEEP
2000 GOSUB 9900:REM CHANGE REMARK
2020 REM SHOW ALL PARAMETERS ON SCREEN
2030 PRINT"** PUSH 'G' TO GO ON,"
2040 PRINT"   THEN HOLD 'CTRL' KEY TO VIEW"
2050 PRINT
2060 GET A$:IF A$<>"G" THEN 2060
```

```
2070 GOSUB 9700:REM SHOW SAMPLE ID
2080 GOSUB 9000:REM SHOW EXPT. CONDITIONS
2100 INPUT"ARE ALL ABOVE CORRECT(Y/N)";DM$
2120 PRINT
2140 IF DM$="Y" THEN 2200
2160 PRINT"** MAKE CORRECTION THEN TYPE 'CONT' !!":STOP
2180 PRINT:GOTO 2000:REM RECHECK INFORMATION
2200 REM CHECK APPLIED VOLTAGE ON ELECTRODE
2220 PRINT
2240 PRINT"ELECTRODE","VOLT.APPLIED"
2260 PRINT
2280 FOR M=1 TO 16
2300 PRINT "    # ";M,RS(M,0)
2320 NEXT M
2340 PRINT
2400 RF=0:RL=0
2420 FOR M=1 TO 16
2440 SF(M)=0:SL(M)=0
2460 NEXT M
2500 REM CHOOSE RANGES FOR RESI:CURRENT & SAMP.CURRENT SETS
2520 BN=2:ED=21:REM START FROM SET 3 TO SET 23
2600 PRINT"** ENTER ELECTRODE #'S TO CHECK !!"
2620 PRINT"    (END OF CHECK IF 1ST INPUT <=0)"
2640 PRINT
2660 INPUT"    1ST & 2ND ELECTRODE(<=16)";X1,X2
2680 INPUT"    ARE BOTH OK(Y/N)";DM$
2700 PRINT
2720 IF DM$<>"Y" THEN 2600
2740 IF X1<=0 THEN 3500
2800 PRINT"** PUSH 'G' TO GO ON.  THEN".
2820 PRINT"    DETERMINE THE WAY & FIND RANGES"
2840 PRINT"    TO NORMALIZE ELECTRODE SURFACE AREA"
2860 PRINT
2900 GET A$:IF A$<>"G" THEN 2900
2920 GOSUB 8800:REM FIND RANGE
3000 PRINT" 1ST ELECTRODE CHECKED :";X1
3020 PRINT" 2ND ELECTRODE CHECKED :";X2
3040 PRINT" INITIAL SET TO CHECK :";BN
3060 PRINT" END SET TO CHECK :";ED
3080 PRINT
3100 INPUT" IS CHECK RANGE OK(Y/N)";DM$
3120 PRINT
3140 IF DM$="Y" THEN 2600
3200 PRINT"** INPUT INITIAL & END SET TO CHECK"
3210 PRINT"    END SET MUST BE SAMLLER THAN";NT
3220 PRINT
3240 INPUT"    INITIAL SET & END SET ";BN,ED
3260 INPUT"    ARE BOTH OK(Y/N)";DM$
3280 PRINT
3300 IF DM$<>"Y" THEN 3200
3400 IF ED<=NT THEN 2600
3420 PRINT" ** END SET TO CHECK IS OVER RANGE **"
3440 PRINT
3460 GOTO 3200
3500 INPUT"INPUT RANGE FOR RESI.CURRENT";RF,RL
3510 INPUT"ARE BOTH OK(Y/N)";DM$
3520 PRINT
3540 IF DM$<>"Y" THEN 2600
3550 GOSUB 12000:REM CHECK RANGES SETUP
3560 INPUT"ARE ALL OK(Y/N)";DM$
3570 PRINT
3580 IF DM$<>"Y" THEN 2600
3600 INPUT"PRINT OUT DATA TO PLOT(Y/N)";DM$
3620 PRINT
3640 IF DM$="N" THEN 3800
3660 INPUT"HAVE PARAMETERS PRINTED OUT(Y/N)";DM$
```

```
3680 PRINT
3700 IF DM$="Y" THEN 3790
3720 OPEN4,4:CMD4
3740 GOSUB 9000
3750 PRINT CHR$(12):REM TOP OF THE NEXT PAGE
3760 PRINT#4
3780 CLOSE4
3790 GOSUB 16000
3800 INPUT"GOT ALL RANGES(Y/N)";DM$
3820 PRINT
3840 IF DM$="Y" THEN 4000
3860 INPUT"CHECK THE SAME SET AGAIN(Y/N)";DM$
3880 PRINT
3900 IF DM$<>"N" THEN 2600
3920 INPUT"LOAD ANOTHER DATA SET(Y/N)";DM$
3940 PRINT
3960 IF DM$="Y" THEN 500
3980 STOP
4000 REM GET RESI.CURRENT & TOTL.SAMP.CURRENT
4010 PRINT"WHICH WAY TO NORM. ELECTRODE AREA ?"
4020 INPUT" (1)BY PEAK AREA; (2)BY PEAK HEIGHT";OP
4030 INPUT" IS IT OK(Y/N)";DM$
4040 PRINT
4050 IF DM$<>"Y" THEN 4010
4060 IF OP=1 THEN GOSUB 15000
4070 IF OP=1 THEN 4100
4080 IF OP=2 THEN GOSUB 15500
4100 REM SHOW AVERAGED CURRENTS ON SCREEN
4140 PRINT"ELECTRODE  RESI.CURRENT*  NET SAMP.CURRENT"
4160 PRINT
4180 FOR M=1 TO 16
4200 PRINT " # ";M;RC(M);SC(M,SS)
4220 NEXT M
4240 PRINT
4300 INPUT"PRINT OUT RESULTS(Y/N)";DM$
4320 PRINT
4340 IF DM$="N" THEN 5000
4360 GOSUB 8400:REM SURE PRINTER ONLINE
4400 INPUT"HAVE PARAMETERS PRINTED OUT(Y/N)";DM$
4420 PRINT
4440 IF DM$="Y" THEN 4600
4460 OPEN4,4:CMD4
4480 GOSUB 9000:REM PARAMETERS
4500 PRINT CHR$(12):REM TOP OF THE NEXT PAGE
4520 PRINT#4
4540 CLOSE4
4600 GOSUB 9900:REM CHANGE REMARK
4700 OPEN4,4:CMD4
4720 GOSUB 9700:REM SHOW SAMPLE ID & REMARK
4740 GOSUB 17000:REM RESULTS OF CURRRENTS
4760 PRINT CHR$(12):REM GET TO THE TOP OF THE NEXT PAGE
4780 PRINT#4:CLOSE 4
4800 INPUT"IS PRINTOUT OK(Y/N)";DM$
4820 PRINT
4840 IF DM$<>"Y" THEN 4300
5000 INPUT"ARE RESULTS OK(Y/N)";DM$
5020 PRINT
5040 IF DM$="Y" THEN 5400
5100 INPUT"CHECK THE SAME SET AGAIN(Y/N)";DM$
5120 PRINT
5140 IF DM$<>"N" THEN 3000
5200 INPUT"LOAD ANOTHER SET DATA(Y/N)";DM$
5220 PRINT
5240 IF DM$="Y" THEN 500
5260 PRINT"WHAT DO YOU WANT ?":STOP
5280 PRINT
```

```
5300 GOTO 5000
5400 INPUT"RESULTS FOR STATISTICS(Y/N)";DM$
5420 PRINT
5440 IF DM$="Y" THEN 5500
5460 GOTO 5100
5500 PRINT"PRESENT DATA FILE ID : ";ID$
5520 PRINT"PRESENT SET # FOR REPEATABILITY : ";SS
5540 PRINT
5600 INPUT"DONE REPEATABILITY CALC.(Y/N)";DM$
5620 PRINT
5640 IF DM$="Y" THEN 5800
5660 INPUT"MORE? ARE YOU SURE(Y/N)";DM$
5680 PRINT
5700 IF DM$="Y" THEN 400
5720 STOP
5740 GOTO 5600
5800 INPUT"DONE? ARE YOU SURE(Y/N)";DM$
5820 PRINT
5840 IF DM$="N" THEN 5720
5900 PRINT"-- APPLY STATISTICS TO THE RESULTS NOW!"
5920 PRINT
5940 I=SS:REM TOTAL SET FOR REPEATABILITY IS 'SS'
5960 GOSUB 10000
6000 REM CALCULATE NORM.AREA FROM A SINGLE SET OF DATA
6100 PRINT"** NORMALIZE ELECTRODE SURFACE AREA !"
6120 PRINT"   #";ES;"ELECTRODE AS STANDARD"
6140 INPUT"   IS IT OK(Y/N)";DM$
6160 PRINT
6180 IF DM$="Y" THEN 6300
6200 INPUT"   NEW STANDARD ELECTRODE(2)";ES
6220 PRINT
6240 GOTO 6100
6300 BA=MN(ES):REM TAKE ES ELECTRODE AS STANDARD
6320 FOR M=1 TO 16
6340 NA(M)=MN(M)/BA
6360 NEXT M
6380 GOSUB 7500:REM SHOW NORM.AREA
6400 INPUT"PRINT OUT THE NORM.AREA(Y/N)";DM$
6410 PRINT
6420 IF DM$="N" THEN 6500
6430 GOSUB 9900:REM CHANGE REMARK
6440 OPEN4,4:CMD4
6450 GOSUB 18000:REM SHOW SAMPLE, EXPT. DATE, & REMARK
6460 GOSUB 7500:GOSUB 7700
6480 PRINT CHR$(12):REM TOP OF THE NEXT PAGE
6490 PRINT#4:CLOSE4
6500 INPUT"SAVE NORM. AREA ON DISK(Y/N)";DM$
6520 PRINT
6540 IF DM$="N" THEN 7000
6560 PRINT"** MAKE SURE RIGHT DISK IN DRIVE !!"
6580 PRINT
6600 INPUT"   WANT TO CHECK DISK(Y/N)";DM$
6620 PRINT
6640 IF DM$="N" THEN 6700
6660 STOP
6680 GOTO 6500
6700 REM SAVE ELECTRODE SURFACE AREA TO A SEQ. FILE
6720 REM N-A-* (N-H-*) = NORM. ELECTRODE SURFACE AREA
6740 PRINT
6760 PRINT"LATEST DATA FILE ID : ";ID$
6800 INPUT"NORM.AREA ID(N-A/H-*)";NI$
6820 INPUT"IS FILE NAME OK(Y/N)";DM$
6840 PRINT
6860 IF DM$="N" THEN 6800
6900 OPEN 2,8,2,NI$+",S,W"
6920 FOR M=0 TO 16
```

```
6940 PRINT#2,NA(M)
6960 NEXT M
6980 CLOSE2
7000 INPUT"CHECK SAME SET AGAIN(Y/N)";DM$
7020 PRINT
7040 IF DM$="Y" THEN 3000
7100 INPUT"ADD ONE MORE SET FOR STAT.(Y/N)";DM$
7120 PRINT
7140 IF DM$="Y" THEN 400
7200 INPUT"REDO STATISTICS W/O LAST SET(Y/N)";DM$
7220 PRINT
7240 IF DM$<>"Y" THEN 7300
7260 SS=SS-1
7280 GOTO 5600
7300 INPUT"START OVER AGAIN(Y/N)";DM$
7320 PRINT
7340 IF DM$="Y" THEN 300
7360 PRINT"WHAT DO YOU WANT ?":PRINT:STOP
7380 GOTO 7000
7400 END
7500 REM SHOW APPLIED VOLTAGE & NORMALIZED AREA
7520 PRINT"ELECTRODE","POTENTIAL   NORM.AREA"
7540 PRINT
7560 FOR M=1 TO 16
7580 PRINT"  # ";M,RS(M,0);NA(M)
7600 NEXT M
7620 PRINT
7640 PRINT
7660 RETURN
7700 REM MESSAGE TO SHOW THE METHOD
7720 IF OP=1 THEN PRINT"  **  RESULTS ARE BASED ON PEAK AREA !"
7740 IF OP=2 THEN PRINT"  **  RESULTS ARE BASED ON PEAK HEIGHT !"
7760 PRINT
7780 PRINT
7800 RETURN
8000 REM CHECK EACH SET DATA FOR ALL ELECTRODE
8020 PRINT"** END OF CHECK IF NN < 0 !"
8040 INPUT" NEW DATA SET # TO CHECK(NN)";NN
8080 PRINT
8100 IF NN<0 THEN 8360
8200 PRINT" M      DATA(NN)          DATA(NN+1)"
8220 FOR M=0 TO 16
8240 PRINT M;RS(M,NN);RS(M,NN+1)
8260 NEXT M
8280 PRINT
8300 PRINT" DATA SET # : ";NN
8320 PRINT
8340 GOTO 8020
8360 RETURN
8400 REM CHECK WHETHER PRINTER IS READY
8420 PRINT"** MAKE SURE PRINTER ONLINE"
8440 PRINT"   THEN PUSH 'G' TO GO ON !"
8460 PRINT
8470 GET A$:IF A$<>"G" THEN 8470
8480 RETURN
8500 REM SHOW A SINGLE SET DATA
8520 PRINT
8540 PRINT N;"TH SET DATA OF SAMPLE"
8560 PRINT"  DATA COLLECTED AT";RS(0,N);"SEC"
8580 PRINT"  INTEGRATION TIME IS";TP(N);"SEC"
8600 PRINT
8620 PRINT"ELECTRODE","TOTL.SAMP.CURRENT"
8640 PRINT
8660 FOR M=1 TO 16
8680 PRINT"  # ";M,RS(M,N)
8700 NEXT M
```

```
8720 PRINT
8740 RETURN
8800 REM SUBROUTINE TO SEE ALL DATA ON TWO ELECTRODES
8820 PRINT"SET";" ELECTRODE";X1;"    ELECTRODE";X2
8840 FOR N=BN TO ED
8860 PRINT N;RS(X1,N);RS(X2,N)
8880 NEXT N
8900 PRINT
8920 GOSUB 13500:REM RECORD RANGE
8940 RETURN
9000 REM SHOW ALL PARAMETERS ON SCREEN
9020 PRINT"EXPERIMENTAL CONDITIONS --"
9040 PRINT
9060 PRINT" FLOW RATE -- ";FR$
9080 PRINT
9100 PRINT" SQUARE WAVE FOR PRECONDITION --"
9120 PRINT"  POTENTIAL OF UPPER LIMIT :";UL;"VOLT"
9140 PRINT"  POTENTIAL OF LOWER LIMIT :";LL;"VOLT"
9160 PRINT"  FREQUENCY :";HZ;"HERTZ"
9180 PRINT"  DURATION :";DU;"SEC"
9200 PRINT
9220 PRINT IV;"VOLTS OUTPUT FROM DAC7548 #1"
9240 PRINT FV;"VOLTS OUTPUT FROM DAC7548 #2"
9260 PRINT
9280 PRINT" WAIT";TD;"SEC TO SUBSIDE CHARGING CURRENT DOWN !"
9300 PRINT
9320 PRINT" U2ALO IS";U2
9340 PRINT" TOTAL COVERED TIME IS";TT;"SEC"
9360 PRINT" U1 TIMER SETUP AS":U1;"* (1/60) SEC"
9380 PRINT" TIME OF RESOLUTION IS ABOUT";TR;"SEC"
9400 PRINT NT;"SETS OF DATA COLLECTED"
9420 PRINT
9440 PRINT" REFERENCE ELECTRODES : ZINC IN 1 M SODIUM ACETATE SOLUTION."
9460 PRINT" WORKING ELECTRODES : CARBON FIBER ARRAY ELECTRODE"
9480 PRINT
9500 PRINT
9520 PRINT" ** REMARK : ";RM$
9540 PRINT
9600 RETURN
9700 REM SHOW SAMPLE ID
9720 PRINT"SAMPLE -- ";LB$
9740 PRINT" AREA DATA FILE ID : ";ID$
9760 PRINT" DATE OF EXPERIMENT : ";DA$
9780 PRINT
9800 PRINT" ** REMARK : ";RM$
9820 PRINT
9840 PRINT
9860 RETURN
9900 REM CHANGE REMARK
9910 PRINT"PREVIOUS REMARK : ";RM$
9920 INPUT"IS IT OK(Y/N)";DM$
9930 PRINT
9940 IF DM$="Y" THEN 9990
9960 INPUT"NEW REMARK";RM$
9970 PRINT
9980 GOTO 9910
9990 RETURN
10000 REM STATISTICS FOR MEAN, STANDARD DEVIATION(SD), AND RELATIVE SD
10100 REM MEAN
10200 FOR M=1 TO 16
10240 D1=0
10260 FOR X=1 TO I
10280 D1=SC(M,X)+D1
10300 NEXT X
10340 MN(M)=D1/I
10500 REM SD & RELATIVE SD (RD)
```

```
10600 D2=0
10620 D3=0
10640 FOR X=1 TO I
10660 D2=SC(M,X)-MN(M)
10680 D3=D2*D2+D3
10700 NEXT X
10720 SD(M)=SQR(D3/(I-1)):REM SUBSTITUTE I-1 WITH I
10740 RD(M)=SD(M)/MN(M)*100
10760 NEXT M
10800 GOSUB 11500:REM SHOW RESULTS
11000 INPUT"PRINT OUT STATISTIC RESULTS(Y/N)";DM$
11020 PRINT
11040 IF DM$="N" THEN 11300
11060 GOSUB 9900:REM CHANGE REMARK
11100 OPEN4,4:CMD4
11200 GOSUB 18000:REM SAMPLE, EXPT. DATE, & REMARK
11220 GOSUB 11500:REM SHOW RESULTS
11240 GOSUB 7700:REM SHOW METHOD
11260 PRINT CHR$(12)
11280 PRINT#4:CLOSE4
11300 RETURN
11500 REM SHOW STATISTIC RESULT
11600 PRINT"ELECTRODE","     CURRENTS FOR AREA NORMALIZATION"
11620 PRINT"          "," MEAN         STD DEV       REL STD DEV(%)"
11640 PRINT
11700 FOR M=1 TO 16
11720 PRINT" #";M,MN(M);"   ";SD(M);"   ";RD(M)
11740 NEXT M
11760 PRINT
11780 PRINT
11800 PRINT"  ** THE STATISTICS IS BASED ON";I;"DATA SETS"
11840 PRINT
11860 RETURN
12000 REM SUBROUTINE SHOWN ALL RANGES
12020 PRINT"ELECTRODE","RF RL SF SL"
12040 PRINT
12100 FOR M=1 TO 16
12120 PRINT" #";M,RF;RL;SF(M);SL(M)
12140 NEXT M
12160 PRINT
12180 PRINT"** WRITE DOWN WHICH ONES NOT RIGHT !"
12200 PRINT
12300 RETURN
13000 REM SUBROUTINE TO LOAD CAPACITANCE FOR EACH INTEGRATOR
13020 REM BASED ON THE RESULTS OBTAINED ON 10/31
13100 CA(1)=9.026E-10:CA(2)=8.618E-10
13120 CA(3)=8.941E-10:CA(4)=8.398E-10
13140 CA(5)=8.369E-10:CA(6)=8.985E-10
13160 CA(7)=8.932E-10:CA(8)=8.661E-10
13180 CA(9)=9.095E-10:CA(10)=8.982E-10
13200 CA(11)=8.954E-10:CA(12)=8.951E-10
13220 CA(13)=9.105E-10:CA(14)=8.888E-10
13240 CA(15)=8.190E-10:CA(16)=8.500E-10
13300 RETURN
13500 REM RECORD RANGE OF SAMPLE CURRENT MAXIMUN
13520 PRINT"** RANGES OF PEAK HEIGHT MAXIMUM"
13560 PRINT
13600 PRINT"   FOR ELECTRODE #";X1
13640 INPUT"   RANGE FOR SAMP.CURRENT";SF(X1),SL(X1)
13660 PRINT
13800 PRINT"   FOR ELECTRODE #";X2
13840 INPUT"   RANGE FOR SAMP.CURRENT";SF(X2),SL(X2)
13860 PRINT
13880 INPUT"   ARE ALL OK (Y/N))";DM$
13900 PRINT
13920 IF DM$<>"Y" THEN 13600
```

```
13940 RETURN
14000 REM GENERATE A BEEPER(REF. P.185)
14020 PRINT"   PUSH 'S' TO STOP BEEPING &"
14040 PRINT"   WATCH SCREEN FOR HINT !"
14060 PRINT
14100 GET A$:IF A$="S" THEN 14400
14200 S=54272
14220 FOR L=S TO S+24:POKE L,0:NEXT
14240 POKE S+5,9:POKE S+6,0
14260 POKE S+24,15
14280 HF=37:LF=162:DR=500
14300 POKE S+1,HF:POKE S,LF
14320 POKE S+4,33
14340 FOR T=1 TO DR:NEXT
14360 POKE S+4,32:FOR T=1 TO 50:NEXT
14380 GOTO 14100
14400 RETURN
15000 REM GET RESI.CURRENT & TOTL.SAMP.CURRENT BY PEAK AREA
15020 PRINT"-- HANG ON, CALC. PEAK AREA !"
15040 PRINT
15100 REM CALC. AVERAGE RESI.CURRENT
15110 FOR M=1 TO 16
15120 RC(M)=0
15130 FOR N=RF TO RL
15140 RC(M)=RC(M)+RS(M,N)
15150 NEXT N
15160 RC(M)=RC(M)/(RL-RF+1)
15170 NEXT M
15200 REM CALC. NET SAMPLE CURRENT PEAK AREA
15220 PRINT"THE FOLLOWING 'N' VALUE SHOULD"
15240 PRINT"  NOT BE GREATER THAN";NT+1
15260 PRINT
15300 FOR M=1 TO 16
15310 SC(M,SS)=0
15320 N=RL+1
15330 SC(M,SS)=(RS(M,N)-RC(M))*RS(0,N)+SC(M,SS)
15340 N=N+1
15350 IF N>NT THEN 15400
15360 IF N<=20 THEN 15330
15370 IF RS(M,N)>=RC(M) THEN 15330
15380 PRINT"  M =";M;"; N =";N
15400 NEXT M
15420 PRINT
15440 GOSUB 14000:REM BEEP
15460 RETURN
15500 REM GET RESI.CURRENT & TOTL.SAMP.CURRENT BY PEAK HEIGHT
15520 PRINT"-- HANG ON, CALC. PEAK HEIGHT !"
15540 PRINT
15600 REM CALC. AVERAGE RESI.CURRENT
15610 FOR M=1 TO 16
15620 RC(M)=0
15630 FOR N=RF TO RL
15640 RC(M)=RC(M)+RS(M,N)
15650 NEXT N
15660 RC(M)=RC(M)/(RL-RF+1)
15670 NEXT M
15700 REM CALC. NET SAMPLE CURRENT PEAK HEIGHT
15720 FOR M=1 TO 16
15740 SC(M,SS)=0
15760 FOR N=SF(M) TO SL(M)
15780 SC(M,SS)=SC(M,SS)+RS(M,N)
15800 NEXT N
15820 SC(M,SS)=SC(M,SS)/(SL(M)-SF(M)+1)
15840 SC(M,SS)=SC(M,SS)-RC(M)
15860 NEXT M
15900 GOSUB 14000:REM BEEP
```

```
15920 RETURN
16000 REM PRINT OUT DATA FOR PLOTTING
16020 PRINT"** INPUT THE RANGE OF DATA TO PRINT"
16040 PRINT"   END OF PRINT IF 1ST<0 !"
16060 PRINT
16100 INPUT"   1ST SET, LAST SET";BN,ED
16120 INPUT"   ARE BOTH OK(Y/N)";DM$
16140 PRINT
16160 IF DM$<>"Y" THEN 16100
16180 IF BN<0 THEN 17000
16200 REM PRINT OUT THE TIME AT WHICH DATA WERE COLLECTED
16220 OPEN 4,4:CMD 4
16240 PRINT"AREA DATA FILE ID : ";ID$
16260 PRINT
16280 PRINT
16300 PRINT"SET","TIME(DATA COLLECTED)"
16320 PRINT
16340 FOR N=BN TO ED
16360 PRINT N,RS(0,N)
16380 NEXT N
16400 PRINT CHR$(12):REM GET TO THE TOP OF NEXT PAGE
16420 PRINT#4
16440 CLOSE4
16500 PRINT"** END OF PRINT IF FT<0 !!"
16540 PRINT"   CHOOSE 4 ELECTRODES TO PRINT DATA !"
16560 INPUT"   1ST,2ND,3RD,4TH ELECTRODE";FT,SD,TD,FH
16620 INPUT"ARE ALL ABOVE OK(Y/N)";DM$
16640 PRINT
16660 IF DM$<>"Y" THEN 16500
16680 IF FT<0 THEN 17000
16700 OPEN 4,4:CMD 4
16720 PRINT"SET","                  ELECTRODE"
16740 PRINT" # ";"      #";FT," LL POT. TO DIGITAL
16620 DM%=INT(LL*4095/6.013+2042)
16640 RH%=INT(DM%/256)
16660 RL%=INT(DM%-RH%*256)
16700 RETURN
17000 REM PRINT OUT AVE. RESIDUAL & NET SAMPLE CURRENT
17100 PRINT"ELECTRODE","             CURRENT*             SAMPLE RANGE"
17120 PRINT" ","             RESIDUE       NET SAMPLE      1ST   LAST"
17140 PRINT
17160 FOR M=1 TO 16
17180 PRINT"  # ";M,"  ";RC(M);SC(M,SS);"   ";SF(M);"   ";SL(M)
17200 NEXT M
17220 PRINT
17240 PRINT
17260 PRINT" * PRESENT AS AVERAGED RESULTS !!"
17280 PRINT
17300 PRINT"   FOR THE RANGE OF AVE. RESIDUAL CURRENTS"
17320 PRINT"    1ST SET IS";RF;"& LAST SET IS";RL
17400 RETURN
18000 REM SHOW SAMPLE, EXPT. DATE, & REMARK
18100 PRINT"SAMPLE -- ";LB$
18120 PRINT
18140 PRINT" DATE OF EXPERIMENT : ";DA$
18160 PRINT
18180 PRINT" ** REMARK : ";RM$
18200 PRINT
18220 PRINT
18300 RETURN
20000 REM PRINT OUT ORIGINAL DATA
20100 OPEN4,4:CMD4
20200 PRINT"  SAMPLE LABEL : ";LB$
20220 PRINT
20240 PRINT"  FLOW RATE : ";FR$
20260 PRINT
```

```
20280 PRINT"  INI. VOLT :";VI;" VOLT"
20300 PRINT"  FINAL VOLT :";VF;" VOLT"
20320 PRINT
20340 PRINT"  U1 VALUE :";U1
20360 PRINT"  LEAST U2 BYTE =";U2
20380 PRINT"  U2 CLOCK PERIOD(CP) =";CP;" SEC"
20400 PRINT"  SET-UP TOTAL COVERED TIME =";CT;"SEC"
20420 PRINT
20440 PRINT"  AFTER RECONDITIONING ELECTRODES,"
20450 PRINT"  ";TD;"SEC LATER, STARTED TO COLLECT DATA!"
20460 PRINT
20480 PRINT#4:CLOSE4
20500 PRINT"** Z MUST <=";N;" & = MULTIPLE OF 5"
20520 PRINT"   IF Z<0 THEN END OF PRINTING "
20540 INPUT"   NEW STARTING SET #";Z
20560 PRINT
20580 IF Z<0 THEN 21000
20600 OPEN4,4:CMD4
20700 PRINT
20720 PRINT" ** Z =";Z
20730 PRINT
20740 PRINT" M  DD%Z DD%Z+1 DD%Z+2 DD%Z+3 DD%Z+4"
20760 FOR M=0 TO 16
20780 PRINT M;DD%(M,Z);DD%(M,Z+1);DD%(M,Z+2);DD%(M,Z+3);DD%(M,Z+4)
20800 NEXT M
20820 PRINT
20840 PRINT#4:CLOSE4
20900 GOTO 20500
21000 RETURN
```

APPENDIX F

SOFTWARE
"RESULT"

The program "RESULT", shown at the end of this section, is used to get the normalized amperometric data for the construction of pseudo-voltammograms. The flow chart of this software is shown in Figure 29.

This program first loads the saved coulometric data for the construction of a pseudo-voltammogram from a disk to the RAM of the C-64 and the normalization factors of all 16 CFAEs. Then the applied potentials at each CFAE are obtained as described in the previous section. The coulometric data are normalized with normalization factors, then converted into the amperometric data by dividing by the integration time. The net currents at each CFAE, which are used to construct a pseudo-voltammogram, are obtained as described in the previous section too. Finally, all these normalized net currents for plotting a pseudo-voltammogram are printed out.

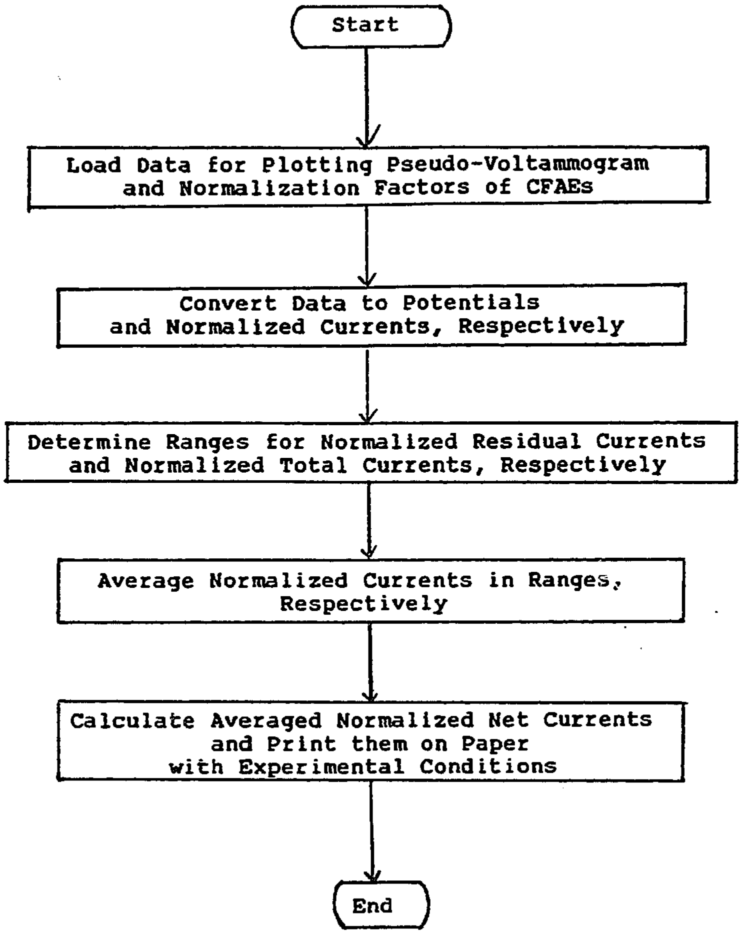


Figure 29. Flow chart of software "RESULT".

```
10 REM ********************************
11 REM *          2/13/1989           *
20 REM *           "RESULT"           *
21 REM *                              *
30 REM * USE CALC. CAPACITANCE &      *
31 REM *   NORM. ELECTRODE AREA TO    *
32 REM *   CALC. PEAK AREA/HEIGHT     *
40 REM *   OF NET SAMPLE CURRENT.     *
41 REM * STATISTICS IS INCLUDED.      *
50 REM ********************************
60 REM DA$= DATE OF RUNNING EXPERIMENT
62 REM LB$= SAMPLE LABEL (SPECIES & CONC.)
64 REM FR$= FLOW RATE (PUMP SCALE)
66 REM IV = INITIAL VOLTAGE ON DAC 7548 #1
68 REM FV = FINAL VOLTAGE ON DAC 7548 #2
70 REM TR = TIME RESOLUTION(TR SEC)
71 REM U1 = U1BLO
72 REM U2 = U2ALO
73 REM TT = ACTUAL TOTAL COVERED TIME
74 REM NT = TOTAL DATA SET # SAVED FROM EXPT.
75 REM RM$= EXPT. REMARK
76 REM NR = RESIDUAL CURRENT SET'S #
78 REM NS = SAMPLE CURRENT SET'S #
80 REM RS(M,N)=RESULTS FROM CALCULATION
81 REM RS(0,N)=INTEGRATION TIME
82 REM RS(M,0)=REAL APPLIED VOLTAGE ON EVERY ELECTRODE
83 REM RB(M)=AVE. RESI.CURRENT AT BEGIN
84 REM RE(M)=AVE. RESI.CURRENT AT END
86 REM RC(M,SS)=AVE. RESIDUAL CURRENT
88 REM SC(M,SS)=PEAK AREA FOR SAMP.CURRENT
89 REM SA(M,SS)=AVE. PEAK AREA OF SAMP.CURRENT
90 REM TP(N)=TIME AT WHICH DATA COLLECTED
92 REM NA(M,SS) =NORM.AREA OF ELECTRODE M FROM "SS" DATA SET
94 REM EA(M)=AVE. SURFACE AREA OF ELECTRODE M
96 REM CA(M)=CAPACITANCE OF ELECTRODE M
100 DIM RS(16,200),RC(16,6),SC(16,6),NA(16),TP(200)
110 DIM SD(16),RD(16),R(16),CA(16),SA(16)
120 DIM SF(16),SL(16)
140 ID$="'NONE'":REM DATA FILE ID
160 PRINT
200 PRINT"** MAKE SURE (1)LINE 10720 CORRECT,"
220 PRINT"   (2)RIGHT DISK IN DRIVE, &"
240 PRINT"   (3)BEEP IS HEARD !"
260 PRINT
280 GOSUB 14000:REM BEEP
300 SS=0:REM SET # FOR REPEATABILITY
320 GOSUB 12000:REM LOAD NORM.AREA
400 SS=SS+1
500 INPUT"KNOW SAMPLE DATA FILE ID(Y/N)";DM$
520 PRINT
540 IF DM$="Y" THEN 700
560 PRINT"*****************************"
580 PRINT"* TYPE '@$' & LOOK FILE     *"
600 PRINT"*   NAME STARTS WITH 'S-'   *"
620 PRINT"* THEN TYPE 'CONT'          *"
640 PRINT"*****************************"
660 PRINT
680 STOP
700 PRINT"*****************************"
```

```
720 PRINT"* FOR SAMPLE DATA FILE ID, *"
740 PRINT"*    IT STARTS WITH 'S-'    *"
760 PRINT"****************************"
780 PRINT
800 PRINT"PREVIOUS SAMPLE DATA FILE ID : ";ID$
820 INPUT"NEW SAMPLE DATA FILE ID(S-*)";ID$
840 INPUT"IS FILE NAME OK(Y/N)";DM$
860 PRINT
880 IF DM$<>"Y" THEN 500
900 PRINT"-- IF DRIVE LIGHT BLINKS,"
910 PRINT"   STOP PROGRAM IMMEDIATELY.  THEN"
920 PRINT"   TYPE 'CLOSE 2', FOLLOWED BY"
930 PRINT"   TYPING 'GOTO 500' !!"
940 PRINT
950 PRINT"   WAIT (ABOUT 5 MINUTES)"
960 PRINT"     TO LOAD & TREAT DATA !!"
980 PRINT
1000 REM GET SAMPLE DATA TO NORMALIZE
1020 OPEN 2,8,2,ID$+",S,R"
1040 INPUT#2,DA$
1060 INPUT#2,LB$
1080 INPUT#2,FR$
1100 INPUT#2,UL:REM UPPER LIMIT OF S.W.
1120 INPUT#2,LL:REM LOWER LIMIT OF S.W.
1140 INPUT#2,HZ:REM FREQ. OF S.W.
1160 INPUT#2,DU:REM DUATION OF S.W.
1180 INPUT#2,TD:REM TIME OF DELAY
1200 INPUT#2,IV
1220 INPUT#2,FV
1230 INPUT#2,U1
1240 INPUT#2,TR
1260 INPUT#2,U2
1280 INPUT#2,TT
1300 INPUT#2,NT
1310 INPUT#2,RM$
1320 IF IV<FV THEN 1500
1340 CLOSE 2
1400 PRINT"** PROGRAM TO NORMALIZE SAMPLE DATA"
1420 PRINT"   LOAD WRONG DATA FILE !!"
1440 PRINT
1460 STOP
1500 REM TREAT DATA BEFORE PUT INTO A MATRIX
1520 CY=1.023E6:REM CY=FREQUENCY OF TIMER
1540 GOSUB 13000:REM LOAD CAPACITANCE FOR EACH INTEGRATOR
1560 REM ORIGINAL SET UP OF U2 TIMER
1580 INPUT#2,TM%
1600 RS(0,0)=TM%*U2/CY
1620 REM CALC. REAL APPLIED POTENTIAL
1640 FOR M=1 TO 16
1660 INPUT#2,TM%
1680 RS(M,0)=(TM%-2043)/208
1700 NEXT M
1720 TP(0)=0
1740 FOR N=1 TO NT
1760 INPUT#2,TM%
1780 RS(0,N)=TM%*U2/CY:REM INTEGRATION TIME
1800 TP(N)=RS(0,N)+TP(N-1):REM TIME SCALE
1820 FOR M=1 TO 16
1840 INPUT#2,TM%
1860 RS(M,N)=TM%/208*CA(M)/RS(0,N)/NA(M)
1880 NEXT M
1900 NEXT N
1920 CLOSE 2
1940 GOSUB 14000:REM BEEP
2000 GOSUB 9900:REM CHANGE REMARK
2010 REM SHOW ALL PARAMETERS ON SCREEN
```

```
2020 PRINT"** PUSH 'G' TO GO ON,"
2030 PRINT"   THEN HOLD 'CTRL' KEY TO VIEW"
2040 PRINT
2050 GET A$:IF A$<>"G" THEN 2050
2060 GOSUB 9700:REM SHOW SAMPLE ID
2070 GOSUB 9000:REM SHOW EXPT. CONDITIONS
2100 INPUT"ARE ALL ABOVE CORRECT(Y/N)";DM$
2120 PRINT
2140 IF DM$="Y" THEN 2200
2160 PRINT"** MAKE CORRECTION, THEN TYPE 'CONT'":STOP
2180 PRINT:GOTO 2000
2200 REM CHECK APPLIED VOLTAGE ON ELECTRODE
2220 PRINT
2240 PRINT"ELECTRODE    APPLIED VOLTAGE"
2260 PRINT
2280 FOR M=1 TO 16
2300 PRINT "   # ";M;"        ";RS(M,0)
2320 NEXT M
2340 PRINT
2400 RF=0:RL=0
2420 FOR M=1 TO 16
2440 SF(M)=0:SL(M)=0
2460 NEXT M
2500 REM CHOOSE RANGES FOR RESI:CURRENT & SAMP.CURRENT SETS
2520 BN=3:ED=23:REM START FROM SET 3 TO SET 23
2600 PRINT"** ENTER ELECTRODE #'S TO CHECK !!"
2620 PRINT"   (END OF CHECK IF 1ST INPUT <=0)"
2640 PRINT
2660 INPUT"   1ST & 2ND ELECTRODE(<=16)";X1,X2
2680 INPUT"   ARE BOTH OK(Y/N)";DM$
2700 PRINT
2720 IF DM$<>"Y" THEN 2600
2740 IF X1<=0 THEN 3500
2800 PRINT"** PUSH 'G' TO GO ON & THEN"
2820 PRINT"   HOLD 'CTRL' KEY TO CHECK DATA "
2840 PRINT"   & FIND RANGES FOR RESI.& SAMP.CURRENT"
2860 PRINT
2900 GET A$:IF A$<>"G" THEN 2900
2920 GOSUB 8800
3000 PRINT" 1ST ELECTRODE CHECKED :";X1
3020 PRINT" 2ND ELECTRODE CHECKED :";X2
3040 PRINT" INITIAL SET TO CHECK :";BN
3060 PRINT" END SET TO CHECK :";ED
3080 PRINT
3100 INPUT" IS CHECK RANGE OK(Y/N)";DM$
3120 PRINT
3140 IF DM$="Y" THEN 2600
3200 PRINT"** INPUT INITIAL & END SET TO CHECK"
3210 PRINT"   END SET MUST BE SMALLER THAN";NT
3220 PRINT
3240 INPUT"   INITIAL SET & END SET ";BN,ED
3260 INPUT"   ARE BOTH OK(Y/N)";DM$
3280 PRINT
3300 IF DM$<>"Y" THEN 3200
3400 IF ED<=NT THEN 2600
3420 PRINT" ** END SET TO CHECK IS OVER RANGE **"
3440 PRINT
3460 GOTO 3200
3500 INPUT"INPUT RESIDUAL CURRENT RANGE";RF,RL
3510 INPUT"ARE BOTH OK(Y/N)";DM$
3520 PRINT
3540 IF DM$<>"Y" THEN 2600
3550 GOSUB 13500:REM SHOW RANGE
3560 INPUT"ARE ALL OK(Y/N)";DM$
3570 PRINT
3580 IF DM$<>"Y" THEN 2600
```

```
3600 INPUT"PRINT OUT DATA TO PLOT(Y/N)";DM$
3620 PRINT
3640 IF DM$="N" THEN 3800
3660 INPUT"HAVE PARAMETERS PRINTED OUT(Y/N)";DM$
3680 PRINT
3700 IF DM$="Y" THEN 3790
3720 OPEN4,4:CMD4
3740 GOSUB 9000
3760 PRINT#4
3780 CLOSE4
3790 GOSUB 16000
3800 INPUT"GOT ALL RANGES(Y/N)";DM$
3820 PRINT
3840 IF DM$="Y" THEN 4000
3860 INPUT"CHECK THE SAME SET AGAIN(Y/N)";DM$
3880 PRINT
3900 IF DM$<>"N" THEN 3000
3920 INPUT"LOAD ANOTHER DATA SET(Y/N)";DM$
3940 PRINT
3960 IF DM$="Y" THEN 500
3980 STOP
4000 REM GET RESI.CURRENT & NET SAMPLE CURRENT
4020 PRINT"WHICH WAY TO GET DATA FOR VOLTAMMOGRAM"
4040 INPUT" (1)BY PEAK AREA; (2)BY PEAK HEIGHT";OP
4050 INPUT" IS IT OK(Y/N)";DM$
4060 PRINT
4080 IF DM$<>"Y" THEN 4020
4100 IF OP=1 THEN GOSUB 15000:REM BY AREA
4120 IF OP=1 THEN 4200
4140 IF OP=2 THEN GOSUB 15500:REM BY HEIGHT
4200 REM SHOW AVERAGED CURRENTS ON SCREEN
4220 PRINT"ELECTRODE  RESI.CURRENT*  NET SAMP.CURRENT"
4240 PRINT
4260 FOR M=1 TO 16
4280 PRINT " # ";M;RC(M,SS);SC(M,SS)
4300 NEXT M
4320 PRINT
5000 INPUT"PRINT OUT RESULTS(Y/N)";DM$
5020 PRINT
5040 IF DM$="N" THEN 6000
5060 GOSUB 7700:REM SURE PRINTER ONLINE
5100 INPUT"HAVE PARAMETERS PRINTED OUT(Y/N)";DM$
5120 PRINT
5140 IF DM$="Y" THEN 5400
5200 OPEN4,4:CMD4
5240 GOSUB 9000
5260 PRINT CHR$(12):REM GET TO THE TOP OF THE NEXT PAGE
5280 PRINT#4
5300 CLOSE4
5400 GOSUB 9900:REM CHANGE REMARK
5420 OPEN4,4:CMD4
5440 GOSUB 9700:REM SAMPLE ID
5500 REM PRINT OUT AVE. RESIDUAL & TOTAL SAMPLE CURRENT
5520 PRINT"ELECTRODE","VOLT.APPLY   RESI.CURRENT*  NET SAMP.CURRENT*"
5540 PRINT
5560 FOR M=1 TO 16
5580 PRINT"  # ";M,RS(M,0);"  ";RC(M,SS);"  ";SC(M,SS)
5600 NEXT M
5620 PRINT
5640 PRINT
5660 PRINT" * ABOVE ARE AVERAGED RESULTS !!"
5670 GOSUB 7900:REM STATE METHOD
5680 PRINT
5690 PRINT
5700 PRINT"THE DATA RANGES ARE AS FOLLOWING :"
5710 PRINT
```

```
5720 PRINT"ELECTRODE"," RESIDUAL CURRENT     NET SAMPLE CURRENT"
5730 PRINT"    #    ","  1ST SET  LAST SET      1ST SET LAST SET"
5740 PRINT
5760 FOR M=1 TO 16
5780 PRINT"    ";M,"   ";RF;"       ";RL,SF(M);"   ";SL(M)"
5800 NEXT M
5820 PRINT
5840 PRINT CHR$(12):REM GET TO THE TOP OF THE NEXT PAGE
5860 PRINT#4:CLOSE 4
5900 INPUT"IS PRINTOUT OK(Y/N)";DM$
5920 PRINT
5940 IF DM$<>"Y" THEN 5000
6000 INPUT"ARE RESULTS OK(Y/N)";DM$
6020 PRINT
6040 IF DM$="Y" THEN 6500
6100 INPUT"CHECK THE SAME SET AGAIN(Y/N)";DM$
6120 PRINT
6140 IF DM$<>"N" THEN 2600
6200 INPUT"LOAD NEW DATA SET(Y/N)";DM$
6220 PRINT
6240 IF DM$="Y" THEN 500
6260 GOTO 7000
6500 INPUT"RESULT FOR STATISTICS(Y/N)";DM$
6520 PRINT
6540 IF DM$="Y" THEN 6600
6560 GOTO 6100
6600 PRINT"PRESENT DATA FILE ID : ";ID$
6620 PRINT"PRESENT SET # FOR REPEATABILITY : ";SS
6640 PRINT
6660 INPUT"DONE REPEATABILITY CALC.(Y/N)";DM$
6680 PRINT
6700 IF DM$="Y" THEN 6800
6720 INPUT"ARE YOU SURE(Y/N)";DM$
6740 PRINT
6760 IF DM$="Y" THEN 400
6770 STOP
6780 GOTO 6660
6800 INPUT"ARE YOU SURE(Y/N)";DM$
6820 PRINT
6840 IF DM$="N" THEN 6770
6900 PRINT" ** NOW APPLY STATISTICS TO THE RESULTS"
6920 PRINT
6940 I=SS:REM TOTAL SET FOR REPEATABILITY IS 'SS'
6960 GOSUB 10000
7000 INPUT"CHECK SAME SET AGAIN(Y/N)";DM$
7020 PRINT
7040 IF DM$="Y" THEN 2600
7100 INPUT"ADD ANOTHER DATA SET(Y/N)";DM$
7120 PRINT
7140 IF DM$="Y" THEN 400
7200 INPUT"GET RID OFF PREVIOUS ONE(Y/N)";DM$
7220 PRINT
7240 IF DM$="N" THEN 7300
7260 SS=SS-1
7280 GOTO 6660
7300 PRINT"WANT TO START OVER/END! RIGHT?"
7320 STOP
7340 PRINT
7360 GOTO 7000
7500 END
7700 REM CHECK PRINTER ONLINE
7720 PRINT"** MAKE SURE PRINTER IS ONLINE."
7740 PRINT"   THEN PUSH 'G' TO GO ON !"
7760 PRINT
7780 GET A$:IF A$<>"G" THEN 7780
7800 RETURN
```

```
7900 REM STATE METHOD
7920 IF OP=1 THEN PRINT" ** RESULTS ARE BASED ON PEAK AREA !"
7940 IF OP=2 THEN PRINT" ** RESULTS ARE BASED ON PEAK HEIGHT !"
7960 PRINT
7980 RETURN
8000 REM SUBROUTINE TO CHECK WHOLE SET DATA
8020 PRINT"** END OF CHECK IF NN < 0 !"
8040 INPUT" NEW DATA SET # TO CHECK(NN)";NN
8080 PRINT
8100 IF NN<0 THEN 8360
8200 PRINT" M     DATA(NN)          DATA(NN+1)"
8220 FOR M=0 TO 16
8240 PRINT M;RS(M,NN);RS(M,NN+1)
8260 NEXT M
8280 PRINT
8300 PRINT" DATA SET # : ";NN
8320 PRINT
8340 GOTO 8020
8360 RETURN
8500 REM SHOW A SINGLE SET DATA
8520 PRINT
8540 PRINT N;"TH SET DATA OF SAMPLE"
8560 PRINT"  DATA COLLECTED AT";RS(0,N);"SEC"
8580 PRINT"  INTEGRATION TIME IS";TP(N);"SEC"
8600 PRINT
8620 PRINT"ELECTRODE","TOTL.SAMP.CURRENT"
8640 PRINT
8660 FOR M=1 TO 16
8680 PRINT"  # ";M,RS(M,N)
8700 NEXT M
8720 PRINT
8740 RETURN
8800 REM SUBROUTINE TO SEE ALL DATA ON TWO ELECTRODES
8820 PRINT"SET";" ELECTRODE";X1;"   ELECTRODE";X2
8840 FOR N=BN TO ED
8860 PRINT N;RS(X1,N);RS(X2,N)
8880 NEXT N
8900 PRINT
8920 GOSUB 14500:REM SET RANGE
8940 RETURN
9000 REM SHOW ALL PARAMETERS ON SCREEN
9020 PRINT"EXPERIMENTAL CONDITIONS --"
9040 PRINT
9060 PRINT" FLOW RATE -- ";FR$
9080 PRINT
9100 PRINT" SQUARE WAVE FOR PRECONDITIONING --"
9120 PRINT"  POTENTIAL OF UPPER LIMIT :";UL;"VOLT"
9140 PRINT"  POTENTIAL OF LOWER LIMIT :";LL;"VOLT"
9160 PRINT"  FREQUENCY :";HZ;"HERTZ"
9180 PRINT"  DURATION :";DU;"SEC"
9200 PRINT
9220 PRINT IV;"VOLTS OUTPUT FROM DAC7548 #1"
9240 PRINT FV;"VOLTS OUTPUT FROM DAC7548 #2"
9260 PRINT
9280 PRINT" WAIT";TD;"SEC TO SUBSIDE CHARGING CURRENT DOWN"
9300 PRINT
9320 PRINT" U2ALO IS";U2
9340 PRINT" TOTAL COVERED TIME IS";TT;"SEC"
9360 PRINT" U1 TIMER SETUP AS";U1;"* (1/60) SEC"
9380 PRINT" TIME OF RESOLUTION IS ABOUT";TR;"SEC"
9400 PRINT NT;"SETS OF DATA COLLECTED"
9420 PRINT
9440 PRINT" REFERENCE ELECTRODES : ZINC IN 1 M SODIUM ACETATE SOLUTION."
9460 PRINT" WORKING ELECTRODES : CARBON FIBER ARRAY ELECTRODE"
9480 PRINT
9500 PRINT
```

```
9520 PRINT" ** REMARK : ";RM$
9540 PRINT
9560 PRINT
9580 RETURN
9600 REM SHOW SAMPLE, EXPT. DATE, & REMARK
9610 PRINT"SAMPLE -- ";LB$
9620 PRINT" NORM.AREA FILE ID : ";NF$
9630 PRINT" DATE OF EXPERIMENT : ";DA$
9640 PRINT
9650 PRINT" ** REMARK : ";RM$
9660 PRINT
9670 PRINT
9680 RETURN
9700 REM SHOW SAMPLE ID
9720 PRINT"SAMPLE -- ";LB$
9740 PRINT" SAMPLE DATA FILE ID : ";ID$
9760 PRINT" NORM.AREA FILE ID : ";NF$
9780 PRINT" DATE OF EXPERIMENT : ";DA$
9800 PRINT
9820 PRINT" ** REMARK : ";RM$
9840 PRINT
9860 PRINT
9880 RETURN
9900 REM CHANGE REMARK
9910 PRINT"PREVIOUS REMARK : ";RM$
9920 INPUT"IS IT OK(Y/N)";DM$
9930 PRINT
9940 IF DM$="Y" THEN 9990
9950 INPUT"NEW REMARK";RM$
9960 INPUT"IS IT OK(Y/N)";DM$
9970 PRINT
9980 IF DM$<>"Y" THEN 9950
9990 RETURN
10000 REM STATISTICS FOR MEAN, STANDARD DEVIATION(SD), AND RELATIVE SD
10100 REM MEAN
10200 FOR M=1 TO 16
10240 D1=0
10260 FOR X=1 TO I
10280 D1=SC(M,X)+D1
10300 NEXT X
10340 SA(M)=D1/I
10500 REM SD & RELATIVE SD (RD)
10600 D2=0
10620 D3=0
10640 FOR X=1 TO I
10660 D2=SC(M,X)-SA(M)
10680 D3=D2*D2+D3
10700 NEXT X
10720 SD(M)=SQR(D3/(I-1)):REM MAY SUBSTITUTE I-1 WITH I
10740 RD(M)=SD(M)/SA(M)*100
10760 NEXT M
10800 GOSUB 11500:REM SHOW RESULTS
11000 INPUT"PRINT OUT STATISTIC RESULTS(Y/N)";DM$
11020 PRINT
11040 IF DM$="N" THEN 11460
11100 GOSUB 9900
11200 OPEN4,4:CMD4
11300 GOSUB 9600:REM SAMPLE, EXPT. DATE, & REMARK
11320 GOSUB 11500:REM SHOW RESULTS
11340 PRINT CHR$(12)
11360 PRINT#4
11380 CLOSE4
11400 INPUT"IS PRINTOUT OK(Y/N)";DM$
11420 PRINT
11440 IF DM$<>"Y" THEN 11000
11460 RETURN
```

```
11500 REM SHOW STATISTIC RESULT.
11600 PRINT"ELECTRODE","          NET SAMPLE CURRENT"
11620 PRINT"         "," MEAN            STD DEV      REL STD DEV(%)"
11640 PRINT
11700 FOR M=1 TO 16
11720 PRINT" #";M,SA(M);"  ";SD(M);"  ";RD(M)
11740 NEXT M
11760 PRINT
11780 PRINT
11800 PRINT"  ** THE STATISTICS IS BASED ON";I;"DATA SETS"
11820 IF OP=1 THEN PRINT"     & ALSO BASED ON PEAK AREA !"
11840 IF OP=2 THEN PRINT"     & ALSO BASED ON PEAK HEIGHT !"
11860 PRINT
11880 PRINT
11900 RETURN
12000 REM SUBROUTINE TO LOAD NORMALIZED AREA
12100 INPUT"KNOW NORM.AREA FILE ID(Y/N)";DM$
12120 PRINT
12140 IF DM$="Y" THEN 12300
12200 PRINT"-- NORM.AREA FILE ID STARTS WITH 'N-*'"
12240 PRINT"   TYPE '@$', THEN TYPE 'CONT'"
12260 PRINT:STOP
12300 PRINT
12320 PRINT"** FILE ID MUST START WITH 'N-A/H-*'"
12340 PRINT
12400 INPUT"   NORM.AREA FILE ID";NF$
12420 INPUT"   IS FILE NAME OK(Y/N)";DM$
12440 PRINT
12460 IF DM$<>"Y" THEN 12100
12500 PRINT"-- HANG ON, LOADING NORM.AREA !!"
12520 PRINT
12600 REM LOAD NORM.AREA
12700 OPEN 2,8,2,NF$+",S,R"
12720 FOR M=0 TO 16
12740 INPUT#2,NA(M)
12760 NEXT M
12780 CLOSE 2
12800 RETURN
13000 REM SUBROUTINE TO LOAD CAPACITANCE FOR EACH INTEGRATOR
13020 REM BASED ON THE RESULTS OBTAINED ON 10/31
13100 CA(1)=9.026E-10:CA(2)=8.618E-10
13120 CA(3)=8.941E-10:CA(4)=8.398E-10
13140 CA(5)=8.369E-10:CA(6)=8.985E-10
13160 CA(7)=8.932E-10:CA(8)=8.661E-10
13180 CA(9)=9.095E-10:CA(10)=8.982E-10
13200 CA(11)=8.954E-10:CA(12)=8.951E-10
13220 CA(13)=9.105E-10:CA(14)=8.888E-10
13240 CA(15)=8.190E-10:CA(16)=8.500E-10
13300 RETURN
13500 REM SUBROUTINE SHOWN RANGES
13520 PRINT"ELECTRODE","RF RL SF SL"
13540 PRINT
13600 FOR M=1 TO 16
13620 PRINT" #";M;RF;RL;SF(M);SL(M)
13640 NEXT M
13660 PRINT
13680 RETURN
14000 REM GENERATE A BEEPER(REF. P.185)
14020 PRINT"   PUSH 'S' TO STOP BEEPING &"
14040 PRINT"   WATCH SCREEN FOR HINT !"
14060 PRINT
14100 GET A$:IF A$="S" THEN 14400
14200 S=54272
14220 FOR L=S TO S+24:POKE L,0:NEXT
14240 POKE S+5,9:POKE S+6,0
14260 POKE S+24,15
```

```
14280 HF=37:LF=162:DR=500
14300 POKE S+1,HF:POKE S,LF
14320 POKE S+4,33
14340 FOR T=1 TO DR:NEXT
14360 POKE S+4,32:FOR T=1 TO 50:NEXT
14380 GOTO 14100
14400 RETURN
14500 REM SET RANGE FOR SAMP.CURRENT PEAK HEIGHT MAXIMUM
14600 PRINT"  FOR ELECTRODE #";X1
14640 INPUT"  RANGE OF SAMPLE CURRENT";SF(X1),SL(X1)
14660 PRINT
14700 PRINT"  FOR ELECTRODE #";X2
14740 INPUT"  RANGE OF SAMPLE CURRENT";SF(X2),SL(X2)
14760 PRINT
14800 INPUT"  ARE BOTH OK(Y/N)";DM$
14820 PRINT
14840 IF DM$<>"Y" THEN 14600
14860 RETURN
15000 REM GET RESI.CURRENT & TOTL.SAMP.CURRENT BY PEAK AREA
15020 PRINT"-- HANG ON, CALC. PEAK AREA !"
15040 PRINT
15100 REM CALC. AVERAGE RESI.CURRENT
15110 FOR M=1 TO 16
15120 RC(M,SS)=0
15130 FOR N=RF TO RL
15140 RC(M,SS)=RC(M,SS)+RS(M,N)
15150 NEXT N
15160 RC(M,SS)=RC(M,SS)/(RL-RF+1)
15170 NEXT M
15200 REM CALC. PEAK AREA OF NET SAMPLE CURRENT
15220 PRINT"-- THE FOLLOWING 'N' VALUE SHOULD BE"
15240 PRINT"   NOT GREATER THAN";NT+1
15260 PRINT
15300 FOR M=1 TO 16
15310 SC(M,SS)=0
15320 N=RL+1
15330 SC(M,SS)=(RS(M,N)-RC(M,SS))*RS(0,N)+SC(M,SS)
15340 N=N+1
15350 IF N>NT THEN 15410
15360 IF N<=20 THEN 15330
15370 IF RS(M,20)<RC(M,SS) THEN 15400
15380 IF RS(M,N)>RC(M,SS) THEN 15330
15390 GOTO 15410
15400 IF RS(M,N)<RC(M,SS) THEN 15330
15410 PRINT"  M =";M;"; N =";N
15420 NEXT M
15440 PRINT
15460 GOSUB 14000:REM BEEP
15480 RETURN
15500 REM GET RESI.CURRENT & SAMP.CURRENT BY PEAK HEIGHT
15520 PRINT"-- HANG ON, CALC. PEAK HEIGHT !"
15540 PRINT
15600 REM CALC. AVERAGE RESI.CURRENT
15610 FOR M=1 TO 16
15620 RC(M,SS)=0
15630 FOR N=RF TO RL
15640 RC(M,SS)=RC(M,SS)+RS(M,N)
15650 NEXT N
15660 RC(M,SS)=RC(M,SS)/(RL-RF+1)
15670 NEXT M
15700 REM CALC. PEAK HEIGHT OF NET SAMPLE CURRENT
15720 FOR M=1 TO 16
15740 SC(M,SS)=0
15760 FOR N=SF(M) TO SL(M)
15780 SC(M,SS)=SC(M,SS)+RS(M,N)
15800 NEXT N
```

```
15820 SC(M,SS)=SC(M,SS)/(SL(M)-SF(M)+1)
15840 SC(M,SS)=SC(M,SS)-RC(M,SS)
15860 NEXT M
15900 GOSUB 14000:REM BEEP
15920 RETURN
16000 REM PRINT OUT DATA FOR PLOTTING
16020 PRINT"** INPUT THE RANGE OF DATA TO PRINT"
16040 PRINT"   END OF PRINT IF 1ST<0 !"
16060 PRINT
16100 INPUT"   1ST SET, LAST SET";BN,ED
16120 INPUT"   ARE BOTH OK(Y/N)";DM$
16140 PRINT
16160 IF DM$<>"Y" THEN 16100
16180 IF BN<0 THEN 17000
16200 REM PRINT OUT THE TIME AT WHICH DATA WERE COLLECTED
16220 OPEN 4,4:CMD 4
16240 PRINT"AREA DATA FILE ID : ";ID$
16260 PRINT
16280 PRINT
16300 PRINT"SET","TIME(DATA COLLECTED)"
16320 PRINT
16340 FOR N=BN TO ED
16360 PRINT N,RS(0,N)
16380 NEXT N
16400 PRINT CHR$(12):REM GET TO THE TOP OF NEXT PAGE
16420 PRINT#4
16440 CLOSE4
16500 PRINT"** END OF PRINT IF FT<0 !!"
16540 PRINT"   CHOOSE 4 ELECTRODES TO PRINT DATA !"
16560 INPUT"   1ST,2ND,3RD,4TH ELECTRODE";FT,SD,TD,FH
16620 INPUT"ARE ALL ABOVE OK(Y/N)";DM$
16640 PRINT
16660 IF DM$<>"Y" THEN 16500
16680 IF FT<0 THEN 17000
16700 OPEN 4,4:CMD 4
16720 PRINT"SET","                  ELECTRODE"
16740 PRINT" # ";"      #";FT,"   #";SD,"  #";TD,"  #";FH
16750 PRINT
16760 FOR N=BN TO ED
16780 PRINT N;RS(FT,N);RS(SD,N);RS(TD,N);RS(FH,N)
16800 NEXT N
16820 PRINT CHR$(12)
16840 PRINT#4
16860 CLOSE4
16900 GOTO 16500
17000 RETURN

READY.
```