Instrumentation for Multi-Electrode Voltammetry

I-Pin Ho

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INSTRUMENTATION FOR MULTI-ELECTRODE VOLTAMMETRY

by

I-PIN HO

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

ENVIRONMENTAL SCIENCES AND RESOURCES: CHEMISTRY

Portland State University
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TO THE OFFICE OF GRADUATE STUDIES:

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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.

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 Pacákova (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 Dalhuijzen 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.
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 micro electrode 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 programmed as two separated timers or jointly programmed 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. $-0.6 \, \text{V}$ in Figure 11a. However, in both CVs the currents increased notably with potentials either more positive than $+1.5 \, \text{V}$ or more negative than $-1.4 \, \text{V}$, 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 $-1.4 \, \text{V}$ and $+1.5 \, \text{V}$ with deoxygenation; otherwise, between $-0.3 \, \text{V}$ and $+1.5 \, \text{V}$. 
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 $E_p-E_{p2}$ 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 \( \text{H}_2 \) and \( \text{O}_2 \) by the decomposition of \( \text{H}_2\text{O} \) 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
Figure 22. 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 ($\delta_{bl}$) 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 affect 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,

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

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

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

\[ \text{Volume of the center hole in two Kalrez films} = (\pi r^2 l) \times 2 = 1.30 \times 10^{-3} \text{ cm}^3 \]
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 x 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

<table>
<thead>
<tr>
<th>Pump Scale</th>
<th>Time for 10 mL (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>540</td>
</tr>
<tr>
<td>30.0</td>
<td>352</td>
</tr>
<tr>
<td>40.0</td>
<td>265</td>
</tr>
<tr>
<td>50.0</td>
<td>210</td>
</tr>
<tr>
<td>60.0</td>
<td>180</td>
</tr>
</tbody>
</table>

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:

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

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;
- $i_{\text{leak}}$: 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 multi-
meter. 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

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

* 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 \( \text{H}_2\text{O} \) and of the noise level caused by the evolution of \( \text{O}_2 \) 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 $5.45 \times 10^{-4}$ 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 ultrade 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**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Current (Amp) at Flow Rate of 1.67 mL/Min</th>
<th>Current (Amp) at Flow Rate of 2.22 mL/min</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>5.26E-10 3.11E-8</td>
<td>4.96E-10 3.19E-8</td>
</tr>
<tr>
<td># 2</td>
<td>4.81E-10 3.61E-8</td>
<td>4.77E-10 3.88E-8</td>
</tr>
<tr>
<td># 3</td>
<td>5.39E-10 4.82E-8</td>
<td>4.90E-10 5.11E-8</td>
</tr>
<tr>
<td># 4</td>
<td>2.56E-10 4.02E-8</td>
<td>2.44E-10 4.19E-8</td>
</tr>
<tr>
<td># 5</td>
<td>1.41E-09 5.74E-8</td>
<td>1.17E-09 5.82E-8</td>
</tr>
<tr>
<td># 6</td>
<td>1.61E-09 6.08E-8</td>
<td>1.35E-09 6.31E-8</td>
</tr>
<tr>
<td># 7</td>
<td>1.93E-09 3.99E-8</td>
<td>1.69E-09 4.03E-8</td>
</tr>
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<td># 8</td>
<td>9.87E-10 5.36E-8</td>
<td>8.95E-10 5.80E-8</td>
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<tr>
<td># 9</td>
<td>1.60E-09 4.96E-8</td>
<td>1.31E-09 5.02E-8</td>
</tr>
<tr>
<td># 10</td>
<td>1.88E-09 4.82E-8</td>
<td>1.62E-09 5.06E-8</td>
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<tr>
<td># 11</td>
<td>2.10E-09 4.88E-8</td>
<td>1.71E-09 5.04E-8</td>
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<td># 13</td>
<td>7.79E-10 5.07E-8</td>
<td>6.90E-10 5.40E-8</td>
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<tr>
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<td>1.07E-09 5.48E-8</td>
<td>9.98E-10 5.82E-8</td>
</tr>
<tr>
<td># 15</td>
<td>2.22E-09 6.03E-8</td>
<td>2.10E-09 6.36E-8</td>
</tr>
<tr>
<td># 16</td>
<td>4.80E-09 5.60E-8</td>
<td>4.07E-09 5.89E-8</td>
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<table>
<thead>
<tr>
<th>Electrode</th>
<th>Current (Amp) at Flow Rate of 2.86 mL/Min</th>
<th>Current (Amp) at Flow Rate of 3.33 mL/min</th>
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<tbody>
<tr>
<td># 1</td>
<td>6.12E-10 3.16E-8</td>
<td>6.12E-10 3.27E-8</td>
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</tr>
<tr>
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<td>3.06E-10 4.22E-8</td>
<td>3.10E-10 4.27E-8</td>
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<td>1.85E-09 6.06E-8</td>
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<tr>
<td># 16</td>
<td>6.49E-09 6.24E-8</td>
<td>6.27E-09 6.23E-8</td>
</tr>
<tr>
<td>Electrode</td>
<td>Normalization Factor at Flow Rate (mL/Min)</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>1.62</td>
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<td># 8</td>
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<td>1.49</td>
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<td>1.29</td>
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<td># 16</td>
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<td>1.52</td>
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<table>
<thead>
<tr>
<th>Electrode</th>
<th>Normalization Factor</th>
<th>Mean</th>
<th>Std. Dev.</th>
<th>Rel. Std. Dev.(%)</th>
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</thead>
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<td>3.6</td>
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<td>0.03</td>
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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 $5.45 \times 10^{-4}$ 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**

<table>
<thead>
<tr>
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<th>Set 2</th>
<th>Set 3</th>
</tr>
</thead>
<tbody>
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<td>3.11E-8</td>
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<td>4.35E-8</td>
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<td>4.37E-8</td>
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<th>Std. Dev.</th>
<th>Rel. Std. Dev. (%)</th>
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TABLE VI
REPRODUCIBILITY OF CARBON FIBER ARRAY ELECTRODE
RESPONSE CURRENTS AT THE APPLIED
POTENTIAL OF +1.95 V

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<th>Set 3</th>
</tr>
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<thead>
<tr>
<th>Electrode</th>
<th>Mean</th>
<th>Std. Dev.</th>
<th>Rel. Std. Dev. (%)</th>
</tr>
</thead>
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<td>1.60E-09</td>
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<td># 9</td>
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<td>1.66E-09</td>
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<td>4.0</td>
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<td>3.14E-09</td>
<td>4.7</td>
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<td># 15</td>
<td>6.93E-8</td>
<td>2.42E-09</td>
<td>3.4</td>
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<tr>
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<td>3.36E-09</td>
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</table>
TABLE VII
CARBON FIBER ARRAY ELECTRODE NORMALIZATION FACTORS FOR PSEUDO-VOLTAMMGRAMS

<table>
<thead>
<tr>
<th>Electrode</th>
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<th>Normalization Factor</th>
</tr>
</thead>
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</tr>
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<td>1.10</td>
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<td># 14</td>
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</tr>
<tr>
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</table>

zinc/zinc acetate reference electrode.

HQ concentrations ranging from 7.26 x 10⁻⁵ M up to 5.45 x 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 x 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**

<table>
<thead>
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<th>Net Current (Amp)</th>
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<td>2.51E-09</td>
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</tr>
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<td>1.95</td>
<td>3.92E-08</td>
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<table>
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<th>Std. Dev.</th>
<th>Rel. Std. Dev. (%)</th>
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</thead>
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<td>6.25E-12</td>
<td>1.2</td>
</tr>
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<td># 8</td>
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</table>
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
Sample: Hydroquinone in 0.1 M Acetate Buffer.
Flow Rate: 3.33 mL/min.
Potential for CFAE Normalization Factors: +1.95 V.

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

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

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

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Net Current (Amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at Concentration (M) of</td>
</tr>
<tr>
<td></td>
<td>7.26E-5</td>
</tr>
<tr>
<td># 1</td>
<td>-3.56E-11</td>
</tr>
<tr>
<td># 2</td>
<td>-2.96E-11</td>
</tr>
<tr>
<td># 3</td>
<td>-4.42E-12</td>
</tr>
<tr>
<td># 4</td>
<td>-5.96E-12</td>
</tr>
<tr>
<td># 5</td>
<td>-2.52E-11</td>
</tr>
<tr>
<td># 6</td>
<td>-1.44E-11</td>
</tr>
<tr>
<td># 7</td>
<td>3.74E-11</td>
</tr>
<tr>
<td># 8</td>
<td>4.65E-10</td>
</tr>
<tr>
<td># 9</td>
<td>4.45E-10</td>
</tr>
<tr>
<td># 10</td>
<td>1.31E-09</td>
</tr>
<tr>
<td># 11</td>
<td>2.16E-09</td>
</tr>
<tr>
<td># 12</td>
<td>2.69E-09</td>
</tr>
<tr>
<td># 13</td>
<td>4.20E-09</td>
</tr>
<tr>
<td># 14</td>
<td>5.48E-09</td>
</tr>
<tr>
<td># 15</td>
<td>5.99E-09</td>
</tr>
<tr>
<td># 16</td>
<td>6.07E-09</td>
</tr>
</tbody>
</table>
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 $5 \times 10^{-5}$ M HQ at 95% confidence level, i.e., 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.
REFERENCES


(34) J. Dash, Professor, Physics Dept., Portland State Univ., P.O. Box 751, Portland, OR 97201.


APPENDIX A

SCHEMATIC DIAGRAM OF THE CIRCUITRY WITH COMPONENT IDENTIFICATIONS
SCHEMATIC DIAGRAM OF THE CIRCUITRY WITH COMPONENT IDENT
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$="Y" THEN GOTO 2000
1000 PRINT
1020 PRINT
1040 PRINT*** IF VH<0 THEN END OF THIS PART !!
1060 PRINT
1200 INPUT"ENTER VH & VL FOR BOTH DACS";VH%,VL$
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 VOLTAGE 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 VOLTAGE 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", 1
10 REM ******************************
11 REM * 2/9/1988 *
12 REM * "COLLECT DATA" *
20 REM * DATA ARE COLLECTED BY *
30 REM * AN ASSEMBLY SUBROUTINE *
40 REM * ALSO SAVE INTO A FILE *
50 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$="N" THEN 300
400 REM DD%(M,N)=DIGITAL DATA OBTAINED
410 REM TR=TIME OF RESOLUTION
420 REM LL=LOWER POTENTIAL LIMIT OF SQUARE WAVE
440 REM TT=TOTAL COVERED TIME
450 REM DA$= DATE OF EXPERIMENT
460 REM DD04 IS THE TA-LO ADDRESS OF 6526 U1
470 REM $C000 TO SET UP PIA
496 REM DA$= DATE OF EXPERIMENT
500 REM DDR-A & CR-A OF PIA
510 REM DDR-B & CR-B OF PIA
520 REM ADDRESS OF CD4514
530 REM ADDRESS OF 74HC273
540 REM ADDRESS OF DAC7548 #1
550 REM $D04 IS THE TB-LO ADDRESS OF 6526 U1
570 REM ADDRESS OF DAC7548 #2
600 REM POKE 640 IS EQUIVALENT TO 600, 610, & 620
640 SYS 49152: REM $C000 TO SET UP PIA
660 IDE$="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 IF A$<>"G" THEN 790
800 PRINT"** IF BEEP IS NOT HEARD,"
820 PRINT" TURN THE VOLUME UP!!"
840 PRINT
860 GOSUB 8800: REM TEST BEEP
1000 GOSUB 13000: REM SET STANDBY POTENTIAL
1100 GOSUB 12500: REM APPLY STANDBY POTENTIALS TO ELECTRODES
1200 PRINT"** EVACUATE FLOW SYSTEM &"
1220 PRINT" THEN CONNECT CABLE TO IT"
1240 PRINT" PUSH 'G' TO GO ON !"
1260 PRINT
1280 IF A$<> "G" THEN 1290
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$="Y" THEN 1400
1480 Ti$="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
2300 BT=TD:GOSUB 92000:REM LET OVERSHOOT CURRENT SUBSIDE DOWN
2320 PRINT "-- NOW, COLLECTING DATA !!"
2340 PRINT
2360 POKE 56928,0:REM PIN 1 & 19 OF 74HC244 LOW
2380 SYS 492009:REM #039 OBTAIN DATA
2400 PRINT "-- DATA HAVE BEEN COLLECTED !"
2420 PRINT
2440 POKE 56928,128:REM KEEP ALL SWITCHES CLOSED
2460 GOSUB 13500:REM APPLY STANDBY POTENTIAL
2480 PRINT "-- HANG ON, CHECKING DATA !"
2500 PRINT
2520 GOSUB 12500:REM FIND OUT HOW MANY SETS OBTAINED
2540 GOSUB 8000:REM BEEP
2560 PRINT "** MOVE FLOW OUTLET BACK TO CYLINDER !"
2580 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$="N" THEN 5000
3260 REM COMBINE DATA TOGETHER ACCORDING TO RESOLUTION TIME
3280 PRINT " WANT TO COMBINE DATA"
3300 INPUT " ACCORDING TO TR(Y/N)"; DM$
3320 PRINT
3340 IF DM$="Y" THEN 5000
3360 GOSUB 11000:REM COMBINE DATA
3380 GOSUB 8000:REM BEEP
3400 GOSUB 9600:REM CHECK COMBINED RESULTS
4000 INPUT " PRINT OUT THESE DATA(Y/N)"; DM$
4100 PRINT
4120 IF DM$="Y" THEN 4200
4140 GOSUB 20000
4200 INPUT " IS TIME RESOLUTION OK(Y/N)"; DM$
4220 PRINT
4240 IF DM$="Y" THEN 4300
4400 INPUT " WANT TO SAVE RESULTS ON DISK(Y/N)"; DM$
4420 PRINT
4440 IF DM$="N" THEN 5000
4460 GOSUB 99000:REM CHECK DISK
4480 PRINT
4500 PRINT " SAMPLE LABEL : "; LB$
4520 PRINT " FLOW RATE : "; FR$
4540 PRINT " INIT. VOLT : "; IV; " VOLT"
PRINT"FINAL VOLT: ";FV;" VOLT"
PRINT
PRINT"PREVIOUS REMARK: ";RM$
PRINT
PRINT"****************************"
PRINT"FOR AREA, FILE NAME STARTS WITH A- *
PRINT"FOR SAMP, FILE NAME STARTS WITH S- *
PRINT"****************************"
PRINT
PRINT"PREVIOUS DATA FILE ID: ";ID$
INPUT"NEW DATA FILE ID";ID$
INPUT"REMARK <NO>";RM$
INPUT"ARE THEY OK<Y/N>";DM$
PRINT
IF DM$<"Y" THEN 4800
PRINT"HANG ON, RECORDING DATA !"
PRINT
GOSUB 6000:REM RECORD DATA
GOSUB 8000:REM BEEP
INPUT"ANOTHER RUN<Y/N>";DM$
PRINT
IF DM$="Y" THEN 5100
PRINT"YOU ARE SURE, RIGHT?":STOP
GOTO 5000
GOSUB 14000:REM SET UP EXPT. CONDITIONS
GOSUB 13500:REM SET STANDBY POTENTIALS
GOSUB 13500:REM APPLY STANDBY POTENTIALS
PRINT"** MAKE SURE**
PRINT"A SAMPLE IS READY TO INJECT"
PRINT"THEN PUSH 'G' TO GO ON !"
PRINT
GET A$:IF A$<"G" THEN
INPUT"WANT TO CLEAN ELECTRODE<Y/N>";DM$
PRINT
IF DM$="Y" THEN
INPUT"TIME OF DELAY";TD
PRINT
IF DM$="Y" THEN
INPUT"TIME OF DELAY>=240 SEC";TD
GOTO 5400
GOSUB 7500:REM SET UP PARAMETERS OF SQUARE WAVE
GOSUB 8500:REM APPLY SQUARE WAVE
GOSUB 8800:REM EXPT. POTENTIAL READY
TIS="000000"
PRINT"-- TIMING BEGIN --"
GOSUB 8000:REM BEEP
GOSUB 10000:REM CLEAR MATRIX
GOSUB 8000:REM BEEP
GOTO 21111111
END
REM SUBROUTINE TO SAVE DATA
PRINT"-- IF DRIVE LIGHT BLINKS, STOP"
PRINT"PROGRAM IMMEDIATELY. THEN TYPE"
PRINT"'CLOSE 2', FOLLOWED BY TYPING"
PRINT"'GOTO 4000' !!"
PRINT
REM SAVE DATA INTO A SED. FILE
OPEN 2,B,0,"DATA+DATA++",S,W
PRINT2,DA$
PRINT2,LB$
PRINT2,FR$
PRINT2,UL
6320 PRINT#2, LL
6340 PRINT#2, HZ
6360 PRINT#2, DU
6380 PRINT#2, TD
6410 PRINT#2, IV
6420 PRINT#2, FV
6440 PRINT#2, UI
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
6610 PRINT#2, DD%<M, S>
6640 NEXT S
6660 CLOSE 2
6810 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$="Y" THEN 7800
7700 PRINT "INPUT NEW SQUARE WAVE PARAMETERS --"
7710 INPUT "UPPER LIMIT(+2.05 V)";UL
7720 INPUT "LOWER LIMIT(+0.95 V)";LL
7730 PRINT "FREQ. IS CA. 5 HZ":HZ=5
7740 INPUT "DURATION(30 SEC)";DU
7750 PRINT
7760 INPUT "DELAY(>240 SEC)";TD
7770 PRINT
7780 GOTO 7500
7800 REM CONVERT UL TO DIGITAL
7810 DM%=INT((UL*4095/6.012)+21142)
7820 RHX=INT(DM%/256)
7830 RL%=INT(DM%-RH%*256)
7900 RETURN
8000 REM GENERATE A BEEPER (REF. P.185)
8010 PRINT "PUSH 'S' TO STOP THE BEEP &"
8020 PRINT "WATCH THE SCREEN FOR THE HINT !"
8030 PRINT
8100 GET AS$: IF AS$="S" THEN 8400
8200 S=54272
8220 FOR L=S TO S+24:POKE L,0:NEXT
8240 POKE S+5,9:POKE S+6,0
8260 POKE S+24,15
8280 HF=37:LF=162:DR=500
8300 POKE S+1,LF:POKE S,LF
8320 POKE S+4,33
8340 FOR T=1 TO DR:NEXT
8360 POKE S+4,32:FOR T=1 TO 50:NEXT
8380 GOTO 8100
8400 RETURN
8500 REM SUBROUTINE FOR APPLYING SQUARE WAVE
8520 PRINT"-- NOW, REACTIVATE ELECTRODES --"  
8540 PRINT" WAIT",DU," SEC FOR ELECTRODE CLEAN !"  
8560 PRINT  
8600 REM FREQUENCY OF S.W. IS 5 HZ  
8620 Ti$="11101111111121121"  
8640 REM APPLY UPPER LIMIT FIRST, THEN LOWER LIMIT  
8660 POKE L1,0L%:POKE H1,0H%  
8680 POKE L2,0L%:POKE H2,0H%  
8700 FOR DM=1 TO 8: NEXT DM  
8720 POKE L1,RL%:POKE H1,RH%  
8740 POKE L2,RL%:POKE H2,RH%  
8760 FOR DM=1 TO 7: NEXT DM  
8780 IF TI/6<DU THEN B660  
9790 RETURN  
8800 REM APPLY EXPT. POTENTIAL TO BOTH DAC  
8820 POKE L1,IL%:POKE H1,IL%  
8840 POKE L2,FL%:POKE H2,FL%  
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" IF DM$="Y" THEN STOP  
9160 IF DM$="Y" THEN STOP  
9180 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" IF Z<0 THEN END OF CHECKING DATA"  
9660 INPUT" NEW STARTING SET #:";Z  
9700 PRINT  
9720 IF Z<0 THEN 9800  
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  
9860 PRINT  
9880 GOTO 9620
REM CLEAR THE WHOLE MATRIX
PRINT "HANG ON, EMPTY THE MATRIX :"
FOR DM=0 TO NR+2
FOR M=0 TO 16
DD%(M,DM)=0
NEXT M
NEXT DM
RETURN
REM FIND OUT HOW MANY SETS OF RAW DATA COLLECTED
NR=0
IF DD%(0,NR)>0 THEN 10600
NR=NR-1
GOTO 10540
PRINT "LAST DATA SET(NR) AT ";NR
NR=NR
PRINT
RETURN
REM ROUTINE TO TREAT RAW DATA
REM J REPRESENTS ORIGINAL ROW
REM N REPRESENTS EACH ROW AFTER DATA COMBINATION
REM DD%(0,N) REPRESENTS INTEGRATION TIME
REM M REPRESENTS THE K ELECTRODE
PRINT "TIME OF RESOLUTION(TR) :";TR;"SEC"
PRINT "IS IT OK? Y/N";DM$
IF DM$="Y" THEN 11200
INPUT "NEW TR (=1.00 SEC)";TR
PRINT GOTO 11000
PRINT "WAIT (ABOUT 5 MIN.) TO COMBINE"
PRINT "DATA ACCORDING TO TR !";
PRINT "--IF PROGRAM STOPPED BY ILLEGAL"
PRINT "QUANTITY, TYPE 'GOTO 5000', !"
D1=TR*1.023E6;XX%=INT(D1/U2)
IF DD%(0,1)<DD%(0,2) THEN 12200
DD%(0,1)=DD%(0,1)-DD%(0,2)
FOR M=1 TO 16
DD%CM,1=DD%CM,2-XX%
NEXT M
IF DD%(0,2)>DD%(0,1)+DD%(0,4) THEN 11390
DD%(0,2)=DD%(0,2)+(32767-DD%(0,4))
GOTO 11400
DD%(0,2)=DD%(0,2)-DD%(0,4)
FOR M=1 TO 16
DD%(M,2)=DD%(M,2)-DD%(M,3)
NEXT M
J=5
N=3
FOR M=0 TO 16
DD%(M,N)=0
NEXT M
IF DD%(0,J+1)=0 AND DD%(0,J+3)=0 THEN 12300
IF DD%(0,J-1)>DD%(0,J+1) THEN 11700
DD%(0,N)=DD%(0,J-1)+(32767-DD%(0,J+1))+DD%(0,N)
GOTO 11800
DD%(0,N)=DD%(0,J-1)-DD%(0,J+1)+DD%(0,N)
FOR M=1 TO 16
DD%(M,N)=DD%(M,J-1)-DD%(M,J)+DD%(M,N)
IF DD%(M,N)>30700 THEN 12600
NEXT M
IF DD%(0,N)>XX% THEN 12100
J=J+2
12040 GOTO 11600
12100 N=N+1
12140 GOTO 11500
12200 REM PRINT OUT MESSAGE TO IMPLY RAW DATA NOT RIGHT
12220 PRINT"** SOMETHING WRONG ABOUT RAW DATA"
12240 PRINT
12260 GOSUB 8101:REM BEEP
12280 GOTO 12700
12300 REM CALCULATE THE ACTUAL TOTAL COVERED TIME
12320 NC=N-1:REM LAST SET DO NOT HAVE INT. DATA
12340 TT=0
12360 FOR Z=1 TO NC
12380 TT=TT+DDSC0,Z>
12410 NEXT Z
12420 TT=TT*U2/(1.023E6):REM IN UNIT OF SEC
12440 PRINT"** TOTAL COVERED TIME IS";TT;"SEC"
12460 PRINT";NC;"SETS OF DATA ARE OBTAINED!"
12480 PRINT
12500 N=NC
12520 GOTO 12700
12600 REM TIME OF RESOLUTION NOT RIGHT
12620 PRINT"** TR IS TOO LONG & HAS TO BE SHORTER!"
12640 PRINT
13100 REM SET STANDBY POTENTIAL
13120 PRINT"STANDBY VOLT ON BOTH DAC :";SV;"VOLT"
13140 PRINT
13160 IF DM$="Y" THEN 13300
13200 INPUT"STANDBY VOLT(+1.0)";SV
13220 PRINT
13300 REM CONVERT ANALOG POTENTIALS TO DIGITAL
13320 DM%=INTCSV*4095/6.012+2042>
13340 SH%=INTCDM%/256)
13360 SL%=INTCDM%-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 PRINT"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(6@.0)"
14560 INPUT* FR$ ON SCALE &0.0";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
14710 DM%=INT(FV*4095/6.0)+2037
14720 IL%=INT(DM%/256)
14730 FL%=INT(DM%-IL%*256)
14740 FH%=INT(DM%/256)
14750 FL%=INT(DM%-FH%*256)
14760 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 IF DM$="Y" THEN 15700
15110 PRINT"U1 CLOCK TIME = U1*<1/60) SEC"
15120 INPUT"U1 VALUE WANTED(<=60)";U1
15130 PRINT"LEAST U2 BYTE DEPENDS ON U1 VALUE(<64=2 S)"
15140 INPUT"LEAST U2 BYTE(>=64)";U2
15150 CP=(127*256+255)*U2/(1.023*10^8)
15160 PRINT"CLOCK PERIOD(CP) =";CP;="SEC"
15170 PRINT
15180 IF DM$="Y" THEN 15700
15190 PRINT"TOTAL COVERED TIME = (CH*256+CL)*CP SEC"
15200 INPUT"COUNTER HI-BYTE(=0)";CH
15210 INPUT"COUNTER LO-BYTE(=0)";CL
15220 CP=(CH*256+CL)*CP
15230 PRINT"TOTAL COVERED TIME =";CT;="SEC"
15240 PRINT"AROUND 60 SEC BE OK"
15250 GOTO 15000
15300 POKE 49909,U1:REM $C2F1=U1BLO
15310 POKE 49916,U2:REM $C2F2=U2ALO
15320 POKE 49917,CL:REM $C2F3=CNTLO
15330 POKE 49918,CH:REM $C2F4=CNTHI
15340 RETURN
16660 GOSUB 9000:REM BEEP
20000 REM PRINT OUT ORIGINAL DATA
20100 OPEN4,4:CMD4
20200 PRINT"SAMPLE LABEL : ";LB$
20300 PRINT"FLOW RATE : ";FR$
20400 PRINT"POTENTIAL ON DAC1 : ";IV1;"VOLT"
20500 PRINT"POTENTIAL ON DAC2 : ";IV2;"VOLT"
20600 PRINT
20700 PRINT"U1 VALUE =U1"
20800 PRINT"LEAST U2 BYTE =";U2
20900 PRINT"U2 CLOCK PERIOD(CP) =";CP;="SEC"
21000 PRINT"SET-UP TOTAL COVERED TIME =";CT;="SEC"
21100 GOTO 21500
21200 IF Z<0 THEN END
21300 INPUT"NEW STARTING SET ";Z
21400 PRINT** Z MUST. <=";N;" >= MULTIPLE OF 5"
21500 IF Z<0 THEN END OF PRINTING
21600 REM PRINT OUT ORIGINAL DATA
21700 PRINT"AFTER ELECTRODES REACTIVATED,"
21800 PRINT"PROGRAM STARTED TO COLLECT DATA";TD;"SEC LATER!!"
20600 OPEN 4, 4: CMD 4
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
20830 PRINT
20840 PRINT# 4: CLOSE 4
20900 GOTO 20500
21000 RETURN

READY.
APPENDIX D

SOFTWARE
"DATAQ"
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.
; ADC SUBROUTINE "DATACQ"
; FOR DISSERTATION
; 2/21/89

SET = $DE00
SAX = $FD
SAV = $FE
LATCH = $DE60

; SETUP OF ADC PIA REGISTERS
; FIRST, PUTS S&H IN HOLD STATE
; (NOTE 11 MUST BE IN SAMPLE STATE
; BEFORE ENTRY)
; WILL LEAVE S&H IN SAMPLE STATE

ASETUP LDA #$0

LDA AC
STA AC

LDA #$3C
STA BD

LDA #$3C
STA BC

RTS

; ONE ADC CONVERSION
; LOW DATA IN REG-X & HI DATA IN REG-A

CNVRT LDA #$34

STA AC

LDA BD

LDA #$3C

STA BC

LDA BD

LDA #$3C

LDX AD

STY AC

RTS
# MAIN ROUTINE

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MAIN ROUTINE

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00088 C072 E9 01 SEC $1
00089 C074 BD F3 C2 STA CNTLO
00090 C077 AD F4 C2 LDA CNTHI
00091 C07A E7 06 SEC $0
00092 C07C BD F4 C2 STA CNTHI
00093 C07F DD 05 BNE CHKU1
00094 C081 AD F3 C2 LDA CNTLD
00095 C084 F8 25 BEQ CLRMSK
00096 C086 A9 02 CHKU1 LDA #$00000010
00097 C088 2C 0D DC BIT $DC0D
00098 C08B DD 0F BNE SAVERST
00099 C08D A9 08 LDA $0
00100 C08F BD F9 C2 STA FLAG
00101 C092 28 F3 C1 JSR R7000
00102 C095 AD F0 C2 LDA FLAG
00103 C098 C9 01 CMP $1
00104 C09A DD EA BNE CHKU1
00105 C09C 28 F3 C0 SAVERST JSR STRCLK
00106 C09F 28 36 C2 JSR R9000
00107 C0A2 28 15 C1 JSR MOVPTR
00108 C0A5 A9 90 LDA #$90
00109 C0A8 25 FC CMP ARPTR+1
0010A C0AB 10 BC BPL CHKU2
00111 C0AC 3D CLRMSK CLI
00112 C0AC A9 7E LDA #$7E
00113 C0AE BD 0D DC STA $DD00
00114 C0B1 A9 7F LDA #$7F
00115 C0B3 BD 0D DD STA $DD0D
00116 C0B6 6B RTS
00117 C0B7 A9 FF MSKINT LDA #$FF
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00119 C0BC BD 0D DD STA $DDDD
00120 C0BF 6A RTS
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00122 C0C2 BD 07 DC STA $D007
00123 C0C5 AD F1 C2 LDA UDBL
00124 C0C8 BD 06 DC STA $D006
00125 C0CB 6A RTS
00126 C0CC A9 7F SETU2 LDA $127
00127 C0CE BD 07 DD STA $D007
00128 C0D1 A9 FF LDA $255
00129 C0D3 BD 06 DD STA $D006
00130 C0D6 A9 09 LDA $0
00131 C0DB BD 05 DD STA $D005
00132 C0DB A9 F2 C2 LDA UCLK
00133 C0DE BD 04 DD STA $D004
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00135 C0E2 A9 5A STFCLK LDA #$54
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**ERRORS = 0000B**
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 CFAE. 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$= DATE OF RUNNING EXPERIMENT
62 REM LBS= SAMPLE LABEL (SPECIES & CONC.)
64 REM FR$= 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 = U1LO
72 REM U2 = U2ALO
73 REM TT = ACTUAL TOTAL COVERED TIME
74 REM NT = TOTAL DATA SET # SAVED FROM EXPT.
75 REM RMS= 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
85 REM RC(M)=AVE. RESIDUAL CURRENT
88 REM SC(M,SS)=PEAK AREA/HEIGHT FOR SAMP. CURRENT
89 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 R(16,200), RC(16), SC(16,6), NA(16), TP(200)
120 DIM MN(16), SF(16), RD(16), R(16), CA(16), SF(16), SL(16)
140 IDS="'NONE'": REM DATA FILE ID
150 PRINT
200 PRINT "** MAKE SURE CU LINE 11372@ CORRECT,"
220 PRINT "(2) RIGHT DISK IN DRIVE,"
240 PRINT "(& 3) BEEP IS HEARD!"
260 PRINT
280 GOSUB 14000: REM BEEP
300 SS=1: REM SET # FOR REPEATABILITY
320 IF DM$<>"Y" THEN 700
340 PRINT "***********************
350 PRINT "* TYPE 'Y' & LOOK FILE *
360 PRINT "* NAME STARTS WITH 'A-' *
380 PRINT "* THEN TYPE 'CONT' *
400 PRINT "***********************
420 PRINT
440 STOP
700 PRINT "***********************
720 PRINT "* FOR AREA DATA FILE ID, *
740 PRINT "* IT STARTS WITH 'A-' *
760 PRINT "***********************
780 PRINT
800 PRINT "PREVIOUS AREA DATA FILE ID : "; IDS
820 INPUT "NEW AREA DATA FILE ID(A-*)"; IDS
8413 INPUT"IS FILE NAME OK(Y/N)";DM$
860 PRINT
880 IF DM$<"Y" THEN 500
900 PRINT"** IF DRIVE LIGHT BLINKS,"
920 PRINT" STOP PROGRAM IMMEDIATELY. THEN"
940 PRINT" TYPE 'CLOSE 2', FOLLOWED BY TYPING"
960 PRINT" 'GOTO 500' !!"
980 PRINT
1000 REM GET DATA FROM A FILE TO NORMALIZE ELECTRODE AREA
1020 OPEN 2,8,2.ID$","S,R"
1040 INPUT#2,DA$
1060 INPUT#2,FR$
1080 INPUT#2,UL:REM UPPER LIMIT OF S.W.
1090 INPUT#2,LL:REM LOWER LIMIT OF S.W.
1100 INPUT#2,HZ:REM FREQ. OF S.W.
1120 INPUT#2,DU:REM DUATION OF S.W.
1140 INPUT#2,TD:REM TIME OF DELAY
1160 INPUT#2,IV
1180 INPUT#2,FV
1200 INPUT#2,U1
1220 INPUT#2,U2
1240 INPUT#2,IT
1260 INPUT#2,NT
1280 IF IV=FV THEN 1500
1300 CLOSE 2
1320 PRINT"**********************************"
1340 PRINT"* PROGRAM IS TO NORMALIZE AREA *
1360 PRINT"* LOAD WRONG DATA FILE *
1380 PRINT"**********************************"
1400 STOP
1420 REM TREAT DATA BEFORE PUT INTO A MATRIX
1440 CY=1.02364:REM CY=FREQUENCY OF TIMER
1460 GOSUB 13000:REM LOAD CAPACITANCE FOR EACH INTEGRATOR
1480 REM ORIGINAL U2 SET-UP FOR 1 CYCLE
1500 INPUT#2,TM$
1520 RS(0,0)=TM%*U2/CY
1540 REM CALC. REAL APPLIED POTENTIAL
1560 FOR M=1 TO 16
1580 INPUT#2,TM$
1600 RS(M,N)=TM%/204.5*CA(M)/RS(0,N)
1610 NEXT M
1620 NEXT N
1640 CLOSE 2
1660 GOSUB 14000:REM BEEP
1680 GOSUB 9900:REM CHANGE REMARK
1700 REM SHOW ALL PARAMETERS ON SCREEN
1720 PRINT"** PUSH 'G' TO GO ON,"
1740 PRINT" THEN HOLD 'CTRL' KEY TO VIEW"
1760 GET A$:IF A$<"G" THEN 2600
1780 PRINT
21370 GOSUB 9700:REM SHOW SAMPLE ID
2180 GOSUB 9000:REM SHOW EXPT. CONDITIONS
211110 INPUT "ARE ALL ABOVE CORRECT (Y/N)" ; DM$ 
2120 PRINT 
214111 IF DM$ = "Y" THEN 2200 
2160 PRINT "** MAKE CORRECTION THEN TYPE 'CONT' !!" : STOP 
2180 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 
2301!1 PRINT " # "; M, RS(M,0) 
2320 NEXT 
234121 PRINT 
241210 RF = 0: RL = 0 
242121 FOR M = 1 TO 16 
244111 SFC(M) = 0: SLC(M) = 0 
246111 NEXT 
2500 REM CHECK APPLIED VOLTAGE ON ELECTRODE 
2520 BN = 2: ED = 21: REM START FROM SET 3 TO SET 23 
2600 PRINT "** ENTER ELECTRODE #'S TO CHECK !!" 
2620 PRINT "END SET TO CHECK IS OVER RANGE **" 
2700 PRINT 
2720 IF DM$ <> "Y" THEN 2600 
2740 IF X1 <= 0 THEN 3500 
2800 PRINT "** PUSH 'G' TO GO ON. THEN DETERMINE THE WAY & FIND RANGES" 
2820 PRINT "TO NORMALIZE ELECTRODE SURFACE AREA" 
2860 PRINT 
2900 GET AS: IF AS <> "G" THEN 2900 
2920 GOSUB 9000: 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 SMALLER THAN" ; INT 
3220 PRINT 
3240 INPUT "INITIAL SET & END SET : "; BN, ED 
3260 PRINT "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 
3520 PRINT "ARE BOTH OK (Y/N)" ; DM$ 
3540 PRINT 
3560 IF DM$ <> "Y" THEN 2600 
3580 GOSUB 12000: REM CHECK RANGES SETUP 
3590 INPUT "ARE ALL OK (Y/N)" ; DM$ 
3570 PRINT 
3600 IF DM$ <> "Y" THEN 2600 
3620 INPUT "PRINT OUT DATA TO PLOT (Y/N)" ; DM$ 
3640 PRINT 
3660 IF DM$ = "N" THEN 3600 
3680 INPUT "HAVE PARAMETERS PRINTED OUT (Y/N)" ; DM$
3680 PRINT
3700 IF DM$="Y" THEN 3790
3720 OPEN 4, 4: CMD4
3740 GOSUB 9000
3750 PRINT CHR$ 121: REM TOP OF THE NEXT PAGE
3760 PRINT# 4
3780 CLOSE 4
3790 GOSUB 14000
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$="Y" THEN 5010
3980 STOP
4000 REM SET RESI.CURRENT & TOTL.SAMP.CURRENT
4010 PRINT "WHICH WAY TO NORM. ELECTRODE AREA ?";
4020 INPUT "(1) BY PEAK AREA; (2) BY PEAK HEIGHT" ; OP
4030 INPUT " IS IT OK (Y/N)" ; DM$
4040 PRINT
4050 IF DM$="Y" THEN 4010
4060 IF OP=1 THEN GOSUB 15000
4070 IF OP=1 THEN 4100
4080 IF OP=2 THEN GOSUB 15500
4100 REM SHOW AVERAGED CURRENTS ON SCREEN
4110 PRINT "ELECTRODE RESI.CURRENT + NET SAMP.CURRENT"
4120 PRINT
4130 FOR M=1 TO 16
4140 PRINT " M; RC(M); SC(M, SS)
4160 NEXT M
4180 PRINT
4200 INPUT "PRINT OUT RESULTS (Y/N)" ; DM$
4220 PRINT
4240 PRINT
4260 IF DM$="N" THEN 5000
4280 GOSUB 8400: REM SURE PRINTER ONLINE
4300 GOSUB 9400: REM HAVE PARAMETERS PRINTED OUT (Y/N) ; DM$
4320 PRINT
4340 IF DM$="Y" THEN 4600
4360 OPEN 4, 4: CMD4
4380 GOSUB 9000: REM PARAMETERS
4400 PRINT CHR$ (12): REM TOP OF THE NEXT PAGE
4420 PRINT# 4
4440 CLOSE 4
4460 GOSUB 5900: REM CHANGE REMARK
4480 OPEN 4, 4: CMD4
4500 GOSUB 9700: REM SHOW SAMPLE ID & REMARK
4520 GOSUB 17000: REM RESULTS OF CURRENTS
4540 PRINT CHR$(12): REM GET TO THE TOP OF THE NEXT PAGE
4560 PRINT# 4: CLOSE 4
4580 INPUT "IS PRINTOUT OK (Y/N)" ; DM$
4600 PRINT
4620 PRINT
4640 IF DM$="Y" THEN 4300
4660 INPUT "ARE RESULTS OK (Y/N)" ; DM$
4680 PRINT
4700 IF DM$="V" THEN 5400
4720 INPUT "CHECK THE SAME SET AGAIN (Y/N)" ; DM$
4740 PRINT
4760 IF DM$="N" THEN 3000
4780 INPUT "LOAD ANOTHER SET DATA (Y/N)" ; DM$
4800 PRINT
4820 IF DM$="Y" THEN 3000
4840 PRINT "WHAT DO YOU WANT ?" : STOP
4860 PRINT
5300 GOTO 5000
5400 INPUT "RESULTS FOR STATISTICS (Y/N)" ; DM$
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
5560 INPUT "DONE REPEATABILITY CALC. (Y/N)" ; DM$
5580 PRINT
5600 IF DM$ = "Y" THEN 5810
5620 PRINT
5640 IF DM$ = "N" THEN 5710
5660 INPUT "MORE? ARE YOU SURE (Y/N)" ; DM$
5680 PRINT
5700 IF DM$ = "Y" THEN 4110
5720 STOP
5740 GOTO 5600
5800 INPUT "DONE? ARE YOU SURE (Y/N)" ; DM$
5820 PRINT
5840 IF DM$ = "N" THEN 5910
5900 PRINT "-- APPLY STATISTICS TO THE RESULTS NOW!"
5920 PRINT
5940 IF DM$ = "Y" THEN 6110
5960 INPUT "NEW STANDARD ELECTRODE (2)" ; ES
6000 INPUT "IS IT OK (Y/N)" ; DM$
6020 PRINT
6040 IF DM$ = "Y" THEN 6200
6060 PRINT
6080 IF DM$ = "N" THEN 6300
6100 INPUT "PRESENT ELECTRODE SURFACE AREA" ; ES
6120 INPUT "IS IT OK (Y/N)" ; DM$
6140 PRINT
6160 IF DM$ = "Y" THEN 6310
6180 INPUT "NEXT M" ; M$useppe
6200 GOTO 6000
6220 REM TOTAL SET FOR REPEATABILITY IS 'SS'
6240 GOSUB 10000
6260 REM CALCULATE NORM.AREA FROM A SINGLE SET OF DATA
6280 PRINT "NORMALIZE ELECTRODE SURFACE AREA!"
6300 PRINT "IS IT OK (Y/N)" ; DM$
6320 PRINT
6340 IF DM$ = "Y" THEN 6390
6360 INPUT "MORE? ARE YOU SURE (Y/N)" ; DM$
6380 PRINT
6400 IF DM$ = "N" THEN 7010
6420 GOTO 6100
6440 BA=MN(ES) ; REM TAKE ES ELECTRODE AS STANDARD
6460 FOR M=1 TO 16
6480 NA(M)=MN(M)/BA
6500 NEXT M
6520 GOSUB 7500 ; REM SHOW NORM.AREA
6540 PRINT
6560 IF DM$ = "Y" THEN 6600
6580 PRINT "MAKE SURE RIGHT DISK IN DRIVE!!"
6600 PRINT
6620 INPUT "WANT TO CHECK DISK (Y/N)" ; DM$
6640 PRINT
6660 IF DM$ = "N" THEN 6700
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 GOSUB 9900 ; REM CHANGE REMARK
6780 OPEN 4,4,CHM4
6800 GOSUB 18100 ; REM SHOW SAMPLE, EXPT. DATE, & REMARK
6820 GOSUB 7500 ; GOSUB 7700
6840 PRINT CHR$(12) ; REM TOP OF THE NEXT PAGE
6860 PRINT$;CLOSE4
6880 PRINT "SAVE NORM. AREA ON DISK (Y/N)" ; DM$
6900 PRINT
6920 IF DM$ = "N" THEN 7000
6940 PRINT "MAKE SURE RIGHT DISK IN DRIVE!!"
6960 PRINT
6980 PRINT
7000 INPUT "WANT TO CHECK DISK (Y/N)" ; DM$
7020 PRINT
7040 IF DM$ = "N" THEN 6700
7060 STOP
7080 GOTO 6500
7100 REM SAVE ELECTRODE SURFACE AREA TO A SEQ. FILE
7120 REM N-A-* (N-H-*) = NORM. ELECTRODE SURFACE AREA
7140 PRINT
7160 GOSUB 9900 ; REM CHANGE REMARK
7180 OPEN 4,4,CHM4
7200 GOSUB 18100 ; REM SHOW SAMPLE, EXPT. DATE, & REMARK
7220 GOSUB 7500 ; GOSUB 7700
7240 PRINT CHR$(12) ; REM TOP OF THE NEXT PAGE
7260 PRINT$;CLOSE4
7280 PRINT "SAVE NORM. AREA ON DISK (Y/N)" ; DM$
7300 PRINT
7320 IF DM$ = "N" THEN 7000
7340 PRINT "MAKE SURE RIGHT DISK IN DRIVE!!"
7360 PRINT
7380 PRINT
7400 INPUT "WANT TO CHECK DISK (Y/N)" ; DM$
7420 PRINT
7440 IF DM$ = "N" THEN 6700
7460 STOP
7480 GOTO 6500
7500 PRINT "LATEST DATA FILE ID : " ; ID$
7520 PRINT "NORM. AREA ID (N-A/H-*)" ; NT$
7540 PRINT "FILE NAME OK (Y/N)" ; DM$
7560 PRINT
7580 IF DM$ = "N" THEN 6800
7600 OPEN 2,2,NI$=*,S,W
7620 FOR M=0 TO 16
6940 PRINT#2,NA(M)
6960 NEXT M
6980 CLOSE2
7000 INPUT "CHECK SAME SET AGAIN(Y/N)" ; DM$
7020 PRINT
7040 IF DM$="Y" THEN 7060
7060 INPUT "ADD ONE MORE SET FOR STAT.(Y/N)" ; DM$
7080 PRINT
7100 IF DM$="Y" THEN 7300
7120 PRINT
7140 IF DM$="Y" THEN 7400
7160 INPUT "REDO STATISTICS W/O LAST SET(Y/N)" ; DM$
7180 PRINT
7200 IF DM$="Y" THEN 7500
7220 PRINT
7240 IF DM$="Y" THEN 7600
7260 SE=SS-1
7280 GOTO 5600
7300 INPUT "START OVER AGAIN(Y/N)" ; DM$
7320 PRINT
7340 IF DM$="Y" THEN 7400
7360 PRINT "WHAT DO YOU WANT ?" ; PRINT; STOP
7380 GOTO 7000
7400 END
7500 REM SHOW APPLIED VOLTAGE & NORMALIZED AREA
7520 PRINT "ELECTRODE", "POTENTIAL NORM.AREA"
7540 PRINT
7560 FOR M=1 TO 16
7580 PRINT #1, '";M, RS(M,0); NA(M)
7600 NEXT M
7620 PRINT
7640 PRINT
7660 RETURN
7700 REM MESSAGE TO SHOW THE METHOD
7720 IF OP=1 THEN PRINT" ** RESULTS ARE BASED ON PEAK AREA !"
7740 IF OP=2 THEN PRINT" ** RESULTS ARE BASED ON PEAK HEIGHT !"
7760 PRINT
7780 PRINT
7800 RETURN
8000 REM CHECK EACH SET DATA FOR ALL ELECTRODE
8020 PRINT" ** END OF CHECK IF NN < 0 !"
8040 INPUT" NEW DATA SET # TO CHECK(NN)" ; NN
8060 PRINT
8100 IF NN<0 THEN 8300
8120 PRINT " M DATA(NN)
8140 FOR M=0 TO 16
8160 PRINT M, RS(M,NN); RS(M,NN+1)
8180 NEXT M
8200 PRINT
8220 PRINT " DATA SET # : ";NN
8240 PRINT
8260 GOTO 8220
8280 RETURN
8400 REM CHECK WHETHER PRINTER IS READY
8420 PRINT" ** MAKE SURE PRINTER ONLINE"" 
8440 PRINT " THEN PUSH 'G' TO GO ON !"
8460 PRINT
8470 IF A$<"G" THEN 8470
8470 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
PRINT "SET:";" ELECTRODE";X1;" ELECTRODE";X2
FOR N=EN TO ED
PRINT N;RS(X1,N);RS(X2,N)
NEXT N
GOSUB 13500:REM RECORD RANGE
REM SHOW ALL PARAMETERS ON SCREEN
PRINT "EXPERIMENTAL CONDITIONS --"
PRINT " FLOW RATE -- ";FR$
PRINT " SQUARE WAVE FOR PRECONDITION --";
PRINT " POTENTIAL OF UPPER LIMIT : ";UL;"VOLT"
PRINT " POTENTIAL OF LOWER LIMIT : ";LL;"VOLT"
PRINT " FREQUENCY : ";HZ;"HERTZ"
PRINT " DURATION : ";DU;"SEC"
PRINT IV;"VOLTS OUTPUT FROM DAC7548 #1"
PRINT FV;"VOLTS OUTPUT FROM DAC7548 #2"
PRINT " WAIT";TD;"SEC TO SUBSIDE CHARGING CURRENT DOWN !"
PRINT " U2ALO IS";U2
PRINT " TOTAL COVERED TIME IS";TT;"SEC"
PRINT U1 TIMER SETUP AS";UL1;" (1/60) SEC"
PRINT TIME OF RESOLUTION IS ABOUT";TR;"SEC"
PRINT "SETS OF DATA COLLECTED"
PRINT "REFERENCE ELECTRODES : ZINC IN 1 M SODIUM ACETATE SOLUTION."
PRINT "WORKING ELECTRODES : CARBON FIBER ARRAY ELECTRODE"
10600 D2=0
10620 D3=0
10640 FOR I=1 TO 16
10660 D2=SC(M,I)-MN(M)
10680 D3=D2*D2+D3
10720 FOR X=1 TO I
10740 D3=SDR(D3/(I-1)):REM SUBSTITUTE I-1 WITH I
10760 RD(M)=SD(M)/MN(M)*100
10800 NEXT M
10840 IF DM$="N" THEN 11300
10860 GOSUB 9900:REM CHANGE REMARK
10900 OPEN 4,4:CMD4
11000 GOSUB 182100:REM SAMPLE, EXPT. DATE, & REMARK
11040 GOSUB 11500:REM SHOW RESULTS
11080 PRINT CHR$(12)
11120 PRINT#4:CLOSE4
11160 RETURN
11200 REM RECORD RANGE OF SAMPLE CURRENT MAXIMUM
11240 PRINT"*** RANGES OF SAMPLE CURRENT MAXIMUM***
11280 PRINT FOR ELECTRODE #";X1
11320 PRINT RANGE FOR SAMPLE CURRENT";SF(X1),SL(X1)
11360 PRINT FOR ELECTRODE #";X2
11400 PRINT RANGE FOR SAMPLE CURRENT";SF(X2),SL(X2)
11440 PRINT ARE ALL OK (Y/N)";DM$
11480 IF DM$="Y" THEN 13600

13940 RETURN
14000 REM GENERATE A BEEPER (REF. P. 105)
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,lli:NEXT
14240 POKE S+5,9: POKE S+6,0
14260 POKE S+24,15
14280 HF=37: LF=16: 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
15600 REM GET RESI.CURRENT & TOTAL.SAMP.CURRENT BY PEAK AREA
15820 PRINT"-- HANG ON, CALC. PEAK AREA !"
15940 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 SCM(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 & TOTAL.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 SCM(SS)=0
15760 FOR N=SF(M) TO SL(M)
15780 SCM(SS)=SC(M,SS)+RS(M,N)
15800 NEXT N
15820 SCM(SS)=SC(M,SS)/SL(M)-SF(M)+1
15840 SCM(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
!6040 PRINT" END OF PRINT IF I<0 !"
16060 PRINT
16100 INPUT" 1ST SET, LAST SET"; BN, ED
16120 INPUT" ARE BOTH OK(Y/N)"; DM$
16140 PRINT
16160 IF DM$="Y" THEN 16100
16180 IF BN<0 THEN 17000
16200 REM PRINT OUT THE TIME AT WHICH DATA WERE COLLECTED
16220 OPEN 4,4:CMD
16240 PRINT"AREA DATA FILE ID : ";ID$
16260 PRINT
16280 PRINT" SET", "TIME DATA COLLECTED"
16300 PRINT"SET","TIME(DATA COLLECTED)"
16320 PRINT
16340 FOR N=BN TO ED
16360 PRINT N,RSC$,
16380 NEXT N
16400 PRINT CHR$(12):REM GET TO THE TOP OF NEXT PAGE
16420 PRINTit4
16440 CLOSE4
16500 PRINT** END OF PRINT IF FT<0 !"
16520 PRINT" CHOOSE 4 ELECTRODES TO PRINT DATA !"
16540 INPUT" 1ST,2ND,3RD,4TH ELECTRODE";FT,SD,TD,FH
16560 PRINT" ARE ALL ABOVE OK(Y/N)"; DM$
16580 PRINT
16600 IF DM$="Y" THEN 18000
16620 OPEN 4,4:CMD
16640 PRINT"ELECTRODE";
16660 PRINT" # ";FT," LL POT. TO DIGITAL"
16680 DM$=INT(DM$/4095/0.6111+2)
16700 RL$=INT(DM$-RH$*256)
16720 RETURN
17000 REM PRINT OUT AVE. RESIDUAL & NET SAMPLE CURRENT
17100 PRINT"ELECTRODE"," CURRENT", " RESIDUE NET SAMPLE 1ST LAST"
17200 PRINT" # ";M," RC(M),SC(M),SS,",;SF(M),",;SL(M)
17280 NEXT M
17300 PRINT
17400 PRINT
17500 PRINT" PRESENT AS AVERAGED RESULTS !!"
17600 RETURN
17700 REM SHOW SAMPLE, EXPT. DATE, & REMARK
17800 PRINT"SAMPLE -- ";LB$
17900 RETURN
18100 PRINT" DATE OF EXPERIMENT : ";DA$
18200 RETURN
18300 RETURN
20000 REM PRINT OUT ORIGINAL DATA
20100 OPEN 4,4:CMD
20200 PRINT" SAMPLE LABEL : ";LB$
20220 RETURN
20300 PRINT
2020 PRINT" INIT VOLT :";VI;" VOLT"
2030 PRINT" FINAL VOLT :";VF;" VOLT"
2040 PRINT
2050 PRINT" U1 VALUE :";U1
2060 PRINT" LEAST U2 BYTE =";U2
2070 PRINT" U2 CLOCK PERIOD (CP) =";CP;" SEC"
2080 PRINT" SET-UP TOTAL COVERED TIME =";CT;" SEC"
2090 PRINT
2100 PRINT" AFTER RECONDITIONING ELECTRODES,"
2110 PRINT" TD;SEC LATER, STARTED TO COLLECT DATA!"
2120 PRINT
2130 PRINT 2140 PRINT#4:CLOSE4
2150 PRINT** Z MUST <=";N;" & = MULTIPLE OF 5"
2160 PRINT" IF Z<0 THEN END OF PRINTING "
2170 INPUT" NEW STARTING SET #:";Z
2180 PRINT
2190 IF Z<0 THEN 21000
2200 OPEN4,4:CMD4
2210 PRINT
2220 PRINT" Z =";Z
2230 PRINT
2240 PRINT" M DD%Z DD%Z+1 DD%Z+2 DD%Z+3 DD%Z+4"
2250 FOR M=0 TO 16
2260 PRINT M;DD%(M,Z);DD%(M,Z+1);DD%(M,Z+2);DD%(M,Z+3);DD%(M,Z+4)
2270 NEXT M
2280 PRINT
2290 PRINT#4:CLOSE4
2300 GOTO 20500
23100 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".

Start

Load Data for Plotting Pseudo-Voltammogram and Normalization Factors of CFAEs

Convert Data to Potentials and Normalized Currents, Respectively

Determine Ranges for Normalized Residual Currents and Normalized Total Currents, Respectively

Average Normalized Currents in Ranges, Respectively

Calculate Averaged Normalized Net Currents and Print them on Paper with Experimental Conditions

End
REM *******************************
2/13/1989
* RESULT *
* USE CALC. CAPACITANCE & *
* NORM. ELECTRODE AREA TO *
* CALC. PEAK AREA/HEIGHT *
* OF NET SAMPLE CURRENT. *
* STATISTICS IS INCLUDED. *
* DA$= DATE OF RUNNING EXPERIMENT *
* LB$= SAMPLE LABEL (SPECIES & CONC.) *
* FR$= FLOW RATE (PUMP SCALE) *
* IV INITIAL VOLTAGE ON DAC 7548 #1 *
* FV FINAL VOLTAGE ON DAC 7548 #2 *
* TR TIME RESOLUTION(TR SEC) *
* U1 U1BLO *
* U2 U2ALO *
* TT ACTUAL TOTAL COVERED TIME *
* NT TOTAL DATA SET # SAVED FROM EXPT. *
* RS(M,N)=RESULTS FROM CALCULATION *
* RS(M,N)=INTEGRATION TIME *
* RS(M,N)=REAL APPLIED VOLTAGE ON EVERY ELECTRODE *
* RB(M)=AVE. RESI.CURRENT AT BEGIN *
* RE(M)=AVE. RESI.CURRENT AT END *
* RC(M,SS)=AVE. RESIDUAL CURRENT *
* SC(M,SS)=PEAK AREA FOR SAMP.CURRENT *
* SA(M,SS)=AVE. PEAK AREA OF SAMP.CURRENT *
* TP(N)=TIME AT WHICH DATA COLLECTED *
* NA(M,SS)=NORM.AREA OF ELECTRODE M FROM "SS" DATA SET *
* EA(M)=AVE. SURFACE AREA OF ELECTRODE M *
* CA(M)=CAPACITANCE OF ELECTRODE M *
* TD(16),RD(16),SC(16,6),NA(16),TP(200) *
* SD(16),RD(16),R(16),CA(16),SA(16) *
* SF(16),SL(16) *
* ID$="NONE":REM DATA FILE ID *
* MAKE SURE (1)LINE 1072(-1 CORRECT , " ** *
* (2) RIGHT DISK IN DRIVE, &"
* BEEP IS HEARD !"
* (3)BEEP IS HEARD !"
* REM BEEP *
* REM SET # FOR REPEATABILITY *
* INPUT"NOW SAMPLE DATA FILE ID(Y/N)":DM$ *
* IF DM$="Y" THEN 700 *
* Type "DM" & LOOK FILE " ** *
* NAME STARTS WITH 'S'- " ** *
* THEN TYPE 'CONT' &"
* Printing"***************" *
* STOP *
* PRINT ""
729 PRINT"* FOR SAMPLE DATA FILE ID, *"
740 PRINT* IT STARTS WITH 'S-' *"
760 PRINT*******************************
780 PRINT
800 PRINT"PREVIOUS SAMPLE DATA FILE ID: ";ID$
820 INPUT"NEW SAMPLE DATA FILE ID(S-)*";ID$
840 INPUT"IS FILE NAME OK(Y/N)";DM$
860 IF DM$<"Y" THEN 500
900 PRINT"-- IF DRIVE LIGHT BLINKS,"
910 PRINT"STOP PROGRAM IMMEDIATELY. THEN"  
920 PRINT"TYPE 'CLOSE 2', FOLLOWED BY"  
930 PRINT"TYPING 'GOTO 50' !!"  
940 PRINT  
950 PRINT"WAIT (ABOUT 5 MINUTES)"
960 PRINT"TO LOAD & TREAT DATA !!"
980 PRINT
1000 REM GET SAMPLE DATA TO NORMALIZE
1020 OPEN 2,8,2,ID$+,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 DURATION 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
1320 IF IV<FV THEN 1500
1340 CLOSE 2
1360 PRINT"** PROGRAM TO NORMALIZE SAMPLE DATA"
1380 PRINT"LOAD WRONG DATA FILE !!"  
1400 PRINT  
1420 REM TREAT DATA BEFORE PUT INTO A MATRIX
1440 CY=1.023E6:REM CY=FREQUENCY OF TIMER
1460 GOSUB 13000:REM LOAD CAPACITANCE FOR EACH INTEGRATOR
1480 REM ORIGINAL SET UP OF U2 TIMER
1500 INPUT#2,TM$
1520 RS(0,0)=TM%*U2/CY
1540 REM CALC. REAL APPLIED POTENTIAL
1560 FOR M=1 TO 16
1580 INPUT#2,TM$
1600 RS(M,0)=TM%/298*CA(M)/RS(0,0)/NA(M)
1620 NEXT M
1640 NEXT N
1660 GOSUB 14000:REM BEEP
1680 GOSUB 99001:REM CHANGE REMARK
2000 REM SHOW ALL PARAMETERS ON SCREEN
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$="Y" THEN 3790
3720 OPEN4,4:CMD4
3740 GOSUB 9000
3760 PRINT 
3780 IF DM$="Y" THEN 3790
3800 INPUT"GET ALL RANGES(Y/N)";DM$
3820 PRINT
3840 IF DM$="Y" THEN 41111
3860 INPUT"CHECK THE SAME SET AGAIN(Y/N)";DM$
3880 PRINT
3900 IF DM$="Y" THEN 3790
3920 INPUT"LOAD ANOTHER DATA SET<Y/N)";DM$
3940 PRINT
3960 IF DM$="Y" THEN 51110
3980 STOP
4000 REM GET RESI.CURRENT & NET SAMPLE CURRENT
4020 PRINT"WHICH WAY TO GET DATA FOR VOLTAMMOGRAM"
4040 INPUT" (1)BY PEAK AREA; (2)BY PEAK HEIGHT";OP
4060 INPUT" IS IT OK(Y/N)";DM$
4080 PRINT
4100 IF DM$="Y" THEN 4200
4120 IF OP=1 THEN GOSUB 15000:REM BY AREA
4140 IF OP=2 THEN GOSUB 15500:REM BY HEIGHT
4200 REM SHOW AVERAGED CURRENTS ON SCREEN
4220 PRINT"ELECTRODE RESI.CURRENT* NET SAMP.CURRENT"
4240 PRINT
4260 FOR N=1 TO 16
4280 PRINT " #: RC(M,SS);SC(M,SS)
4300 NEXT M
4320 PRINT
5000 INPUT"PRINT OUT RESULTS(Y/N)";DM$
5020 PRINT
5040 IF DM$="N" THEN 6000
5060 GOSUB 77000:REM SURE PRINTER ONLINE
5100 INPUT"HAVE PARAMETERS PRINTED OUT(Y/N)";DM$
5120 PRINT
5140 IF DM$="N" THEN 5400
5160 OPEN4,4:CMD4
5180 GOSUB 9000
5200 PRINT CHR$(112):REM GET TO THE TOP OF THE NEXT PAGE
5220 PRINT#4
5300 CLOSE4
5400 GOSUB 99000:REM CHANGE REMARK
5420 OPEN4,4:CMD4
5440 GOSUB 97000:REM SAMPLE ID
5500 REM PRINT OUT AVE. RESIDUAL & TOTAL SAMPLE CURRENT
5520 PRINT"ELECTRODE","VOLT.APPLY RES.I.CURRENT* NET SAMP.CURRENT"
5540 PRINT
5560 FOR M=1 TO 16
5580 PRINT" #: RC(M,SS);SC(M,SS)
5600 NEXT M
5620 PRINT
5640 PRINT
5660 PRINT" ARE ABOVE AVERAGED RESULTS !"
5680 GOSUB 79000:REM STATE METHOD
5700 GOSUB 90000:REM PRINT OUT
5720 PRINT
5740 PRINT" THE DATA RANGES ARE AS FOLLOWING : "
5760 PRINT
5720 PRINT"ELECTRODE"," RESIDUAL 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$(12):REM GET TO THE TOP OF THE NEXT PAGE  
5860 PRINT:CLOSE 4  
5900 INPUT"IS PRINTOUT OK<Y/N)";DM$  
5920 PRINT  
5940 IF DM$< >"Y" THEN 5000  
6000 INPUT"ARE RESULTS OK<Y<IN>";DM$  
6020 PRINT  
6100 INPUT"CHECK THE SAME SET AGAIN<Y/N)";DM$  
6120 PRINT  
6140 IF DM$< >"N" THEN 2580  
6200 PRINT"LOAD NEW DATA SET<Y<IN>";DM$  
6220 PRINT  
6240 IF DM$="Y" THEN 500  
6260 GOTO 7000  
6500 PRINT"RESULT FOR STATISTICS<Y<IN>";DM$  
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<IN>";DM$  
6680 PRINT  
6700 IF DM$="Y" THEN 6800  
6720 INPUT"ARE YOU SURE<Y<IN>";DM$  
6740 PRINT  
6760 IF DM$="Y" THEN 400  
6780 GOTO 6660  
6800 PRINT"ARE YOU SURE<Y<IN>";DM$  
6820 PRINT  
6840 IF DM$="N" THEN 6770  
6900 PRINT"*** NOW APPLY STATISTICS TO THE RESULTS"  
6920 PRINT  
6940 I=SS:REM TOTAL SET FOR REPEATABILITY IS 'SS'  
6960 GOSUB 10000  
7000 PRINT"CHECK SAME SET AGAIN<Y/N)";DM$  
7020 PRINT  
7040 IF DM$="Y" THEN 2600  
7100 PRINT"ADD ANOTHER DATA SET<Y/N)";DM$  
7120 PRINT  
7140 IF DM$="Y" THEN 400  
7200 INPUT"GET RID OF PREVIOUS ONE<Y/N)";DM$  
7220 PRINT  
7240 IF DM$="N" THEN 7300  
7260 SS=SS-1  
7280 GOTO 6660  
7300 PRINT"WANT TO START OVER/END RIGHT?"  
7320 STOP  
7340 PRINT  
7360 GOTO 7000  
7500 END  
7780 REM CHECK PRINTER ONLINE  
7790 PRINT"*** MAKE SURE PRINTER IS ONLINE."  
7740 PRINT" THEN PUSH 'G' TO GO ON !"  
7760 PRINT  
7780 GET A$:IF A$< >"G" THEN 7780  
7800 RETURN
REM STATE METHOD

IF OP=1 THEN PRINT" ** RESULTS ARE BASED ON PEAK AREA!"

IF OP=2 THEN PRINT" ** RESULTS ARE BASED ON PEAK HEIGHT!"

PRINT

RETURN

REM SUBROUTINE TO CHECK WHOLE SET DATA

IF NN<0 THEN 8360

PRINT M DATA(NN) DATA(NN+1)

FOR M=0 TO 16

PRINT M;RS(M,NN);RS(M,NN+1)

NEXT M

PRINT

GOTO 8620

RETURN

REM SHOW A SINGLE SET DATA

PRINT N;"TH DATA SET OF SAMPLE"

FOR NN=0 TO ED

PRINT NN;RS(0,NN);RS(0,NN+1)

NEXT NN

PRINT

RETURN

REM SUBROUTINE TO SEE ALL DATA ON TWO ELECTRODES

FOR N=BN TO ED

PRINT N;RS(N,1);RS(N,2)

NEXT N

PRINT

GOSUB 14501:REM SET RANGE

PRINT

REM SHOW ALL PARAMETERS ON SCREEN

PRINT"EXPERIMENTAL CONDITIONS --"

PRINT"FLOW RATE -- ";FR$:VOLTS"

PRINT"SQUARE WAVE FOR PRECONDITIONING --"

PRINT"POTENTIAL OF UPPER LIMIT : ";UL;"VOLT"

PRINT"POTENTIAL OF LOWER LIMIT : ";LL;"VOLT"

PRINT"FREQUENCY : ";HZ;"HERTZ"

PRINT"DURATION : ";DU;"SEC"

PRINT IV;"VOLTS OUTPUT FROM DAC7548 #1"

PRINT FV;"VOLTS OUTPUT FROM DAC7548 #2"

PRINT

PRINT IV;"WAIT";TD;"SEC TO SUBSIDE CHARGING CURRENT DOWN"

PRINT

PRINT"U1ALO IS";U2

PRINT"TOTAL COVERED TIME IS";TT;"SEC"

PRINT"UI TIMER SETUP AS";UI;"* (1/60) SEC"

PRINT"TIME OF RESOLUTION IS ABOUT";TR;"SEC"

PRINT NT;"SETS OF DATA COLLECTED"

PRINT

PRINT"REFERENCE ELECTRODES : ZINC IN 1 M SODIUM ACETATE SOLUTION."

PRINT"WORKING ELECTRODES : CARBON FIBER ARRAY ELECTRODE"

PRINT

PRINT
9520 PRINT ** REMARK : ";RM$
9540 PRINT
9560 PRINT
9580 RETURN
9600 REM SHOW SAMPLE, EXPT. DATE, & REMARK
9620 PRINT"SAMPLE -- ";LB$
9640 PRINT" NORM.AREA FILE ID : ";NF$
9660 PRINT" DATE OF EXPERIMENT : ";DA$
9680 PRINT
9700 PRINT ** REMARK : ";RM$
9720 PRINT
9740 PRINT
9760 RETURN
9780 REM SHOW SAMPLE ID
9800 PRINT"SAMPLE -- ";LB$
9820 PRINT" NORM.AREA FILE ID : ";NF$
9840 PRINT" DATE OF EXPERIMENT : ";DA$
9860 PRINT
9880 PRINT
9900 REM CHANGE REMARK
9920 PRINT"PREVIOUS REMARK : ";RM$
9940 INPUT"IS IT OK CY/N?";OM$
9960 IF DM$="Y" THEN 9990
9980 INPUT"NEW REMARK:";RM$
9990 PRINT
10000 IF DM$< >"Y" THEN 9950
10020 RETURN
10040 REM STATISTICS FOR MEAN, STANDARD DEVIATION(SD), AND RELATIVE SD
10060 REM MEAN
10080 FOR M=1 TO 16
10100 D1=0
10120 FOR X=1 TO I
10140 D1=SC(M,X)+D1
10160 NEXT X
10180 SACM=01/I
10200 REM SD & RELATIVE SD (RD)
10220 D2=0
10240 D3=0
10260 FOR X=1 TO I
10280 D2=SC(M,X)-SA(M)
10300 D3=D2*D2+D3
10320 NEXT X
10340 SD(M)=SQR(D3/(I-1));REM MAY SUBSTITUTE 1-1 WITH I
10360 RD(M)=SD(M)/SA(M)*100
10380 NEXT M
10400 GOSUB 11500;REM SHOW RESULTS
10420 INPUT"PRINT OUT STATISTIC RESULTS(Y/N)?";DM$
10440 PRINT
10460 IF DM$="Y" THEN 11460
11100 GOSUB 9900
11120 OPEN4,4,CMD4
11140 GOSUB 9600;REM SAMPLE, EXPT. DATE, & REMARK
11160 GOSUB 11500;REM SHOW RESULTS
11180 PRINT CHR$(12)
11200 PRINT
11220 CLOSE4
11240 INPUT"IS PRINTOUT OK(Y/N)?";DM$
11260 PRINT
11280 IF DM$< >"Y" THEN 11000
11300 RETURN
11500 REM SHOW STATISTIC RESULT.
11600 PRINT"ELECTRODE","NET SAMPLE CURRENT"
11620 PRINT","MEAN STD DEV REL STD DEV(%)"
11640 PRINT
11700 FOR M=1 TO 16
11720 PRINT #";M,SA(M);";SD(M);";RD(M)
11740 NEXT M
11760 PRINT
11780 PRINT
11800 PRINT** THE STATISTICS IS BASED ON";I;"DATA SETS"
11820 IF OP=1 THEN PRINT" & ALSO BASED ON PEAK AREA !"
11840 IF OP=2 THEN PRINT" & ALSO BASED ON PEAK HEIGHT !"
11860 PRINT
11880 RETURN
11900 REM SUBROUTINE TO LOAD NORMALIZED AREA
12100 OPEN 2,8,2,NF$+,S,R
12120 FOR M=0 TO 16
12140 INPUT#:NA(M)
12160 NEXT M
12180 RETURN
12200 REM SUBROUTINE TO LOAD CAPACITANCE FOR EACH INTEGRATOR
12300 REM BASED ON THE RESULTS OBTAINED ON 10/31
12320 CA(1)=9.92E-10;CA(2)=8.61E-10
12340 CA(3)=9.94E-10;CA(4)=8.39E-10
12360 CA(5)=8.36E-10;CA(6)=9.95E-10
12380 CA(7)=8.92E-10;CA(8)=8.66E-10
12400 CA(9)=9.95E-10;CA(10)=8.92E-10
12420 CA(11)=8.95E-10;CA(12)=8.95E-10
12440 CA(13)=9.10E-10;CA(14)=8.95E-10
12460 CA(15)=9.10E-10;CA(16)=9.50E-10
12480 RETURN
12500 REM SUBROUTINE TO LOAD NORMALIZED AREA
12520 FOR M=9 TO 16
12540 INPUT#:NA(M)
12560 NEXT M
12580 RETURN
12800 REM SUBROUTINE TO LOAD CAPACITANCE FOR EACH INTEGRATOR
12900 REM BASED ON THE RESULTS OBTAINED ON 10/31
13000 REM SHOW RANGES
13300 REM SUBROUTINE TO LOAD NORMALIZED AREA
13500 PRINT"ELECTRODE","RF RL SF SL"
13540 PRINT
13600 FOR M=1 TO 16
13620 PRINT #";M,RF;RL;SF;SL"
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 GET A$:IF A$="S" THEN 14400
14080 S=54272
14100 POKE S+5,L:POKE S+6,L:POKE S+24,15
14280 HF=37:LF=142:DR=5e0
14300 POKE S+1,TF: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
14420 REM SET RANGE FOR SAMPL.CURRENT PEAK HEIGHT MAXIMUM
14440 PRINT" FOR ELECTRODE ":X1
14460 INPUT": RANGE OF SAMPLE CURRENT":SF(X1),SL(X1)
14480 PRINT
14500 PRINT" FOR ELECTRODE ":X2
14540 INPUT": RANGE OF SAMPLE CURRENT":SF(X2),SL(X2)
14560 PRINT
14580 INPUT": ARE BOTH OK(Y/N)";DM$
14600 IF DM$<>"V" THEN 14600
14620 RETURN
15000 REM GET RESI.CURRENT & TOTL.SAMPL.CURRENT BY PEAK AREA
15020 PRINT" -- HANG ON, CALC. PEAK AREA !";
15040 PRINT
15100 REM CALC. AVERAGE RESI.CURRENT
15110 FOR M=1 TO 16
15120 RC(M,SS)=0
15130 FOR N=RF TO RL
15140 RC(M,SS)=RC(M,SS)+RS(M,N)
15150 NEXT N
15160 RC(M,SS)=RC(M,SS)/(RL-RF+1)
15170 NEXT M
15200 REM CALC. PEAK AREA OF NET SAMPLE CURRENT
15220 PRINT" -- THE FOLLOWING 'N' VALUE SHOULD BE "
15240 PRINT" NOT GREATER THAN";NT+1
15260 PRINT
15300 FOR M=1 TO 16
15310 SC(M,SS)=0
15320 N=RL+1
15330 SC(M,SS)=(RS(M,N)-RC(M,SS))*RS(M,N)+SC(M,SS)
15340 N=N+1
15350 IF N>NT THEN 15410
15360 IF N<=21Z THEN 15330
15370 IF RS(M,N)<RC(M,SS) THEN 15400
15380 IF RS(M,N)>RC(M,SS) THEN 15330
15390 GOTO 15410
15400 IF RS(M,N)<RC(M,SS) THEN 15330
15410 PRINT M=";M;";N=";N
15420 NEXT M
15440 PRINT
15460 GOSUB 14000:REM BEEP
15480 RETURN
15500 REM GET RESI.CURRENT & TOTL.SAMPL.CURRENT BY PEAK HEIGHT
15520 PRINT" -- HANG ON, CALC. PEAK HEIGHT !"
15540 PRINT
15560 REM CALC. AVERAGE RESI.CURRENT
15610 FOR M=1 TO 16
15620 RC(M,SS)=0
15630 FOR N=RF TO RL
15640 RC(M,SS)=RC(M,SS)+RS(M,N)
15650 NEXT N
15660 RC(M,SS)=RC(M,SS)/(RL-RF+1)
15670 NEXT M
15700 REM CALC. PEAK HEIGHT OF NET SAMPLE CURRENT
15720 FOR M=1 TO 16
15740 SC(M,SS)=0
15760 FOR N=SF(M) TO SL(M)
15780 SC(M,SS)=SC(M,SS)+RS(M,N)
15800 NEXT N
15820 SC(M,SS) = SC(M,SS)/(SL(M)-SF(M)+1)
15840 SC(M,SS) = SC(M,SS) - RC(M,SS)
15860 NEXT M
15900 COSUB 14000: REM BEEP
15920 RETURN
16000 REM PRINT OUT DATA FOR PLOTTING
16020 PRINT"*** INPUT THE RANGE OF DATA TO PRINT"
16040 PRINT" END OF PRINT IF 1ST<0 !""
16060 PRINT
16100 INPUT" 1ST SET, LAST SET";BN,ED
16120 INPUT" ARE BOTH OK(Y/N)";DM$
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$<12>: REM SET TO THE TOP OF NEXT PAGE
16420 PRINT#4
16440 CLOSE4
16500 PRINT"** END OF PRINT IF FT<0 !""
16520 PRINT" CHOOSE 4 ELECTRODES TO PRINT DATA !"
16540 INPUT" 1ST, 2ND, 3RD, 4TH ELECTRODE";FT,SD,TD,FH
16560 PRINT" ARE ALL ABOVE OK (Y/N) ";DM$
16580 PRINT
16600 IF DM$<"Y" THEN 16500
16620 IF FT<0 THEN 17000
16700 OPEN 4,4: CMD 4
16720 PRINT"SET"," ELECTRODE"
16740 PRINT#1,"#";FT, "#";SD, "#";TD, "#";FH
16760 PRINT
16780 FOR N=BN TO ED
16800 PRINT N,RS(FT,N);RS(SD,N);RS(TD,N);RS(FH,N)
16820 NEXT N
16820 PRINT CHR$<12>
16840 PRINT#4
16860 CLOSE4
16900 GOTO 16500
17000 RETURN

READY.