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The development of pulsed waveforms for the electrochemical detection of inorganic and organic compounds in flow-injection analysis and liquid chromatography

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Neuburger, Glen Gary

THE DEVELOPMENT OF PULSED WAVEFORMS FOR THE ELECTROCHEMICAL DETECTION OF INORGANIC AND ORGANIC COMPOUNDS IN FLOW-INJECTION ANALYSIS AND LIQUID CHROMATOGRAPHY. (VOLUMES I AND II)

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The development of pulsed waveforms for the electrochemical detection of inorganic and organic compounds in flow-injection analysis and liquid chromatography

by

Glen Gary Neuburger

Volume 1 of 2

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LIST OF ACRONYMS

A/D	Analog-to-digital
A/DC	Analog-to-digital conversion Analog-to-digital converter
AI	Artificial Intelligence
ASV	Anodic stripping voltammetry
CHEMFET	Chemical field-effect transistor
CPPP	Constant potential pulse polarography
CPPV	Constant potential pulse voltammetry
D/A	Digital-to-analog
D/AC	Digital-to-analog conversion Digital-to-analog converter
DME	Dropping mercury electrode
DPASV	Differential pulse anodic stripping voltammetry
DPP	Differential pulse polarography
DPV	Differential pulse voltammetry
EC	Electrochemical
EPROM	Erasable-programmable-read-only memory
FIA	Flow-injection analysis
FI/CPPP	Flow-injection constant potential pulse polarography
FT	Fourier transform
FT-IR	Fourier transform infrared spectroscopy
FT-MS	Fourier transform mass spectrometry
FT/NMR	Fourier transform nuclear magnetic resonance
FT-UV-vis	Fourier transform ultraviolet-visible spectroscopy

HP	Hewlett Packard
I/O	Input and/or output
ISE	Ion-selective electrode
ISFET	Ion-selective field-effect transistor
k	multiples of 1024
LC	Liquid chromatography
LC/EC	Liquid chromatography with electrochemical detection
MS/MS	Mass spectrometry/mass spectrometry (used to denote parent-daughter structural elucidation)
NMR	Nuclear magnetic resonance
NPP	Normal pulse polarography
NPV	Normal pulse voltammetry
PAD	Pulsed amperometric detection
PAR PARC	Princeton Applied Research Corporation
PCD	Pulsed coulometric detection
PCS	Pulsed coulometric stripping
PS-PCD	Potential sweep pulsed coulometric detection
RAM	Random access read/write memory
RC	Resistor-capacitor
RCPPP	Reverse constant-potential pulse voltammetry
RDE	Rotating disk electrode
RPA	Reverse pulse amperometry
rpm	revolutions per minute
RPP	Reverse pulse polarography
RPV	Reverse pulse voltammetry

RRDE	Rotating ring-disk electrode
S/H	Sample-and-hold
S/N	Signal-to-noise ratio
SCE	Saturated calomel electrode
SDME	Static dropping mercury electrode
SP-PCD	Static potential pulsed coulometric detection
TDW	Triply distilled water
TTL	Transistor-transistor logic
UPD	Underpotential deposition
UV	Ultraviolet
UV-vis	Ultraviolet visible spectroscopy

DEFINITION OF SYMBOLS

ΔE	Potential step increment
τ	Drop lifetime, s
θ	Fractional surface coverage
ϕ	Scan rate, V min^{-1}
A	Area, cm_2
a	Activity of analyte
a_{ox}	Activity of oxidized form of the analyte
a_{red}	Activity of reduced form of the analyte
C^b	Bulk concentration of analyte
D	Diffusion coefficient, cm_2 s^{-1}
$E_{½}$	Half-wave potential
E_d	Detection potential (CPPP)
E_f	Final potential (polarography)
E_i	Initial potential (polarography)
F	Faraday Constant, 96,487 eq mol^{-1}
i_{DC}	Constant potential (dc) polarographic current
i-E	Current-potential, in reference to Figures
i_{NP}	Normal pulse polarographic current
i_{RP}	Reverse pulse polarographic current
i-t	Current-time, in reference to transient flow profiles (CPPP)
n	Equivalent number of electrons
n_{ox}	Equivalent number of electrons in oxidation mechanism
n_{red}	Equivalent number of electrons in reduction mechanism

R	Gas constant, 8.316 J mol^{-1} deg^{-1}
T	Temperature, K
t_p	Potential-pulse lifetime or period
v_f	Flow rate, mL min^{-1}
V_r	Retention volume
V_s	Sample volume injected

DEFINITION OF TERMS

batch	Refers to experiments performed in a cell of constant volume. Commonly used for experiments employing rotating ring-disk electrodes.
detection limit	The lowest measurable concentration for a specified signal-to-noise ratio.
final potential	Used in the description of two-step pulsed polarographic waveforms. Indicates that potential at which the current is measured.
initial potential	Used in the description of two-step pulsed polarographic waveforms. Indicates that potential at which the current is not measured.
irreversible	Reserved for reactions for which oxidative products are not subsequently reduced at a more cathodic potential, or reductive products are not oxidized at a more anodic potential. For example, carbohydrates are irreversibly oxidized at a Au electrode such that their products cannot be reduced at potentials within the boundaries defined by solvent decomposition.
kinetically-controlled	Reserved for reactions which are thought to be slow. That is, the chemical or electron transfer step is slow compared to any following reaction steps or in comparison to the rate of convective-diffusional mass transport to the electrode surface.
mass-transport controlled	Reserved for reactions in which the chemical or electron transfer step is fast relative to the rate of convective-diffusional mass transport to the electrode surface.
potential	Used solely as a synonym for "voltage".

reversible	Reserved for reactions for which oxidative products are subsequently reduced at a more cathodic potential, or reductive products are subsequently oxidized at a more anodic potential. For example, Fe(II) is reversibly oxidized at a Au electrode such that its product Fe(III) can be reduced at potentials within the region defined by solvent decomposition.
sensitivity	The rate of change of the measured signal with the variation of bulk analyte concentration.
surface-controlled	This term implies that the observed reaction is strongly controlled by surface adsorption phenomena and can be described by an appropriate adsorption isotherm for processes in chemical equilibrium.
underpotential deposition	A phenomenon which occurs at solid metal electrodes. It is characterized by the cathodic deposition of metal ions at potentials more positive than predicted by thermodynamics, i.e., the Nernst equation.

ABSTRACT

Methods are described for the electrochemical detection of several classes of electroactive elements and compounds utilizing pulsed waveforms in flow-injection and liquid chromatographic systems. Particular emphasis is placed on the development of waveforms for the rejection of ubiquitous background interferences as well as for the enhancement of sensitivity and detectability.

Constant potential pulse polarography, a variation of normal pulse polarography, is described for the determination of reversible electroactive ions, such as Cd(II), Cu(II) and Pb(II), in the presence of dissolved oxygen with no apparent interferences.

Pulsed amperometric detection schemes based upon the use of a gold electrode instead of platinum are presented with special emphasis on the amperometric detection of carbohydrates in alkaline solutions. The choice of gold over platinum eliminates interference from dissolved oxygen, reducing the observed background current, and thus, increasing detectability.

Pulsed amperometric detection is described for the detection of carbohydrates with an asymmetric two-step waveform at a gold electrode in alkaline media, without a loss in sensitivity in comparison to three-step waveforms. Detection limits are represented by the values 35 and 50 $\mu\underline{M}$

for glucose and sucrose, respectively, in 0.20 M NaOH.

Pulsed coulometric detection at a constant detection potential was introduced to increase the overall linear dynamic range for the detection of carbohydrates through a lowering of detection limits. Detection limits are ca. 25X lower than those obtained with ***pulsed amperometric detection*** and are represented by the values 1.0 and 2.5 μM for glucose and sucrose, respectively.

Pulse coulometric detection at swept detection potentials was developed to reduce automatically background signals resulting from oxide formation and double-layer charging at noble metal electrodes and thus eliminates the need for special offset compensation circuitry. In addition, the background drift commonly observed with ***pulsed amperometric detection*** as a result of electrode surface reformation processes was eliminated. In addition, the background signal was found to be virtually independent of small changes in eluent pH, and thus may be used in liquid chromatographic schemes which employ pH-step or pH-gradient elution.

Pulsed coulometric detection is also extended to the determination of heavy metal ions which are reversibly reduced at a gold electrode. Limits of detection for most metals, e.g., Hg(II), Bi(III), Pb(II), and Cd(II) are 0.1-10 μM for a two-step waveform applied with a frequency of 1 Hz.

PREFACE

There remains a need for the development of liquid chromatographic detectors (LC) which yield much lower detection limits, higher sensitivities, and are capable of functioning as either specific or universal detectors. In addition, emphasis must also be placed on the development of detection mechanisms which reduce automatically the background offset commonly associated with electronic drift or as a result of the alteration of LC eluent composition. An alternate method for reducing low frequency drift would be the inclusion of complex algorithms in microprocessor-controlled instrumentation.

Since it would be redundant to create LC detectors which offer no advantages over existing detectors, emphasis has been placed on the detection of molecules which, at present, are not detected well by nonelectrochemical mechanisms. However, the main goal of this research was placed on the development of new detection mechanisms and no attempt was made to test these methods on a wide variety of compounds. Prior pulsed-potential waveforms have received the greatest attention for the detection of carbohydrates, and for this reason this compound class was used for the testing of the detection mechanism. It should be noted that many of detection mechanisms described in this dissertation are applicable for a wide variety of compound classes.

The organization of this dissertation follows the alternate format; thus, each of the latter chapters comprise a duplication of a publication as it appeared in the literature. With the selection of this format, it was necessary to cover each of several individual subjects in greater detail. Subsequently, because of the diversity of the techniques discussed, it was necessary to cover a greater literature subject range; hence, the following four chapters may seem unrelated with the exception of their electrochemical roots.

It is important to note that it is not this author's intention to describe in grave detail all methods or techniques covered in the general introduction (Chapters I-IV) in grave detail. In fact, many will be mentioned only in passing and the interested reader is encouraged to seek out more exact information in the appropriate reference(s).

Finally, no attempt will be made to cover the literature exhaustively, with the exception of the summary of underpotential deposition (Chapter IV); only those references deemed significant by this author will be considered. Emphasis is also placed on more recent literature, with special mention of authors (papers) responsible for the introduction of new and significant techniques.

DEDICATION

Dedicated to my parents

Dorothy Anna Neuburger
Louis Francis Neuburger

silent, yet strong;

and to my wife and our children

Dawn Marie Neuburger
Chace Alden Neuburger

my link to life.

I. GENERAL SURVEY OF LIQUID CHROMATOGRAPHIC DETECTORS

Detectors designed for liquid chromatography (LC) come from a wide variety of backgrounds and each may offer advantages specific to the method of detection employed. Common categories are: 1) optical detectors, beginning with the simple UV-vis absorption and refraction methods and continuing to more complex and specific methods based on optical activity, 2) electrochemical detectors employing dual indicating electrodes or pulsed waveforms, and 3) more exotic and expensive methods based on mass spectrometry, FT-IR spectroscopy, and NMR. All of these methods will be reviewed presently with the exception of electrochemical detectors which will be discussed separately in Chapter II. Reviews on liquid chromatographic detectors have recently appeared.[1a-2]

The development of a LC detection scheme relies upon the differing responses of the eluent employed for chromatographic separation and the solutes of interest. The response may be designated as positive or negative depending upon the absolute change in the measured signal. For any detection mechanism, it is necessary that these responses be significantly different so that they are measurable by the employed transducer. This is summarized by defining a detection limit for the detector, denoted as the minimum detectable concentration for a specified ratio of the signal obtained and the peak-to-peak noise on the background (S/N). Additional interest lies in the sensitivity of the mechanism, that is, the rate of signal change per unit concentration ($\delta\gamma/\delta C$). Although, they are often used interchangeably, high sensitivity does not imply good detectability, and vice-versa.

Although many LC detectors are limited to quantitative assessments, i.e., the attainment of "good" sensitivity and detectability, it is often desirable for some LC separations that the detector provide qualitative information which complements that encoded in the separation process, i.e., retention time values. These qualitative assessments may be as simple as the selectivity or specificity of the detector for a class of compounds, or they may be more complex owing to variation of one or more parameters of the experiment and may result in 3-dimensional chromatographic maps. The purpose of all qualitative determinations is the reduction in time necessary for compound identification. Conventionally, this has been performed through peak retention time assignments.

The desire for selective or specific detection of a particular class of compounds has been the trend in the development of the most recent LC detectors. These detectors offer an alternate dimension to the qualitative assessment in the determination of a single compound or a mixture of compounds, within a sample matrix. Particular attention is given to the "separation" of co-eluting peaks corresponding to compounds which have similar molecular properties in relation to the separation mechanism, but with differing properties in relation to the method of detection. Thus, it is possible to deconvolute overlapping peaks based solely on differences in detectability.

Depending on the detector employed and the present state of its development, some detector systems, with supporting hardware and software, can offer the use of sophisticated mathematical algorithms for data reduction and analysis. The trend in the development of LC detectors is toward more "intelligent" instrumentation requiring little knowledge of its workings by the user. This is a result of the development of microprocessor-based instrumentation.

Further refinements in the development of LC detectors is demanded by ongoing improvements in separation technology. Presently, the field of LC separations is being overhauled with the advent of microbore (i.e., < ca. 1 mm i.d.) and open tubular capillary (i.e., < ca. 50 μm i.d.) columns. Many of the advantages of these columns are centered around the ability to use low flow rates in the LC separation scheme. Of primary interest is the ability to use more exotic, and hence more expensive solvents for the separation, thus improving efficiency and the overall performance of the analysis. Additional interest rests on the ability to use detectors which were previously considered noncompatible with LC, such as MS or GC-specific detectors like electron capture and photoionization detectors. As a result of these recent developments in separation technology, demands have now been placed on the developers of LC detectors with emphasis placed upon the lowering of detector dead volume but not at the expense of sensitivity and/or detectability.

Additional improvements are needed in the development of LC detectors for rejection of background signal variation due to common physical or instrumental drifts, or from variation in the composition or concentration of components in the LC mobile phase. Most detectors, for example, are incapable of rejecting the background drifts due to pH variation in gradient elution ion chromatography. Other detectors are plagued by ubiquitous background drifts associated commonly with electronic drifts. Methods must be developed for removal of physical or instrumental drifts either by designing the detectors so that drifts are compensated automatically in real time, or by the development and inclusion of algorithms which modify the data set after its acquisition.

The following discussion will be centered on the presentation of a variety of nonelectrochemical LC detectors with their respective traits, advantages, etc. No attempt will be made to discuss the theory behind the detectors or their specific applications for analysis in liquid chromatography. In addition, a discussion of LC separations and their uses will not be presented. In a subsequent section, electrochemical detectors will be discussed in greater detail than the nonelectrochemical detectors presented here.

It is important to point out that a table comparing sensitivities and detection limits of the various detectors has not been included. It is this author's belief that this information is of little significance if the comparisons are not made for the detection of identical compounds under identical conditions. It is also important that comparisons be made for several very different compounds to demonstrate any unique performance of a specific detector(s). Since this information is not presently available such a comparison is purposely omitted.

A. Refractive Index Detection

Refractive index detectors were developed for the detection of compounds which do not have strong adsorption bands in the UV-vis spectrum, such as saturated organic molecules, and thus may not be detected sufficiently well with either absorbance or fluorescence detection. Despite the poor sensitivity and detectability commonly obtained with these detectors, they continue to be in strong use with LC. Detection limits have been improved with the use of a laser-based Fabry-Perot interferometer.[3] Current research is being performed in the development of reduced detector volumes for use in microbore and capillary column LC. Detector volumes (ca. 1 μL) which are ca. 10-fold less than conventional detectors have been reported with laser based instrumentation.[4]

B. UV-vis Absorbance Detection

Detection based on absorption in the UV-vis region is by far the most widely used in routine LC analyses. Detection schemes are commonly based upon single wavelength detection. With the advent of multichannel photodiode arrays,[5] multiwavelength monitoring or rapid wavelength scanning is now possible. This allows for the construction of 3-dimensional chromatograms of absorbance vs. wavelength vs. time, and will allow for quantitation of severely overlapping peaks normally observed in 2-dimensional chromatograms.[6] Additional advantages of 3-dimensional constructions are the ease of selection of an optimal wavelength for use in single wavelength detection schemes, and the determination of peak (compound) purity.[2]

More recent advances are in the development of FT-UV-vis spectrometers. Groton has recently introduced[7] a FT instrument which utilizes a common-path holographic interferometer--an interferometer which encodes the signal in the spacial domain instead of the time domain as in the case for the more common Michelson interferometers. These instruments use a 512-element photodiode array, with a resolution of 1-2 nm over the range of 200-700 nm, and are capable of obtaining 20 spectra/s. Claims have been made by Groton that the observed S/N is better than the dispersive photodiode array detector.

On the other hand, single wavelength detection still holds promise for a large number of pre-characterized separations. Universal detection of most organic compounds may be achieved by absorption monitoring at 185 nm.[8] With proper choice of the eluents, these methods can be applied to gradient elution schemes.

C. Mass Spectrometric Detection

The complication of interfacing MS with LC lay in the complementing of the LC effluent flow rate with the maximum allowable sample intake of the mass spectrometer. This has resulted in a variety of sample introduction methods, including direct liquid introduction,[9] mechanical transfer,[10-11] and thermospray.[12] However, with the advent of microbore and open tubular capillary LC, which utilize much lower flow rates, these two methods, LC and MS, are converging toward their optimized limits. In addition, with the introduction of commercially available FT/MS instruments, increases in several categories are expected. For example, the overall mass range studied, the resolution and S/N of mass spectrometric measurements, and the ability to perform more complicated real time experiments for further compound elucidation, e.g., MS/MS.

Second only to NMR in qualitative information content, MS is one of the most versatile LC detectors, offering several modes of detection. For increased detectability and for operation as a universal detector, the total ion current can be monitored. Selective detection can be obtained by monitoring a specific mass or a set of masses (selective ion monitoring). Additionally, in comparison to its gas phase counterpart GC/MS, LC/MS is applicable for thermally labile compounds.[13]

D. Fourier Transform Nuclear Magnetic Resonance Detection

Because of the fingerprinting capabilities of NMR, there has been considerable interest in the development of this technique as a detector for LC.[14] Advantages that NMR can offer over its greatest competitor MS, are: 1) no molecular weight or volatility requirements, and 2) the overall wealth of unique structural information that may be obtained from the local electronic environment of the active nucleus, such as stereochemical structural elucidation.

However, many difficulties must be overcome before this is considered a suitable and reliable detector. The primary fault of this detector is its poor detection limits which are comparable to that of conventional refractive index detectors. Other complications arise from the application of NMR in flowing systems. For example, the intensity of the resonance signal is a function of the effluent flow rate, and the NMR spectral resolution is a function of solvent viscosity and detector cell volume. Further complications arise with the limited selection of NMR compatible solvents used as LC eluents. For example, mobile phases which contain hydrogen atoms may cause signal saturation in proton NMR and difficulties may arise in the measurement of a small signal, due to the eluting solute, on a large background. This latter effect has been overcome with the use of more expensive deuterated or halogenated solvents.

Initial work has been centered around the use of proton NMR;[15,16] however, studies are expected to appear for other active nuclei, with the limit set by the simultaneous detection of many active nuclei in a single experiment. Recent results have been presented for continuous-flow carbon-13 NMR/LC.[17]

E. Fourier Transform Infrared Spectroscopic Detection

Fourier Transform Infrared Spectroscopy offers many of the same advantages as other qualitative detectors, such as MS. Since FT-IR spectroscopic methods have been well developed as a diagnostic tool, present work centers around adapting this method for use in microbore LC.[18,19] A particular disadvantage of IR, in general, is its inability to distinguish between optically active components.

F. Fluorescence Detection

Fluorescence detection offers many advantages over common transmission based absorption detectors, including an increase in sensitivity and selectivity, a 100-fold decrease in detection limits, and an overall improvement in the obtainable qualitative information. Increases in detectability are primarily a result of the lowering or elimination of background signals by judicious selection of the monitoring wavelength and delay time before signal measurement. Computerized detectors, capable of rapid wavelength scanning, can allow for the variation of several variables to obtain multidimensional plots. Thus, combinations of fluorescence intensity, retention time, excitation wavelength, emission wavelength, and detection time will normally provide sufficient information for compound identification provided a suitable data base is available for comparison. The variation of fluorescence decay time is the basis for phase-resolved fluorescence detection.[20]

Fluorescence detection is not necessarily limited to only those compounds which naturally fluoresce, but may be extended to nonfluorescing compounds which have been labeled with a fluorescence tag, or to compounds known to be active quenchers of certain fluorophores.

Present interest in the development of fluorescence based detectors is center around the use of lasers as excitation sources for increased detectability, and the overall simplicity of using these detectors in microbore and capillary column LC.[21] These detectors are also gaining advantage with the use of photodiode arrays in conjunction with low volume detection cells.[22]

G. Optical Activity Detection

Optical activity detectors were developed because of the need for the determination of naturally occurring compounds or biomolecules. Most LC detectors up to this time, with the exception of NMR, provide little or no information about the stereochemistry of the molecule, and the use of derivatization methods are unreliable because of racemization. Detectors have been presented based upon either polarimetry[23-26] or circular dichroism.[27] This latter technique may provide more specificity because molecules will not be detected unless they adsorb at the excitation wavelength. Detection of optically inactive compounds can be achieved with the use of an optically active eluent with no apparent loss in detectability.[24]

H. Conductivity Detection

Conductivity detection is the universal detector for ionic constituents and has been widely used in ion chromatography.[28] Detection limits can be competitive with conventional absorbance detectors if proper attention is given to temperature control of the chromatographic system.[28,29]

I. Element Specific Detection

Several flame-based detectors have been introduced for use in LC. Of these, the most common are flame photometric,[30,31] flame ionization[32] and thermionic detection.[33,34]

Initial studies which involved the use of these detectors with conventional packed column (macrobore) LC, suffered because of flame instability with the introduction of large volumes of solvent, but have been overcome with the advent of microbore and capillary column LC.

J. Other Photometric Based Detectors

Many other LC detectors have been introduced but at present have not found widespread use. These methods are based upon thermal lens effects,[35-37] light scattering,[38] indirect absorption based polarimetric measurements,[39] photothermal deflection,[40] photothermal refraction,[41] multiphoton effects,[42-45] the Raman Effect,[46] and photo-acoustic measurements.[47-48]

II. ELECTROCHEMICAL DETECTORS FOR FLOW INJECTION ANALYSIS AND LIQUID CHROMATOGRAPHY

Electrochemical detection for use in LC and FIA has advanced greatly in the last decade; however, the use of the term "electrochemical detection" is often equated with the more popular techniques of voltammetry and amperometry. Several techniques are often regarded as being not suitable for LC detection and are therefore implicitly excluded. This discussion has been added to introduce several recent techniques which are being applied for detection. Emphasis is placed on the most recent papers, and there has been no attempt to cover the literature exhaustively. Several recent reviews have appeared on the use of electrochemical detectors in FIA and LC.[1-5]

Present work is being performed in three primary categories: voltammetry, including polarography, and all of its subtechniques, potentiometry, and coulometry. Of these categories, voltammetry and coulometry seem to be dominant in the American market for use in LC, while potentiometry is dominant in the European market for use in FIA. Although FIA is common in the United States and Canada, it is primarily used for preliminary testing of detection schemes. The most common LC detectors in North America are based upon constant potential (dc) amperometry with carbon or noble metal electrodes; however, surface fouling has caused the need for *in* *situ* electrochemical cleaning. A great deal of work is also being performed with mercury electrodes, and the use of various pulsed waveforms, such as normal pulse, differential pulse, and square wave. Present work being performed in the United Kingdom and Australia is centered around the use of potentiometric EC detectors for detection and separation. State-of-the-art FIA potentiometric detectors are comprised of an array of ISFETs or CHEMFETs.

Although detectors based upon conductometry and high-frequency impedance measurements are certainly electrochemical in nature they are not covered in this chapter (see the discussion of conductometric detection in the previous chapter). The lack of recent significant advances in these two fields has warranted their absence here.

A. Potentiometric Detection

Of all the electrochemical detectors, potentiometric detectors have gone through the greatest change in the last decade. Traditionally, these detectors, equated with ISEs, have been characterized as being not suitable for LC detection. Reasons for their poor performance as LC detectors have often been contributed to: 1) slow response, 2) selectivity for a specific ion(s), 3) the need for a constant and high ionic strength of the effluent, and 4) the measured potentials are generally insensitive and inadequately reproducible leading to high detection limits. However, many benefits may be had with these detectors; 1) no interferences from dissolved gases, i.e., oxygen, 2) signal independence from variation of carrier stream flow rate, 3) ease of cell design with small internal volume (< 1 μL), and 4) nondestructive detection.

Few modern potentiometric membrane electrodes are suitable for use as LC detectors because of their compound specificity. However, electrodes which may be characterized as having a nonspecific response (i.e., nonselective electrodes) have been applied in LC for the detection of halides and thiocyanate with a silver/silver-silicylate coated electrode,[6] sulfide and cyanide with a silver sulfide membrane electrode,[7] and monovalent cations with a neutral ligand plastic membrane electrodes.[8] Indirect detection methods have also been applied to potentiometric detection in LC; several anions have been detected with a chloride electrode,[9] amino acids,[10] transition and rare earth metal ions[11] with a copper sensitive membrane electrode, and carboxylic acids with a pH electrode.[12]

More recent studies involve the use of metallic indicating electrodes for detection in FIA and LC, and yield lower detection limits, have faster response times, and are in general more universal or nonspecific in nature than membrane electrodes.[13] Potentiometric detection with chemically or electrochemically pretreated silver electrodes[14,15] or copper electrodes[16] have been used for the determination of L-cysteine and several proteins. Of particular interest is the use of metallic copper indicating electrodes for the detection of amino acids,[13,17] organic acids,[18] alkaline earth metal ions,[19,20] transition metal ions,[20,21] inorganic anions (e.g., nitrite, nitrate[20] and bromate, chlorate, iodate[22]), oxidizing inorganic anions (e.g., CN^-, Cl^-, Br^-, I^- and SCN^-),[22] reducing inorganic anions (e.g., ascorbic acid, hydrazine, and hydroxylamine),[23] and several complexing organic ligands, such as, glycine, histidine, L-cysteine, EDTA, ethylenediamine, dopamine, and imidazole.[24] All of these detection schemes can be placed under one of three modes of detection: 1) direct detection in which organic and inorganic complexing agents reduce the amount of free copper ions at the electrode surface; 2) indirect detection in which a 'vacancy' in the eluent flow stream is measured due to a decrease in the concentration of a copper complexing agent in the eluent; and, 3) redox detection in which a strong reducing or a strong oxidizing agent alters the free copper ion concentration at the electrode surface by oxidation of $Cu \rightarrow Cu^{n+}$, or reduction of copper ions onto the electrode surface.

Ion selective electrodes have not found widespread use as potentiometric detectors because of their selectivity and slow response. These problems are expected to be carried over into the development of ISFETs and CHEMFETs for use in LC. The latter electrodes have not been developed as rapidly as ISEs owing to the lack of expertise and synthesis/encapsulation methods in common electrochemical laboratories. However, the development of mixed array potentiometric detectors may offer simultaneous detection of a wide variety of analytes.

B. Coulometric Detection

Coulometric methods, as traditionally defined, involve the conversion of all electroactive species to an electro-inactive form, i.e., 100% conversion efficiency; however, it is this authors opinion that detection methods based on chronocoulometric experiments, i.e., the measurement of charge with time, with conversion efficiencies much less than 100% must still be considered coulometric in nature, simply as the result of the measurement of charge and not current. Presented here are detection schemes which utilize coulometric electrodes which are capable of 100% conversion efficiencies. Methods involving pulsed coulometric detection are presented in the following section.

In practice, coulometric electrodes, do not offer higher sensitivity or lower detection limits than their amperometric counterparts. This is due primarily to the necessary increase in electrode area for coulometric determinations which, in turn, causes a proportional increase in the background noise. Additionally, coulometric cells used in LC are often characterized as being clumsy owing to the common use of indicating electrode particle beds. Coulometric detectors are also characterized as being totally destructive.

Advantages of coulometric detection can be the characterization of reaction products, and the possible increase in precision and accuracy of quantitative determinations. However, these advantages are not always obtained. Characterization of electrochemical reactions with Faraday's Law may fail if side reactions occur; and, quantitative determinations may not be limited by the precision and accuracy of the detector but rather by the reproducibility of the sample injector. These advantages, if they exist for the particular chemical system and LC apparatus, are not provided by other electrochemical methods of detection.

Few applications have appeared in recent literature for which coulometric detectors are used in conjunction with FIA and LC. Series coulometric cells have been introduced[25] for the determination of neurotransmitters. "Gate cells" were used for the elimination of electrochemically irreversible substances, and "array cells" for the separation of co-eluting compounds based on differences in their cyclic voltammograms. A coulometric reticulated vitreous carbon indicating electrode has been introduced[26] for use in FIA and conventional HPLC with flow rates less than ca. 1 mL/min.

C. Voltammetric and Polarographic Detection

Amperometric detection at single phase working electrodes continues to be the largest field in the development of electrochemical detectors for FIA and LC. Methods involving the application of constant-potential (dc) amperometric detection are considered commonplace and are not presented here. Amperometric detectors have the advantages of large sensitivity and low limits of detection, rapid response, and are applicable for the determination of a wide variety of electroactive and electroinactive compounds, organic as well as inorganic. However, several disadvantages exist for amperometric detectors in comparison to electrochemical detectors based on coulometry or potentiometry. The greatest disadvantage for all voltammetric detectors is the response dependence on the surface area and the surface state of the indicating electrode. Detector response is also dependent on the hydrodynamic conditions of the flow system and the composition of the supporting electrolyte. This latter effect results in the general inability to use these methods with gradient elution chromatography. Similar effects are seen with polarographic detectors with the exception of the surface state of the electrode since it is renewed with each drop. Several approaches have been taken to alleviate some of these problems and are presented below.

Detection at dual series electrodes (an extension of the more common ring-disk experiments) continues to be useful for the selection and identification of electroactive analytes. Dual series glassy carbon electrodes were used for the determination of phenolic constituents in commercial beverages and the determination of metabolites of acetaminophen in urine.[27] Series and parallel dual electrodes have been used for the characterization of the chemical and electrochemical mechanisms of 6-methylpterin.[28] Several advantages can be gained by monitoring current differences for both series and parallel configurations.[29] For parallel electrodes, an increase in the detectability is expected with the subtraction of common background interferants; furthermore, the selectivity can be increased with a small difference in potentials applied to the working electrodes. In the series configuration, the sensitivity and detectability can be increased for electrochemically reversible species; and, the S/N can be increased for all analytes if operated in the equipotential mode.

Microelectrodes have received recent attention for use in FIA and LC. They offer several advantages over conventional electrodes, including the ability to construct low dead-volume detectors compatible with microbore and capillary column LC, reduced iR drop, and a much smaller dependence on effluent flow rate. A graphite microarray amperometric detector[30] can be used for the discrimination of reactions limited by mass transport and reactions limited by electron transfer or other surface controlled processes at high applied potentials.[31] Microarray electrodes may afford a greater S/N than a single electrode of equal area.[30] The first report of the use of a single graphite fiber electrode (9 μm o.d.) inserted into an open tubular capillary column (15 μm i.d.) demonstrates the amperometric detection of electroactive components in urine.[32] In this latter study, nearly 100% conversion efficiencies were observed due to the combined effects of the small difference between the electrode diameter and the internal diameter of the capillary column, and the relatively large length of the carbon fiber electrode. Similar experiments have demonstrated the use of on-column voltammetric detection for the analysis of human urine.[33]

Several pulsed amperometric techniques applied to solid and mercury electrodes, e.g., normal pulse, differential pulse, and square wave, have been geared for use as detectors in LC. Of these waveforms applied to mercury electrodes, square wave holds the most promise, allowing for very rapid analysis and the construction of 3-dimensional chromatograms for compound identification and quantitation. An excellent review of square wave voltammetry and its comparison to other pulsed techniques has appeared recently.[34] Pulsed amperometric techniques have also been described for use with solid noble metal electrodes.[35-44] These waveforms were constructed to combat the problem of surface fouling observed with oxidative electrochemical detection at noble metal electrodes. A significant increase in detectability is not observed with the use of pulsed waveforms at solid metal electrodes over conventional dc detection because of the large charging currents associated with these electrodes. As an extension of pulsed amperometric detection, pulsed coulometric methods have recently been introduced in an effort to increase the detectability of electroactive analytes through an increase in conversion efficiency. For a thorough discussion of pulsed amperometric and pulsed coulometric detection, see the latter chapters of this dissertation. Electrode fouling can also be reduced with the low-frequency electrochemical pretreatment of solid electrodes.[45-52] Chemical coating of electrodes also has been described[53] for reducing surface fouling effects.

Additional amperometric detection methods have been reported for the determination of proteins,[54] and demonstrated with the detection of phenolic ethers,[55] which utilize techniques involving bromine microtitrations.

Several new electrochemical detectors have appeared. Biamperometric detection has been applied for the FI determination of Fe(II) in multivitamin preparations; no interference was reported for ascorbic acid which is more easily oxidized on platinum electrodes.[56] Coulostatic pulse amperometry--the injection of small known charge pulses into the electrochemical cell to maintain the indicating electrode at a fixed potential--have been demonstrated with caffeic acid and phenolic derivatives.[57] Three-dimensional voltammograms can be obtained for a single injection for quantitation and an estimation of half wave potentials. Spectroelectrochemical detection schemes have drawn recent attention. The amperometric photoelectrochemical detection of several organic molecules, e.g., alkyl and aryl ketones and aldehydes, has been recently discussed[58] in conjunction with reverse phase HPLC.

III. PULSE POLAROGRAPHIC METHODS

Since their inception by J. Heyrovsky[1], polarographic methods have become a strong force in analytical chemistry. Thousands of papers have appeared in the literature on various aspects of past, present and future polarographic methods, including the development of new and improved waveforms, noise reduction techniques, and the omnipresent determination of hundreds of classes of compounds, inorganic as well as organic, in a variety of matrices. For the present discussion, interest is centered upon the development of pulsed waveforms for increased signal-to-noise (S/N) and for the avoidance of ubiquitous interferants. All waveforms presented are summarized in the last section of this chapter for ease of reference and comparison. For more thorough discussions, the interested reader is encouraged to consult the extensive literature on this subject.[2-9]

After its introduction in the beginning of this century, and after a dramatic expansion period of ca. thirty years, techniques involving dc polarography were under serious scrutiny by the scientific and industrial communities as to their future potential in analytical chemistry. This was in part due to the crude and unpleasant nature of the dc polarographic technique, which was ultimately limited by electronic components of that era. In addition, flame atomic absorption spectrometry was at its peak and could compete well with the relatively insensitive dc polarographic methods for trace metal determinations. Ultimately the scientific community continued with the development of polarographic methods, primarily in theory, while users, past or present, fell behind, either by giving up polarographic methods completely or by being restricted to instruments capable of this single technique.

However, the interest in polarographic techniques, and thus, electrochemical methods surged with the introduction of differential pulse polarography and the appearance of improved commercially available instrumentation in the late 1960s and early 1970s.[10-12] In the last twenty years, the techniques have advanced dramatically with the advent of improved low-cost microprocessor-controlled instrumentation and with the extensive development of procedures for heavy metal and organic analyses.

A. Staircase Voltammetry

Although staircase voltammetry is not considered a true potential-pulse technique, it is worthy to note that improvements in detection limits can be obtained by employing this technique over conventional dc or sample dc polarography,[13-14] albeit it is no match for the pulse polarographic techniques which are described below. To further reduce charging current contributions, the current may be sampled twice in the lifetime of one drop (one step), and the current difference displayed as a function of potential.[14] The increase in detectability with this double sampling methodology is at the expense of sensitivity.

B. Normal Pulse Techniques

Normal pulse polarography was introduced by Barker,[15] and Barker and Gardner,[16] as were many of the pulse techniques, as an extension of his initial work on square-wave polarography. These methods involve the application of a potentiodynamic waveform to the DME with special current sampling techniques to discriminate against background noise and/or currents. With the use of integral sample-and-hold circuits this technique has sometimes been referred to as integral pulse polarography.

The popularity of NPP was a result of the increased sensitivity and subsequently the decrease in detection limits, and to a lesser extent the simplicity of the polarograms in comparison to dc polarography. Additionally, mechanisms may be inferred from NP experiments in which the pulse durations are varied; the kinetic restrictions of the reaction may be more obvious with a decrease in the pulse time.

1. Standard normal pulse polarography

Although a single technique is normally inferred with the statement "normal pulse polarography" there are several subtle modifications to what might be considered the most conventional waveform. The most common waveform used by scientists and instrument manufacturers alike is that waveform for which the output is simply the current measured after a selected delay time following the application of the final potential pulse. Here the initial potential is selected to be in a region of zero dc current background and is held constant throughout the entire experiment, whereas the final potential is scanned over the desired potential range. The output is the sampled current displayed as a function of the final potential.

2. Modified normal pulse polarography

This technique differs from standard normal pulse only in that the final potential is fixed for each pulse, and is not varied (scanned) over the period of the final potential pulse. The advantage for this waveform is that it reduces the background charging current due to potential variation. Newer, microprocessor-controlled instruments are implementing this waveform for their "normal pulse" mode.

3. Successive drop (fixed-amplitude) pseudoderivative normal pulse polarography

This method was developed to gain the advantage of increased resolution as commonly observed with differential pulse polarography (below) in addition to the advantages of standard normal pulse polarography. The experiment is usually performed in the exact same manner as standard normal pulse; however, the difference of currents measured at successive drops is displayed as a function of the average of final potential values.

4. *Variable-amplitude pseudoderivative normal pulse polarography*

The ability to vary or expand the pulse amplitude in a single experiment for pseudoderivative techniques leads to detection limits commonly observed with differential pulse polarography while at the same time maintaining the sensitivity at levels common to normal pulse polarography.[17-19] For example, if the standard normal pulse experiment is performed such that the final potential is stepped at -5 mV increments, then a pseudoderivative potential increment (ΔE) of -40 mV may be obtained by subtracting the first from the ninth, the second from the tenth, etc., for any specified range of the data set. A distinct advantage of this technique over differential pulse polarography is the elimination of dc offsets (see Section F, Subcategory 1). Additionally, differential pulse polarograms of varying pulse amplitudes ΔE require separate and distinct experiments whereas any number of curves may be generated from a single data set obtained from a single experiment with pseudoderivative techniques. This technique also retains the advantage of maintaining the working electrode at a fixed and defined initial potential for a majority of the experimental time.[19-21]

5. *Constant pulse amplitude normal pulse polarography*

This technique[22] presents essentially the same information for reversible systems as successive drop pseudoderivative normal pulse polarography; although no mathematical step is necessary for finite differentiation, and thus allows for real-time measurements. For irreversible systems or systems which display adsorption phenomena, the experiment may encode this information because of initial potential variation.

6. *Subtractive normal pulse polarography*

This waveform is similar in all respects with that for modified normal pulse polarography except the output is now the difference of two currents--the current measured after the application of the final potential pulse and the current measured just prior to the application of the pulse. This waveform is useful for subtracting out constant background offsets when the initial potential is defined to be in a region where a limiting current faradaic process occurs.[23]

7. *Differential normal pulse polarography*

Differential normal pulse is a hybrid of the normal pulse and differential pulse waveforms. The initial potential is defined to be in a region where no faradaic current flows and is stepped cathodically to the final potential, which is immediately followed by either a positive or negative small-amplitude pulse. In the alternating pulse mode, the small-amplitude pulse is alternately added or subtracted from the final potential with successive drops (or final potential pulses). For each cycle, the amplitude of the final potential is incremented while the value of the small-amplitude pulse is held constant. The differential current response is plotted as a function of the final potential. In addition to excellent charging current discrimination, detection limits and sensitivities are equal to or better than differential pulse polarography.[24]

8. Alternate-drop normal pulse polarography

All of the pulse techniques have been developed to enhance the measured signal-to-noise usually through an increase in signal and/or a decrease in noise. Background limitations are due primarily to potential and drop size variations during the current measurement period. All of the previous techniques make attempts to eliminate some of the background charge, but none have made exact corrections. Alternate-drop normal pulse polarography[25] does accomplish this by measuring the current at the same potential and at the same time in the drop life. This is accomplished by pulsing only alternate drops to the final potential E_2; all other drops are held at the final potential for their entire lifetime. The current output is the difference of the currents measured at the same time in the drop life, and at the same potential. However, since both current measurements are made at the same potential a reduction in the faradaic response is anticipated; the loss in sensitivity being a function of the system studied. Methods employing this waveform have also been applied at high scan rates.[26]

9. Optimized normal pulse polarography

This waveform attempts to reduce the charging current contribution by measuring the current at the beginning and ending of the final potential pulse; the current output is the difference between values measured on the same drop. In addition to lowering the sensitivity of the method in comparison to standard normal pulse polarography, this technique only reduces charging current contributions due to potential variation (i.e., the currents are measure at the same potential for each drop) and not from drop size variation; however, the detection limits are lowered over that for conventional normal pulse waveforms.[14]

C. Reverse Pulse Polarography

This technique utilizes the same waveform as normal pulse polarography and differs only in the regions for assignment of initial and final potential values.[27] The method has been applied for kinetic studies of electrode reactions, and for the determination of species which are hidden by cathodic solvent decomposition waves.

A unique feature of this method is that there exists a region, bounded by the decomposition of the electrode and the first reductive wave for dissolved oxygen, in which no interference is expected with oxygen saturated solutions owing to its irreversibility on this electrode material. This characteristic has led to reverse pulse amperometric methods of detection for which the presence of dissolved oxygen does not interfere.[28,29]

D. Constant Potential Pulse Polarography

This variant of pulse polarographic methods results by fixing the final potential and varying the initial potential between some specified limits. Initially, it was introduced because of the theoretical zero background charging currents,[30] but was latter used for the analysis of alkali and alkaline earth metals which are reduced at potentials far negative of the wave observed for hydrogen reduction.[31,32] Recent studies have shown that complex voltammograms can be obtained over the entire potential range for mercury with no interference from dissolved oxygen (see Chapter VI).

E. Constant-Current Pulse Polarography

This technique differs from all other pulse modes in that the time required to reach a predefined constant current is recorded versus applied potential.[33] The advantage of this method is the elimination of distortions due to current averaging (i.e., 16.7 ms integration periods) which is incorporated in many if not all of the pulse techniques. This is accomplished by the instantaneous measurement of time required to reach a constant sampling current. Waveforms have been developed for normal pulse and differential pulse modes of detection.[33]

F. Differential Pulse Techniques

At present the greatest number of analyses for which polarographic methods are used are performed with differential pulse polarography, primarily due to its increased detectability over many of the other pulse techniques and the availability of instruments which can perform this technique. This method differs from normal pulse techniques in that the pulsed waveform is superimposed upon a dc potential ramp. As with normal pulse polarography, there are many variations to the traditional differential pulse waveform.

1. *Standard differential pulse polarography*

The original, and by far the most common waveform, may be described as the summation of a small-amplitude square-wave potential waveform with a dc potential ramp; current measurement is made late in the drop lifetime at two points in the waveform, before and after pulse application, and the output is simply the difference of these two currents plotted against the applied voltage. In addition to lower detection limits, differential pulse polarography offers a more aesthetic voltammogram than its standard normal pulse counterpart. The lower detection limits are due to a reduction in the charging current background; a result of both the decreased amplitude of the potential step and partial subtraction by taking current differences. However, the sensitivity of the differential pulse technique is ultimately limited either by faradaic dc currents[23,34] (dc distortion effects) or by capacitive charging currents[23] (charging current distortion) which result from taking current measurements at different times (electrode areas) and potentials on the same drop, respectively; the former effect of dc distortion being a result of the inclusion of the dc potential ramp in the differential pulse waveform. However, with the inclusion of the dc potential ramp the technique may be more useful for analyses performed on a single drop.[35,36] Depletion effects may limit this effect with the normal pulse mode or with any such waveforms which have fixed initial potentials.

2. *Modified differential pulse polarography*

To reduce the charging current contributions during current integration the potential is held constant before pulse application; that is, the waveform is defined as discrete pulses and no dc ramp is employed for initial potential variation.[14,37]

3. *Differential single-pulse polarography*

This waveform uses a sampling methodology which increases S/N by subtraction of the oxidative current that flows upon stepping the potential back to its initial value; i.e., the current is now measured after application of the potential pulse and not before as in more conventional differential pulse techniques.[37]

4. *Differential double-pulse polarography*

This is simply an extension of the single-pulse waveform (above), and results from an increase in the negative pulse amplitude, and thus an increase in signal is obtained for a reversible system over that obtained with differential single-pulse polarography.[37] It is very similar to the square-wave methods discussed below; where the symmetry of the waveform allows for more exact correction of background charging current. As with the differential single-pulse technique no increase in signal is expected for irreversible systems.

5. *Alternate-drop differential pulse polarography*

This method differs from standard differential pulse polarography in that the current measurements are taken at exactly the same time in the drop life (however, measurements are carried out on successive drops) and at the same potential. This reduces the dc and charging current distortion effects as seen with the more common standard (single-drop) differential pulse polarographic technique.[38-40] As a result, sensitivities may be increased by ca. an order of magnitude, and the background charging currents are less severe.

6. *Successive-drop differential double-pulse polarography*

The method of successive-drop differential double-pulse voltammetry has been introduced for studies in which reactants or reactant products are adsorbed onto the surface of the electrode.[41] With the unique advantage of electrode surface renewal in polarographic methods and the similarity of this method to pseudoderivative techniques it has not found widespread use.

7. *Optimized differential pulse polarography*

This waveform utilizes the same sampling procedure as optimized normal pulse and optimized staircase techniques--the current is measured at two different times during the pulse period and their difference is recorded as a function of applied potential--in an effort to reduce the charging current contributions in the measured signal. As is true with all double sampling techniques previously discussed, the increase in detectability is at the expense of a severe reduction in sensitivity.[14]

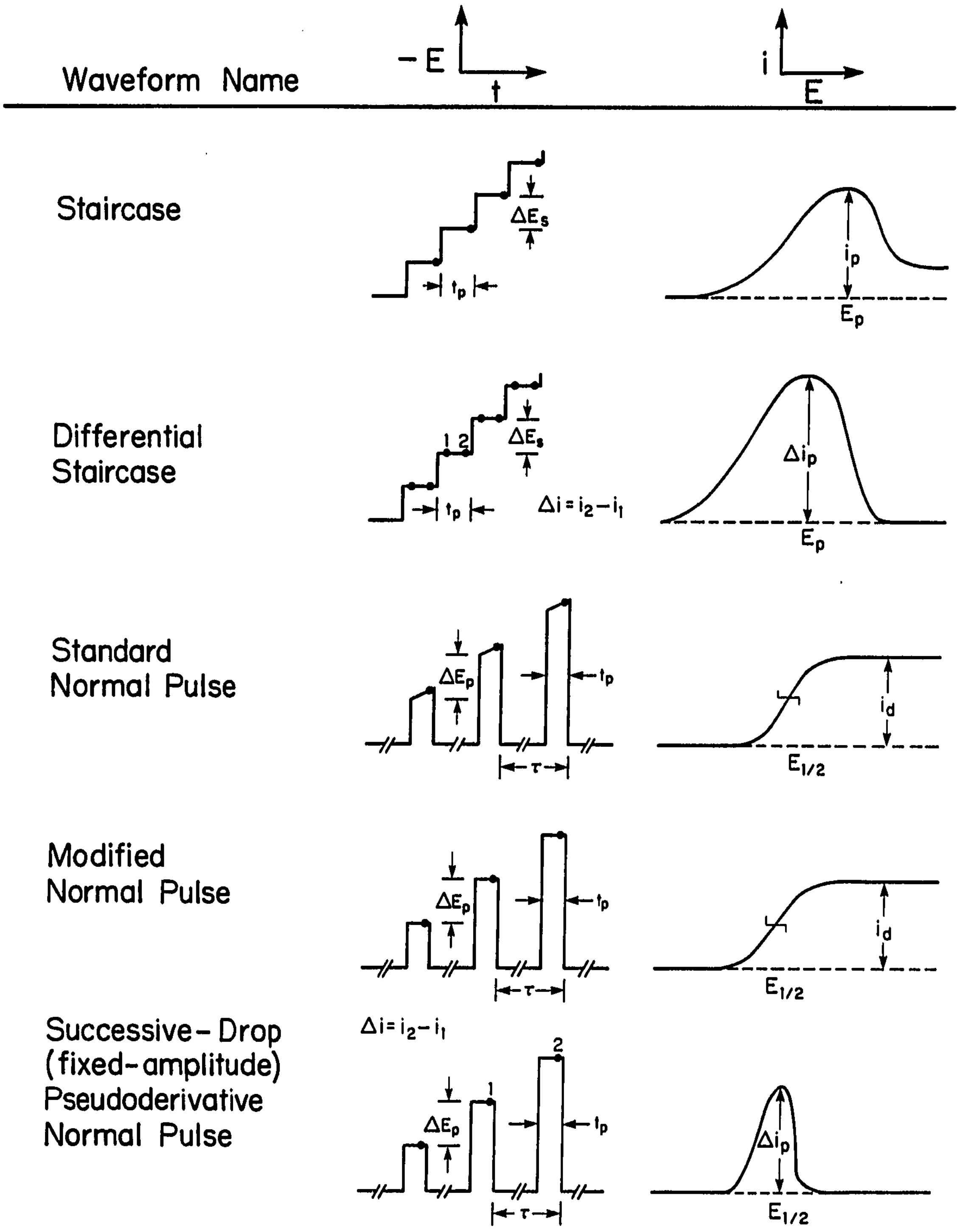
G. Square-Wave Polarography

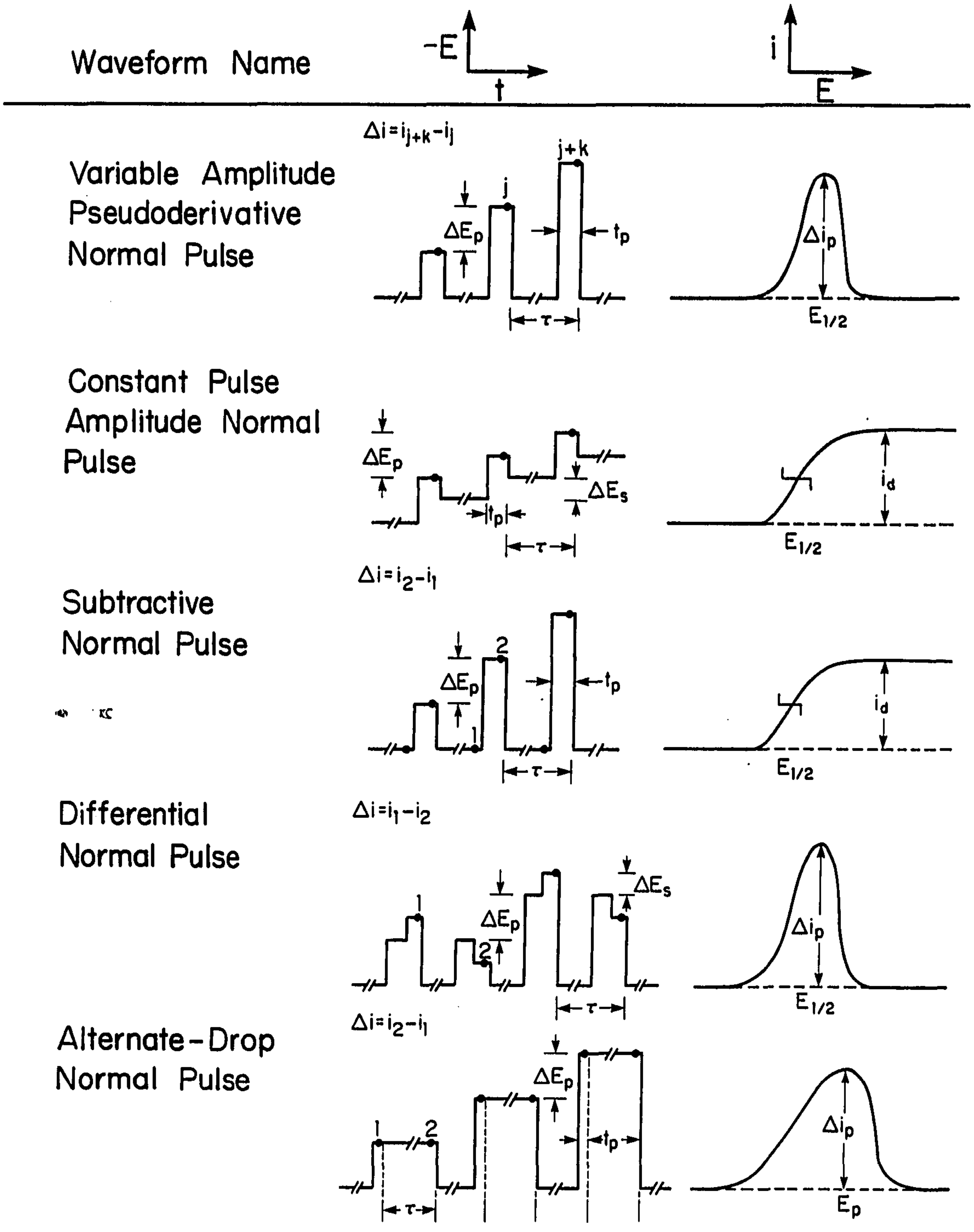
This technique may be described as the combination of a large-amplitude square-wave modulation with a staircase waveform[42,43] and is not to be confused with square-wave modulation introduced by Barker. In addition to 100X lower detection limits in comparison to differential pulse polarography, the experiments can be carried out with frequencies in excess of 1000 Hz (200 Hz is commonly used), and thus, can be carried out on a single drop.[44] With the ability to run the waveform at such high frequencies, without sacrificing detectability, signal averaging techniques may be employed to further increase signal-to-noise. Additional advantages are gained because of the symmetry of the waveform. For example, exact charging current compensation may be achieved as a result of equivalent potential steps before current measurement.

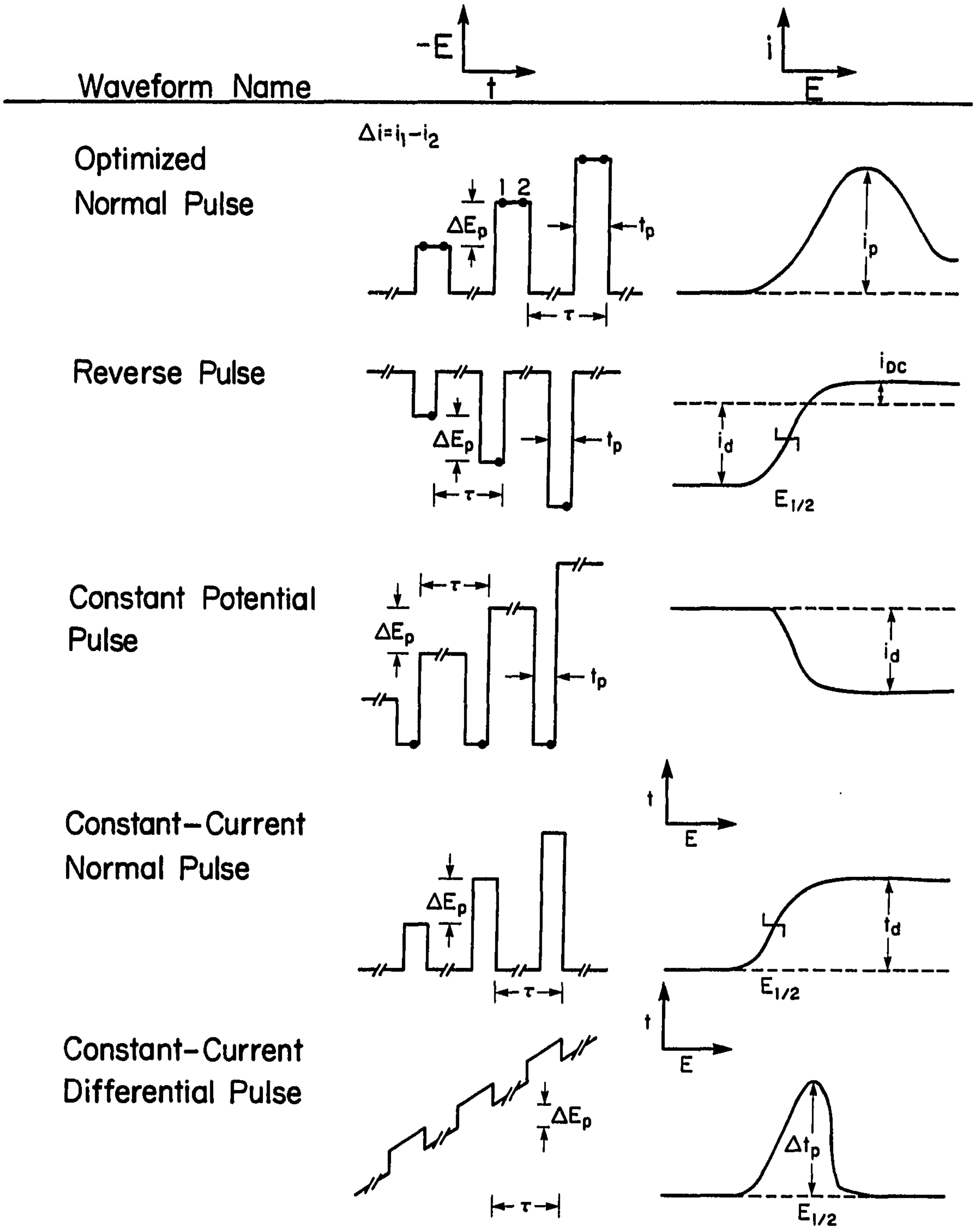
It is this author's belief that the strength of this technique lay in the ability to run the waveform at such high scan rates without distortion from charging current phenomena; hence, reactions which are considered fast on a conventional cyclic voltammetry time scale can be "stopped" for kinetic studies. Additionally, three-dimensional voltammograms (i vs. E vs. t) may be easily obtained and constructed with the use of digital computers for use in FIA and LC. Two instruments, the BAS-100 (Bioanalytical Systems, West Lafayette, IN) and the PAR 384B (EG&G Princeton Applied Research, Princeton, NJ), are currently supporting this technique.

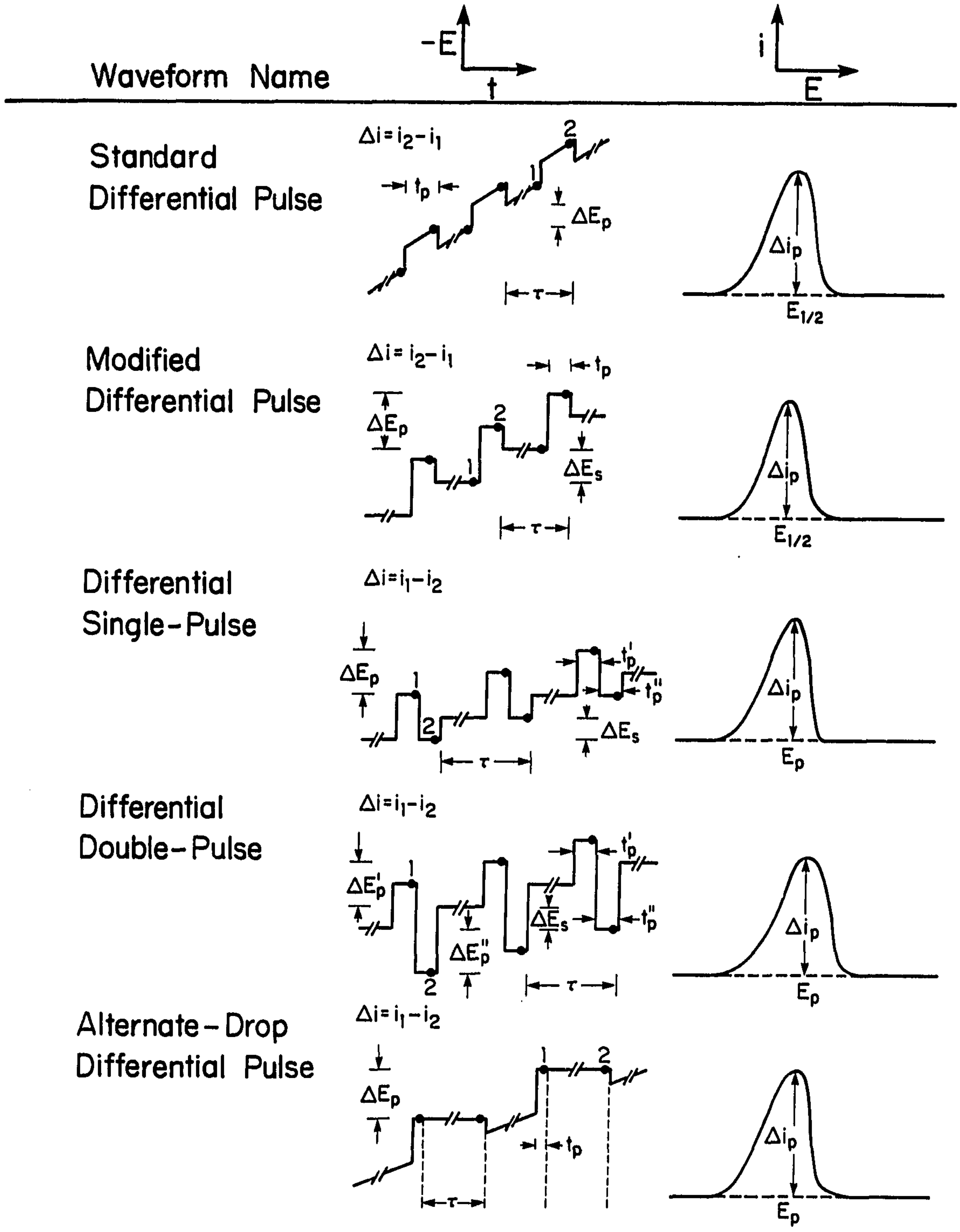
H. Compilation of Pulsed Polarographic Waveforms

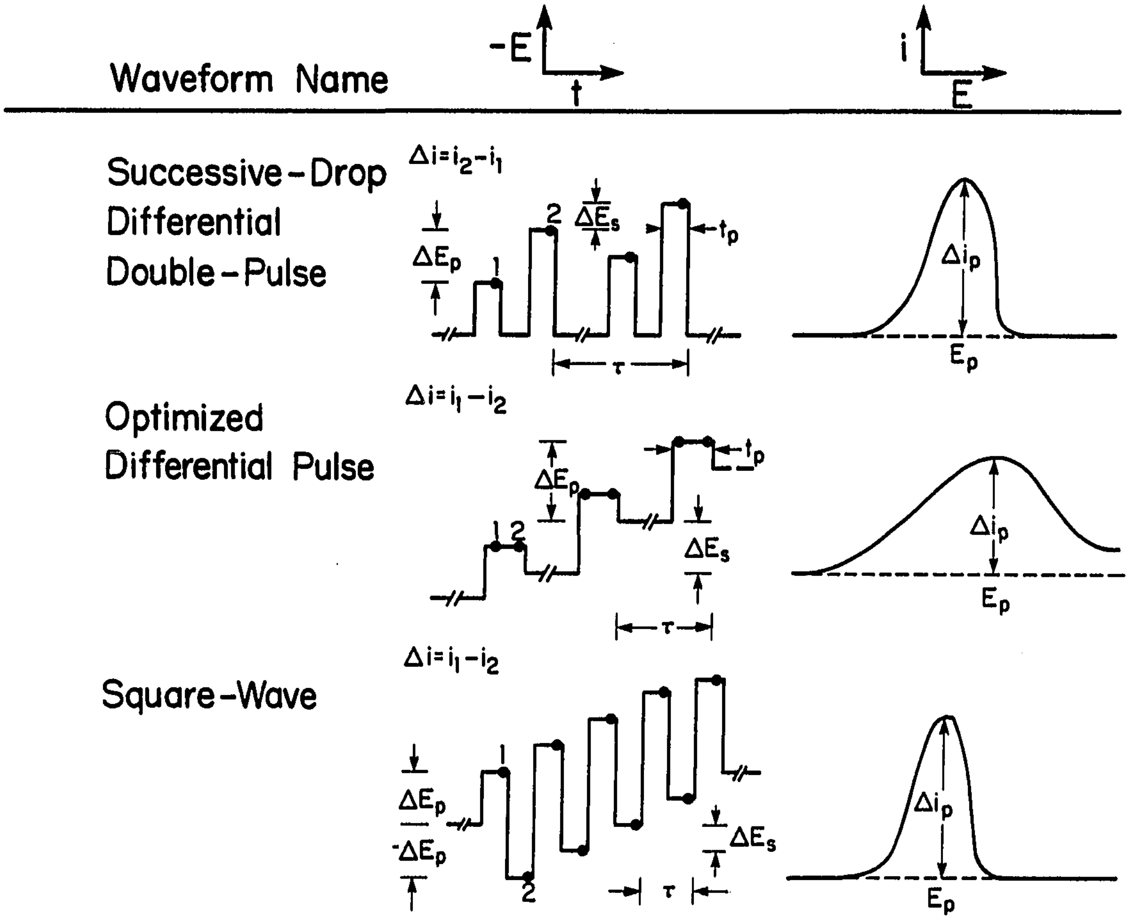
The following five pages contain a pictorial summary of all the waveforms discussed in this chapter. The format of this summary is as follows. 1) The name of the waveform is listed in the first column, and the waveforms are presented in the same order as they appeared in this chapter. However, the names of some waveforms are generic; that is, a great deal of confusion exists in the literature in reference to naming pulsed waveforms (i.e., the same waveform may have different names, or different waveforms may have the same name). Therefore, the most descriptive name was selected for these waveforms, and these names may not appear in the literature. 2) The second column contains pictorial descriptions of the potentiodynamic waveforms applied for a reducible analyte. All variables of the waveforms are included in these figures. 3) The final column shows the expected voltammetric response for a reducible and reversible analyte.


Waveform Name
−E
t
i
E
Staircase
ΔE_s
t_p
i_p
E_p
Differential Staircase
1 2
ΔE_s
t_p
Δi = i_2 − i_1
Δi_p
E_p
Standard Normal Pulse
ΔE_p
t_p
τ
i_d
E_1/2
Modified Normal Pulse
ΔE_p
t_p
τ
i_d
E_1/2
Successive-Drop (fixed-amplitude) Pseudoderivative Normal Pulse
Δi = i_2 − i_1
1
2
ΔE_p
t_p
τ
Δi_p
E_1/2


Waveform Name
-E
t
i
E
Variable Amplitude Pseudoderivative Normal Pulse
Δi = i_{j+k} - i_j
j+k
j
ΔE_p
t_p
τ
Δi_p
E_{1/2}
Constant Pulse Amplitude Normal Pulse
ΔE_p
t_p
ΔE_s
τ
i_d
E_{1/2}
Subtractive Normal Pulse
Δi = i_2 - i_1
2
1
ΔE_p
t_p
τ
i_d
E_{1/2}
Differential Normal Pulse
Δi = i_1 - i_2
1
2
ΔE_p
ΔE_s
τ
Δi_p
E_{1/2}
Alternate-Drop Normal Pulse
Δi = i_2 - i_1
1
2
ΔE_p
t_p
τ
Δi_p
E_p


Waveform Name
-E
t
i
E
$\Delta i = i_1 - i_2$
Optimized Normal Pulse
1 2
ΔE_p
t_p
τ
i_p
Reverse Pulse
ΔE_p
t_p
τ
i_{DC}
i_d
$E_{1/2}$
Constant Potential Pulse
τ
ΔE_p
t_p
i_d
t
E
Constant-Current Normal Pulse
ΔE_p
τ
t_d
$E_{1/2}$
t
E
Constant-Current Differential Pulse
ΔE_p
τ
Δt_p
$E_{1/2}$


Waveform Name
-E
t
i
E
Standard Differential Pulse
Δi = i2 - i1
tp
ΔEp
τ
1
2
Δip
E1/2
Modified Differential Pulse
Δi = i2 - i1
tp
ΔEp
ΔEs
τ
1
2
Δip
E1/2
Differential Single-Pulse
Δi = i1 - i2
ΔEp
t'p
t''p
ΔEs
τ
1
2
Δip
Ep
Differential Double-Pulse
Δi = i1 - i2
ΔE'p
ΔE''p
ΔEs
t'p
t''p
τ
1
2
Δip
Ep
Alternate-Drop Differential Pulse
Δi = i1 - i2
ΔEp
tp
τ
1
2
Δip
Ep


Waveform Name
-E
t
i
E
Successive-Drop Differential Double-Pulse
Δi=i2-i1
ΔEp
1
2
ΔEs
tp
τ
Δip
Ep
Optimized Differential Pulse
Δi=i1-i2
ΔEp
1 2
tp
ΔEs
τ
Δip
Ep
Square-Wave
Δi=i1-i2
ΔEp
-ΔEp
1
2
ΔEs
τ
Δip
Ep

IV. UNDERPOTENTIAL DEPOSITION

> "From the point of view of theoretical electrochemistry the behavior of metallic ions in the electrolysis of very dilute solutions is now more satisfactory than it previously seemed to be. We see, however, that it is dangerous to use the critical potentials measured in these solutions for the calculation of an unknown normal potential. Such an extrapolation should be made only if the potential varies with the concentration and if it is independent of the nature of the electrode, at least for several metals."

Haissinsky and Coche[134], 1949

Underpotential deposition effects were noted as early as 1912 by Hevesy[149,150] and were followed by a series of papers from 1913 to 1915 by Paneth and Hevesy.[246a-c] Their interests at this time lay in the characterization of Polonium, an element available in only trace amounts, by cathodic deposition upon a variety of substrates. This characterization was based upon the calculation of the formal potential from the Nernst equation given the concentration of the reactant and its valency change. In their initial investigations, they noted that some systems did not follow the Nernst equation, i.e., deposition occurred at more positive potentials than expected and there was notable deviation from the expected potential shifts due to concentration variation of the reactant. Explanations of these effects were proposed by several authors in the decades to follow and usually centered around the modification of the Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \qquad [1]$$

Herzfeld[147] proposed that the activity of the electrode surface was not unity, as is normally assumed, and offered the supposition that the activity was a function of the surface coverage θ, for $\theta < 1$. Later workers, such as Rogers and Stehney,[259] introduced other terms to account for specific interactions between the adsorbing or depositing metal ions and the particular substrate.

It is interesting to note that initial investigations of the UPD effect involved the use of "inert" electrodes; that is, electrodes which were believed not to contribute to the observed effect. This early conclusion was specifically addressed by Haissinsky and Coche (preceding quotation) in the 1940s and was shown to be absolutely false.

Concurrently with the development of the theoretical basis for the UPD effect many groups were studying the UPD of a variety of adatoms upon a variety of substrates with particular emphasis placed upon the variation of metal ion concentration, type of supporting electrolyte and its concentration, the presence of interfering anions and complexing agents, etc. Most of these studies were performed in conjunction with the development of UPD for analytical stripping analysis.

During the decade from ca. 1965-1975, Schmidt and co-workers,[246-280] with the availability of more specific and sophisticated techniques, directed their efforts toward the study of the UPD phenomena. Early investigations involved the use of a variety of electrochemical techniques, such as cyclic voltammetry and chronoamperometry, and later efforts centered around studies on single crystal electrodes.

Presently, numerous groups have studied the effects of UPD of metal ions on a variety of single crystal surfaces, with the most common being the Ag and Au 100, 110, and 111 single crystal faces. Several investigations have shown that correlations may be made between the deposition and stripping peaks observed on polycrystalline electrodes and that of their single crystal faces; thus, it is possible to assign the various stripping peaks to their corresponding single crystal faces.

A particularly exciting branch of the UPD phenomena is its "catalytic" effect upon the oxidation and reduction of numerous organic and some inorganic molecules. The use of the word "catalytic" is at present in serious question, since the apparent effects causing the increase in reaction rate, in one case, were shown not to be due to a lowering of the reaction energy barrier. Adzic *et al.*[2-19] have studied the effects of UPD of metal monolayers upon several noble metal electrodes, with special interest upon the oxidation of formic acid, a believed common intermediate for many organic oxidations. Kokkinidis *et al.*[181-191] have performed similar studies for a variety of chemical systems including aliphatic alcohols, pyrocatechol/o-benzoquinone, ammonia, etc. Several groups have studied reductions with particular emphasis upon the reduction of dissolved oxygen on several noble metal electrodes modified by UPD.

Since it would be impossible to summarize the work in literary form which has been accumulated over the last 75 years, it has been compiled and is presented in a detailed summary (Section D). Only that work which specifically involved electrochemical investigations is included; work involving only UHV or vapor phase experiments is specifically excluded. A definition of terms used in the UPD summary is contained in a separate section (Section C) and directly follows this discussion. It is hoped that this compilation will guide future researchers and may hopefully be used in the preparation and presentation of a review on UPD.

Some of the references have been selected as being outstanding in any one or more of several categories and are listed below for easy reference.

Founding papers	147, 149-151, 245, 246a-246c
Historical Discussions	79-84, 130-137, 171, 258-261
Reviews	16, 18b, 67, 88, 118, 175, 190, 199, 217, 223, 314, 333, 336
References (text)	42, 193, 199, 223, 314

Summary of UPD data	117, 193, 194, 334, 335
Theoretical Discussions	21, 63, 67, 87, 89, 190, 194, 201, 247, 263, 284, 287, 321, 322

A. Introduction to UPD Compilation

This section is included to help in the interpretation of the UPD summary; a compilation of the literature on *underpotential deposition*. The general format of this summary is as follows: 1) The substrate used in the study is listed in the first column; short-hand notation is used to signify the use of special electrodes (see Section C for a discussion of these notations). For example, Au/Pt denotes that the electrode is composed of an alloy of Au and Pt, C:graph. denotes that a carbon graphite electrode was used, etc. 2) The UPD adatom(s) are listed in the second column. Short-hand notation is also used. The asterisk (*) is used to denote that the substrate/adatom(s) pair is continued from the previous record. Other notations are summarized in Section C. 3) The third column contains a list of descriptive terms, called attributes, which are used to summarized the conditions of the investigation(s), note special experimental techniques, and comment upon special goals of the investigations. Additionally, for many substrate/adatom(s)/solution pairs the values of ΔE_p or $E_{\frac{1}{2},d}$ are listed; however, this is done only once for each unique substrate/adatom(s) entry, and may be found anywhere within the specific record list. A more thorough discussion of this section may be found in proceeding paragraphs. 4) The references are listed in the fourth and final column. Additional information may be gained by consulting the extended bibliography in Appendix A.

The attribute field is the heart of this summary, and is often the separator between similar records or references. In this field, a variety of information may be found. First, if the reference includes a thorough theoretical discussion this is noted in this field by the symbol T. Second, only methods which involved electrochemical investigations are summarized; however, notations are made for those investigation which used additional non-electrochemical methods. For example, studies which involved low-energy electron diffraction (LEED) are noted by including this acronym in the attribute field. Specific comments are also made of the supporting electrolyte(s) used in the investigation and perhaps the molar concentration of these solutions. From this point on, the similarity between records is almost non-existent. Additional comments may be directed towards the study of specific reactions catalyzed by UPD of metal adatom(s) (cf. r-, section C), the effects of anion or cation adsorption (cf. a-, c-, section C), or comments upon the specific goal of the investigation. For a complete summary of all possible entries, see Section C.

At the time of compilation of this table, a special format was followed to simplify the reading of the table.

The entries in the attribute section are listed in the following order, but they are listed only if they exist: 1) comments about the creation of the substrate; 2) comments about the ionic character of the depositing adatoms, i.e., the anion associated with the depositing cation, however, these are listed only if the anion differs from the supporting electrolyte anion; 3) the inclusion of a theoretical discussion, T; 4) the supporting electrolyte(s) used and their respective concentrations; 5) anion or cation adsorption effects, a-, c-; 6) special reactions studies for electrocatalytic effects from UPD of metal adatom(s), r-; 7) values for ΔE_p or $E_{½,d}$, listed in volts; and, 8) any further comments about the specific investigation. A semicolon (;) is used to separate dislike elements in the attribute definitions, e.g., T; AES; LEED; 0.5 M $HClO_4$. A comma (,) is used to separate elements in a common attribute, e.g., r-reds. of $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5F^{2+}$, $Cr(OH_2)_5OSO_3^{+}$, $Cr(NH_3)_5OH_2^{3+}$, $Cr(en)_3^{3+}$, $Eu(OH_2)_n^{3+}$.

As a final note, at the time of compilation no differentiation was made between the states of the depositing adatom(s); that is, the ionic states of the depositing adatom(s) are not listed, however in most experiments the common valence states may be assumed. Additionally, the state of the substrate is not indicated and experiments may have been performed on any of several electrode types. For example, UPD may have been performed on either a "clean" electrode surface or an electrode covered with an oxide layer. Further information about the specific investigation may be obtained from the extended bibliography in Appendix A.

B. General Overview of Definitions

This following section contains descriptions of the acronyms and abbreviations used in the UPD summary (Section D). Acronyms which are used to define an experiment are expanded to their usual or common form; however, no descriptions of these experimental techniques are given, and the interested reader is encouraged to seek out further information in the appropriate references.

Entries which are preceded by ellipses (...) denote that the suffix pattern is applied in general to a compound name. Square brackets ([]) denote that the word or phase is optional. Usage of these optional phrases may simplify the interpretation of the UPD table attribute. Parentheses are used to define optional forms for a given abbreviation. Braces ({}) are used either to clarify the applicability of some abbreviations, or to define listed punctuation marks. Braces used in this latter manner are printed in italics for clarification.

C. Definition of Terms

Abbreviation	Description
, *{comma}*	used as a separator between like elements in an attribute, e.g., r-oxid. CO, HCOOH, HCOH
; *{semicolon}*	used as a separator between dislike elements in the attribute definitions, e.g., LEED; 0.5 M $HClO_4$
* *{asterisk}*	used to denote the continuation of a substrate/adatom(s) pair
~ *{tilde}*	approximately-equal-to, denotes that the concentrations of the compounds stated are only approximate
...benz.	...benzene
...hydraz.	...hydrazine
...meth.	...methane
('number')	when directly following a listed supporting electrolyte the number in parentheses denotes the pH of the supporting electrolyte. For multiple supporting electrolytes listed for a single reference it refers only to that solution just preceding it, unless stated otherwise.
('number')	when following an attribute other than a supporting electrolyte, this denotes that the attribute preceding it is discussed only in the corresponding relative reference; e.g., SRS (1), denotes that a discussion of SRS applicable to UPD can be found in the first reference listed in the adjacent reference column.

Abbreviation	Description
(compound)	denotes a specific example of a group of compounds listed for electrocatalytic study (cf. r-)
+e	denotes that electrolytes, different than those stated in the attribute section, were used, or the electrolytes used as stated in the attribute section were used in varying concentrations.
+s	denotes that other single crystal faces were studied for the same or a different substrate, and can be listed within the table under the appropriate categories.
-I	denotes that iodide pretreatment of the substrate was used prior to the experiments
ΔE_p (, ,)	The peak voltage difference of the first UPD stripping peak and that for bulk stripping, expressed in units of volts. Information in parentheses may clarify either of the following, the electrodeposited adatom(s), the crystal plane or face, and the supporting electrolyte.
ΔE_p=f(face)	denotes that the peak potential for the specific face has been determined but is probably summarized in graphical form.
A/B {adatom(s)}	codeposition of A and B on the listed substrate
A/B {substrate}	denotes that the substrate used was made from an alloy of A and B
A/m-B {substrate}	denotes the deposition of a monolayer or less of B onto A
A-B {substrate}	denotes that A is deposited electrochemically on B unless otherwise stated in the attributes section

Abbreviation	Description
A:B {substrate}	denotes that the substrate is made of element A but with the special crystallographic form B. For example, C:glassy implies that a carbon electrode was used, and specifically, a glassy carbon electrode.
a- (a,c-)	anion effects of supporting electrolyte(s); may also denote adsorption effects of neutrals, such as CO_2.
a-sup.	see a-
ACN	acetonitrile
ads.	adsorption [of]
ads. kinetics	adsorption kinetics are discussed
AES	Auger Electron Spectroscopy
anal.	analytical
as ...	denotes that the electrodeposited ion was of a different composition that the supporting electrolyte. For example, as PbF_2, denotes that the F^- anion is different from the supporting electrolyte anion.
B-carbide	Boron Carbide
benzoquin.	benzoquinone
benzotriaz.	benzotriazole
buff.	buffer [of]
BuPyCl	butyl pyridinium chloride
c- (a,c-)	cation adsorption effects are discussed
c-sup.	see c-
carb.	carbide

Abbreviation	Description
catal.	catalytic or catalysts
cf.	see the listed reference
char.	characterization
codepos.	codeposition [of]
comp.	comparison [of], or compared [to]
d (depos.)	deposition
depos. (d)	deposition
disc.	discussion [of]
DS	Desorption Spectra
$E_{\frac{1}{2},d}$ (,)	the characteristic half-wave deposition potential, this is directly followed with the information, (supporting electrolyte, pH of the solution)
e-	Concentration variation of either adsorbed anions or supporting electrolyte(s), or both
ED	Electron Diffraction
eff.	effect[s] [of]
Ellip.	Ellipsometry
EM	Electron Microprobe
en	ethylenediamine
EPE	Electronic PhotoEmission
Et_4NClO_4	ethylammonium perchlorate
evol.	evolution [of]
exam.	example, denotes that the UPD example is used for demonstration purposes in a theoretical discussion

Abbreviation	Description
Fe-TsPc	iron tetrasulfonated phthalocyanines
FIM	Field Ion Microscope
gen. disc.	general discussion, applicable to UPD as a whole
gen. theory	general theory, applicable to UPD as a whole
graph.	graphite
HOAc	acetic acid
hydroquin.	hydroquinone
increas.	increase
mc	mica
mech.	mechanism [of]
MeOH	methanol
mono.	monolayer [of]
monosacch.	monosaccharides, listed under catalytic effects of reactions (cf. r-)
mono. red. sep. bulk	denotes that submonolayer or monolayer deposition is separate from bulk deposition
Moss.	Mossbauer Effect
mult.	multiple
NA	adatom or attribute information not available at the time of compilation
OAc	acetate anion
org.	original
oxid.	oxidation [of]

Abbreviation	Description
part.-part. inter.	particle-particle interactions, denotes that interactions between UPD atoms are discussed
pg:graph	pyrolytic graphite
phenyldinitrometh.	phenyldinitromethane
phenylnitrometh.	phenylnitromethane
photo. exam.	photographic examination in conjunction with radiotracer methods (RTM)
pot.	potential
PPC	propylene carbonate
Pt(S)-I	an abbreviation for Pt(S)[6(111)x(111)]-I, an I pretreated crystal face of Pt
QCM	Quartz Crystal Microbalance
r-	compound(s) following this symbol were studied for "catalytic" effects due to UPD
R {bold}	Review of UPD
react.	reactivity [of]
red.	reduction [of]
ref.	reference
reg.	regions, used to denote that separate regions are seen for UPD and bulk deposition, or UPD and bulk stripping. This may also include more than two distinct regions for UPD and/or bulk processes, e.g., 3 or more distinct regions for stripping.
revers.	reversibility

Abbreviation	Description
RHEED	Reflected High Energy Electron Diffraction
RTM	RadioTracer Methods
rxns.	reactions [of]
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
sep.	separate [from]
SERS	Surface Enhanced Raman Scattering
SHG	Second Harmonic Generation, use of, to monitor UPD monolayer growth on substrate
solns.	solutions
SRS	Specular Reflectance Studies {Spectroscopy}, includes differential specular reflectance
strip.	stripping
substr.	substrate
surf.	surface
T {bold}	theoretical discussion of UPD
Temp.	Temperature [effects of]
thermo.	thermodynamics [discussion of]
trans. to Ar electrochem.	see UHV
UHV	UltraHigh Vacuum, denotes that the single crystals were either cut or cleaned in a UHV environment and than transferred to the electrochemical system, usually purged with an inert gas such as Ar.

Abbreviation	Description
UHV single cryst.	see UHV
UPD	UnderPotential Deposition
ver.	verification [of]
ver. third strip.	Studies were performed to determine peak (H UPD) or verify the "source" of three deposition peaks for H (usually on Pt)
w/	with
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

D. Summary of Underpotential Deposition Literature

Following is a thorough examination and summary of the literature on the underpotential deposition of metal ions on foreign metal substrates. With the exception of the first page of this summary, an index of the substrate/adatom(s) pair has been included as the first entry on each page, but is listed in italics to minimize confusion with the other entries of the summary. If the substrate/adatom(s) pair is continued from the previous page the word *continued* will appear in the attribute field. For a detailed discussion of the format of this summary see Section A of this chapter, or for a summary of the terms and symbols see the proceeding section of this chapter. To minimize searching efforts a copy of this compilation is included on the disk accompanying this dissertation.

Substrate	Adatom(s)	Attributes	Reference(s)
Ag	Bi	1 $\underline{M}$ HNO_3	94,95
	*	$HClO_4$; KCl	268
	*	0.5 $\underline{M}$ $HClO_4$; ΔE_p=0.065	193,268
	Bi/Pb	$HClO_4$/KCl	267
	Cd	SERS; 0.1 $\underline{M}$ KCl; a-pyridine	342
	*	1 $\underline{M}$ $HClO_4$; a-Cl^-, HSO_4^-, thiourea	160
	*	T; 0.5 $\underline{M}$ Na_2SO_4	45
	*	XRD; 0.5 $\underline{M}$ NaCl; ΔE_p=0.19 (cf. 193)	279
	*	1 $\underline{M}$ Na_2SO_4 (3); ΔE_p=0.16	
	Cu	1 $\underline{M}$ $HClO_4$; 0.5 $\underline{M}$ Na_2SO_4	274
	Hg	surf. char.	148
	Li	1 $\underline{M}$ $LiClO_4$ in ACN; ΔE_p=0.96	193
	*	1 $\underline{M}$ $LiClO_4$ in PPC; ΔE_p=1.00	193
	Pb	SERS; 0.1 $\underline{M}$ KCl; a-Cl^-, pyridine	124
	*	SHG; 0.1 $\underline{M}$ NaOAc; surf. depos. monitoring	90
	*	0.5 $\underline{M}$ $NaClO_4$ (3.5)	164
	*	SERS; 0.1 $\underline{M}$ KCl/0.05 $\underline{M}$ pyridine (5.5)	123
	*	40 m$\underline{M}$ $La(ClO_4)_3$/3 m$\underline{M}$ $HClO_4$; r-$Cr(NH_3)_6^{3+}$ red.	207,208
	*	0.5 $\underline{M}$ $NaClO_4$/3 m$\underline{M}$ $HClO_4$; r-reds. of $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5F^{2+}$, $Cr(OH_2)_5OSO_3^+$, $Cr(NH_3)_5OH_2^{3+}$, $Cr(en)_3^{3+}$, $Eu(OH_2)_n^{3+}$	207,208
	*	0.1 $\underline{M}$ $LiClO_4$ in MeOH; r-red. of dinitrobenzenes	169
	*	a-I^-	25
	*	1 $\underline{M}$ HNO_3	82
	*	0.5 $\underline{M}$ Na_2SO_4 (2); 0.5 $\underline{M}$ $NaClO_4$ (2); a-Cl^-, Br^-, I^-	198
	*	T; $NaClO_4$/$HClO_4$; H_2SO_4	211
	*	0.1 $\underline{M}$ NaOH; 0.1 $\underline{M}$ Na_2SO_4 (4); 0.1 $\underline{M}$ Na_2CO_3	232
	*	T (2); 0.5 $\underline{M}$ KCl	264,273

Substrate	Adatom(s)	Attributes	Reference(s)
Ag	*Pb*	*Continued*	
	*	$HClO_4$; KCl	268
	*	0.5 M solns. of NH_4ClO_4; NaF; NH_2SO_3H; KI; KCl; KSCN; KBr	266
	*	RTM; comp. w/ Po depos.	81
	*	SHG	91
	*	$NaClO_4/HClO_4$ (5); catal. surf. area measurements	109
	*	SRS	196
	*	RTM; 0.16 M sodium tartrate; 0.3 M NaOH	218
	*	1 M $NaClO_4$ (3); ΔE_p=0.16	
	*	0.5 M KCl; ΔE_p=0.12	193
	Pb/Bi	$HClO_4$/KCl	267
	Pb/Tl	0.5 M NH_4ClO_4; 0.5 M KCl	267
	Po	Photo. exam.; surf. char.	80
	Sn	1 M KCl/10 mM HCl	278
	Tl	SERS; 0.1 M KCl; a-pyridine	342
	*	SERS; 0.1 M KCl (8); a-benzotriaz.	178
	*	T; SRS; 1 M $HClO_4$	308
	*	SRS; 0.5 M Na_2SO_4/1 mM $HClO_4$	34
	*	40 mM $La(ClO_4)_3$/3 mM $HClO_4$; r-$Cr(NH_3)_6^{3+}$ red.	207,208
	*	0.5 M $NaClO_4$/3 mM $HClO_4$; r-reds. of $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5F^{2+}$, $Cr(OH_2)_5OSO_3^+$, $Cr(NH_3)_5OH_2^{3+}$, $Cr(en)_3^{3+}$, $Eu(OH_2)_n^{3+}$	207,208
	*	a-I^-	25
	*	0.5 M Na_2SO_4 (2); 0.5 M $NaClO_4$ (2); a-Cl^-, Br^-, I^-	198
	*	0.5 M KCl	265,210
	*	$NaClO_4$ in MeOH; a-Cl^-	271
	*	RTM; 0.16 M sodium tartrate; 0.3 M NaOH	218
	*	1 M Na_2SO_4 (3); ΔE_p=0.27$_5$	193

Substrate	**Adatom(s)**	**Attributes**	**Reference(s)**
Ag	*Tl*	*Continued*	
	*	0.5 M KCl; $\Delta E_p=0.18_5$	268,193
	Tl/Pb	0.5 M NH_4ClO_4; 0.5 M KCl	267
	Zn	SEM; XRD; 1 M KOH; $\Delta E_p=0.15$	2
Ag-glass	Pb	Au vapor depos.; LEED; RHEED; 0.5 M $NaClO_4$ (2)	349
Ag-mc	Pb	Au vapor depos.; LEED; RHEED; 0.5 M $NaClO_4$ (2)	349
Ag(100)	Bi	0.5 M $HClO_4$; r-O_2 red.; +s	176
	Cd	T; 0.5 M Na_2SO_4	45
	Pb	0.5 M NaCl (3); effects of SDS ΔE_p = 200-300 mV	27
	*	T; 0.5 M $NaClO_4$/5 mM $HClO_4$	44,46
	*	T; 0.5 M Na_2SO_4/5 mM $HClO_4$; ads. kinetics	180
	*	0.5 M $HClO_4$; r-O_2 red.; a-Cl^-	350
	*	T; SRS; 0.3 M NaOAc/0.01 M HOAc; 0.5 M $NaClO_4$/0.2 M NaOH/0.1 M citric acid; $HClO_4$; 2-D nucleation	37
	*	SRS; as PbO; 0.5 M NaOAc/0.1 M HOAc; 0.5 M $HClO_4$; 0.5 M $NaClO_4$ (5.4); mult. layer UPD; comp. w/ Tl depos.	38
	*	0.5 M NaOAc/0.1 M HOAc; 0.5 M Na_2SO_4/1 mM $HClO_4$; surf. char.	35
	*	0.1 M $HClO_4$; r-Fe-TsPc	19
	*	0.5 M $HClO_4$; r-O_2 red.; +s	176
	*	0.2 M $LiClO_4$ in MeOH; r-nitrobenz. oxid., nitrosobenz. oxid.	182
	*	$HClO_4$; H_2SO_4; r-red. of quinone, H^+, persulfate	1
	*	T; isotherm ads.	327

Substrate	Adatom(s)	Attributes	Reference(s)
Ag(100)	*Pb*	*Continued*	
	*	SEM; 0.5 $\underline{M}$ $NaClO_4$/1 m$\underline{M}$ $HClO_4$	298
	*	1 $\underline{M}$ $HClO_4$	98
	*	0.5 $\underline{M}$ $NaClO_4$; 0.5 $\underline{M}$ Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s	219
	Tl	0.5 $\underline{M}$ NaCl (3); effects of SDS ΔE_p = 200-300 mV	27
	*	T; 0.5 $\underline{M}$ Na_2SO_4/5 m$\underline{M}$ $HClO_4$; ads. kinetics	180
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; a-Cl^-	350
	*	0.5 $\underline{M}$ NaOAc/0.1 $\underline{M}$ HOAc; 0.5 $\underline{M}$ Na_2SO_4/1 m$\underline{M}$ $HClO_4$; surf. char.	35
	*	SRS; 0.5 $\underline{M}$ Na_2SO_4/1 m$\underline{M}$ $HClO_4$	34
	*	$HClO_4$; H_2SO_4; r-red. of quinone, H^+, persulfate	1
	*	T; isotherm ads.	327
	*	0.5 $\underline{M}$ KCl	153,210
	*	T; 0.5 $\underline{M}$ KCl; 0.5 $\underline{M}$ $NaClO_4$/10 m$\underline{M}$ $HClO_4$	211
	*	$HClO_4$; KCl	268
	*	SEM; 0.5 $\underline{M}$ Na_2SO_4/1 m$\underline{M}$ $HClO_4$	298
	*	0.5 $\underline{M}$ $NaClO_4$; 0.5 $\underline{M}$ Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s	219
Ag(110)	Bi	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176
	Pb	T; 0.5 $\underline{M}$ Na_2SO_4/5 m$\underline{M}$ $HClO_4$; ads. kinetics	180
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; a-Cl^-	350
	*	T; 0.5 $\underline{M}$ $NaClO_4$/5 m$\underline{M}$ $HClO_4$	44
	*	SRS; as PbO; 0.5 $\underline{M}$ NaOAc/0.1 $\underline{M}$ HOAc; 0.5 $\underline{M}$ $HClO_4$; 0.5 $\underline{M}$ $NaClO_4$ (5.4); mult. layer UPD; comp. w/ Tl depos.	38
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176

Substrate	Adatom(s)	Attributes	Reference(s)
Ag(110)	*Pb*	*Continued*	
	*	0.5 M NaOAc/0.1 M HOAc; 0.5 M Na_2SO_4/1 mM $HClO_4$; surf. char.	35
	*	$HClO_4$; H_2SO_4; r-red. of quinone, H^+, persulfate	1
	*	1 M $HClO_4$	98
	*	0.5 M $NaClO_4$; 0.5 M Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s	219
	Tl	T; 0.5 M Na_2SO_4/5 mM $HClO_4$; ads. kinetics	180
	*	0.5 M $HClO_4$; r-O_2 red.; a-Cl^-	350
	*	T; SRS; 0.3 M NaOAc/0.01 M HOAc; 0.5 M $NaClO_4$/0.2 M NaOH/0.1 M citric acid; $HClO_4$; 2-D nucleation	37
	*	0.5 M NaOAc/0.1 M HOAc; 0.5 M Na_2SO_4/1 mM $HClO_4$; surf. char.	35
	*	SRS; 0.5 M Na_2SO_4/1 mM $HClO_4$	34
	*	$HClO_4$; H_2SO_4; r-red. of quinone, H^+, persulfate	1
	*	0.5 M KCl	153,210
	*	T; 0.5 M KCl; 0.5 M $NaClO_4$/10 mM $HClO_4$	211
	*	0.5 M $NaClO_4$; 0.5 M Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s	219
Ag(111)	Bi	0.5 M $HClO_4$; r-O_2 red.; +s	176
	Cd	T; 0.5 M Na_2SO_4	45
	Cd/Tl	1 mM $HClO_4$; r-nitrate red.; comment to ref. 345	346
	Pb	T; a-0.5 M solns. of ClO_4^-, OAc^-, $C_6H_5O_7^{3-}$	172
	*	T; 0.5 M $NaClO_4$/5 mM $HClO_4$	44,46
	*	0.5 M $HClO_4$; r-O_2 red.; a-Cl^-	350
	*	T; Ellip.; 1 M $NaClO_4$ (3)	236

Substrate	Adatom(s)		Attributes	Reference(s)
Ag(111)	*Pb*		*Continued*	
		*	T; SRS; 0.3 M NaOAC/0.01 M HOAc; 0.5 M $NaClO_4$/0.2 M NaOH/0.1 M citric acid; $HClO_4$; 2-D nucleation	37
		*	SRS; as PbO; 0.5 M NaOAc/0.1 M HOAc; 0.5 M $HClO_4$; 0.5 M $NaClO_4$ (5.4); mult. layer UPD; comp. w/ Tl depos.	38
		*	0.5 M NaOAc/0.1 M HOAc; 0.5 M Na_2SO_4/1 mM $HClO_4$; surf. char.	35
		*	0.5 M $HClO_4$; r-O_2 red.; +s	176
		*	0.5 M $NaClO_4$	281
		*	0.2 M $LiClO_4$ in MeOH; r-nitrobenz. oxid., nitrosobenz. oxid.	182
		*	$HClO_4$; H_2SO_4; r-red. of quinone, H^+, persulfate	1
		*	NaOAc/HOAc	25
		*	T; 0.5 M Na_2SO_4/1 mM $HClO_4$; 2-D growth study	173
		*	SEM; 0.5 M $NaClO_4$/1 mM $HClO_4$	298
		*	1 M $HClO_4$	98
		*	0.5 M $NaClO_4$; 0.5 M Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s	219
	Tl		0.5 M $HClO_4$; r-O_2 red.; a-Cl^-	350
		*	0.5 M NaOAc/0.1 M HOAc; 0.5 M Na_2SO_4/1 mM $HClO_4$; surf. char.	35
		*	SRS; 0.5 M Na_2SO_4/1 mM $HClO_4$	34
		*	0.5 M $NaClO_4$	281
		*	$HClO_4$; H_2SO_4; r-red. of quinone, H^+, persulfate	1
		*	0.5 M KCl	153,210
		*	T; 0.5 M KCl; 0.5 M $NaClO_4$/10 mM $HClO_4$	211

Substrate	Adatom(s)	Attributes	Reference(s)
Ag(111)	*Tl*	*Continued*	
	*	T; 0.5 M Na_2SO_4/1 mM $HClO_4$; 2-D growth study	173
	*	SEM; 0.5 M Na_2SO_4/1 mM $HClO_4$	298
	*	0.5 M $NaClO_4$; 0.5 M Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s	219
Ag(111)-mc	Cd/Tl	Ag vapor depos.; $K_2SO_4/HClO_4$; r-H_2 evolution	345
Ag/m-Au	Pb	0.5 M $NaClO_4$ (2)	301
Ag-T	Ag	as $AgClO_4$; $HClO_4$; greater react. from depos. comp. to org. substr.	202
As	Li	$LiClO_4$ in PPC	32
Au	Ag	1 M $HClO_4$; a-Cl^-, HSO_4^-	160
	*	T; 0.2 M $HClO_4$; part.-part. inter.	306
	*	T; 0.2 M H_2SO_4	255,305
	*	T; gen. theory; kinetics	303
	*	T; 0.2 M $HClO_4$; thermo.	304
	*	T; 0.2 M H_2SO_4	326,296
	*	QCM; 0.2 M H_2SO_4; 0.2 M $NaClO_4$ in ACN	62
	*	T; Ellip.; $HClO_4$; H_2SO_4	75
	*	RTM; 1 M $HClO_4$; a-Cl^-, HSO_4^-	159
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	1 M H_2SO_4; r-Fe^{2+} oxid.	8
	*	r-oxid. of MeOH, HCHO, HCOOH	39
	*	exam.; gen. disc.; 0.1 M $HClO_4$	67,68
	*	T; $NaClO_4/HClO_4$; H_2SO_4	211
	*	T (2); 1 M $HClO_4$	209,262
	*	phosphate buff. (8)	224
	*	RTM; $HClO_4$	251
	*	RTM; 0.1 M $NaClO_4$; $E_{½,d}$(0.1 M KNO_3, pH 4)=0.8	258

Substrate	**Adatom(s)**	**Attributes**	**Reference(s)**
Au	*Ag*	*Continued*	
	*	0.5 $\underline{M}$ H_2SO_4; a-Cl^-; $\Delta E_p=0.59$ (cf. 193)	275
	*	SRS (1); 1 $\underline{M}$ $HClO_4$	311,210
	*	r-O_2 red.	71,254
	*	Ellip.	162
	*	r-O_2 red., H_2 evol.	225
	*	1 $\underline{M}$ H_2SO_4	325
	*	0.5 $\underline{M}$ H_2SO_4; $\Delta E_p=0.50_5$	193
	*	1 $\underline{M}$ $LiClO_4$ in ACN; $\Delta E_p=0.55$	193
	*	NA, isotherms	60
	*	H_2SO_4; HNO_3	226
	As	phosphate buff. (8)	224
	Bi	T; SRS; 1 $\underline{M}$ $HClO_4$	18a,308
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	r-oxid. of MeOH, HCHO, HCOOH	39
	*	0.12 $\underline{M}$ $HClO_4$	73,59,71
	*	1 $\underline{M}$ HNO_3	82,94,95
	*	phosphate buff. (8)	224
	*	~ 0.1 $\underline{M}$ Na_2CO_3	232
	*	1 $\underline{M}$ HCl	272
	*	NaOAc; r-O_2 red.	15
	*	RTM; comp. w/ Po depos.	81
	*	SRS; $HClO_4$	310
	*	NA	84
	*	0.1 $\underline{M}$ $HClO_4$; $\Delta E_p=0.25$	73,193
	Cd	T (1); SRS; 1 $\underline{M}$ $HClO_4$	308,312
	*	RTM; 1 $\underline{M}$ $HClO_4$; a-Cl^-, HSO_4^-	159
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	phosphate buff. (8)	224
	*	1 $\underline{M}$ acetate buff.	285
	*	NaOAc; r-O_2 red.	15
	*	SRS; 0.2 $\underline{M}$ $HClO_4$	309

Substrate	Adatom(s)	Attributes	Reference(s)
Au	*Cd*	*Continued*	
	*	0.5 M Na_2SO_4 (3); $\Delta E_p=0.50_5$	193
	Cu	T (1); SRS; 1 M $HClO_4$	308,312
	*	RTM; 1 M $HClO_4$; a-Cl^-, HSO_4^-	159
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	1 M H_2SO_4; r-Ti^{3+} oxid.	8
	*	SRS; 1 M $NaClO_4$; 0.5 M Na_2SO_4	195
	*	T; $NaClO_4/HClO_4$; H_2SO_4	211
	*	phosphate buff. (8)	224
	*	1 M $HClO_4$; 0.5 M Na_2SO_4	274
	*	NaOAc; r-O_2 red.	15
	*	0.1 M $NaClO_4$; effect of anions, H^+	96
	*	H_2SO_4; a-thiourea	104
	*	r-O_2 red.	71
	*	0.1 M KCl	77
	*	0.5 M H_2SO_4	210
	*	0.5 M Na_2SO_4 (3); $\Delta E_p=0.21_5$	193
	Ga	phosphate buff. (8)	224
	Hg	2 M HNO_3; surf. char.	206
	*	0.2 M H_2SO_4	295
	*	T; 0.2 M H_2SO_4	326,296
	*	phosphate buff. (8)	224
	*	surf. char.	148
	*	e-$HClO_4$, H_2SO_4	294
	*	0.5 M H_2SO_4; $\Delta E_p=0.43$	193
	*	NA, isotherms	60
	In	T; SRS; 1 M $HClO_4$	308
	*	phosphate buff. (8)	224
	Ir	r-oxid. of MeOH, HCHO, HCOOH	39
	Li	1 M $LiClO_4$ in ACN; $\Delta E_p=1.23$	193
	Ni	~ 0.1 M Na_2SO_4	232
	*	0.1 M KSCN; 0.1 M KNO_3	240

Substrate	Adatom(s)	Attributes	Reference(s)
Au	*Pb*		
	Pb	T; 0.2 $\underline{M}$ $HClO_4$; thermo.	304
	*	T (1); SRS; 1 $\underline{M}$ $HClO_4$	308,312,313
	*	T; as PbO; 1 $\underline{M}$ NaOH; r-O_2 red.	17
	*	T; 0.5 $\underline{M}$ $NaClO_4$/1 m$\underline{M}$ $HClO_4$	101,102
	*	XRD; ED; as PbF_2; 0.01 $\underline{M}$ $HClO_4$	139
	*	T; 1 $\underline{M}$ $HClO_4$; r-formic acid oxid.	13
	*	Ellip.; 1 $\underline{M}$ $HClO_4$	163
	*	SRS; 1 $\underline{M}$ $HClO_4$; cf. 6,280	7
	*	0.5 $\underline{M}$ KCl	331,59
	*	0.1 $\underline{M}$ Et_4NClO_4/10 m$\underline{M}$ $HClO_4$ in ACN; comp. w/ aqueous UPD	191
	*	QCM; 0.2 $\underline{M}$ H_2SO_4; 0.2 $\underline{M}$ $NaClO_4$ in ACN	62
	*	T; EPE; as PbF_2; $HClO_4$/$KClO_4$; r-H red. & oxid.	248
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	r-oxid. of MeOH, HCHO, HCOOH	39
	*	1 $\underline{M}$ HNO_3	82
	*	SRS; 1 $\underline{M}$ $NaClO_4$; 0.5 $\underline{M}$ Na_2SO_4	195
	*	0.5 $\underline{M}$ Na_2SO_4 (2); 0.5 $\underline{M}$ $NaClO_4$ (2); a-Cl^-, Br^-, I^-	198
	*	T; $NaClO_4$/$HClO_4$; H_2SO_4	211
	*	phosphate buff. (8)	224
	*	~ 0.1 $\underline{M}$ $Ca(OH)_2$; ~ 0.1 $\underline{M}$ NaOH; ~ 0.1 $\underline{M}$ Na_2CO_3	232
	*	KCl (4.5); KBr (4); KI (5); NH_4ClO_4 (4.5); $HClO_4$ (0.5)	269
	*	0.25 $\underline{M}$ KCl	270
	*	T; HOAc/NaOAc/0.5 $\underline{M}$ $NaClO_4$ (4.7)	276
	*	r-oxalic acid oxid.	106
	*	SRS; $HClO_4$	3,4,5

Substrate	Adatom(s)	Attributes	Reference(s)
Au	*Pb*	*Continued*	
	*	NaOAc; r-O_2 red.	15
	*	RTM; comp. w/ Po depos.	81
	*	0.5 $\underline{M}$ KCl/0.1 m$\underline{M}$ HCl	330
	*	1 $\underline{M}$ $NaClO_4$ (3); ΔE_p=0.40	193
	*	1 $\underline{M}$ $NaClO_4$/0.2 $\underline{M}$ KCl (3); ΔE_p=0.33	193
	Pd	1 $\underline{M}$ H_2SO_4	121
	*	r-oxid. of MeOH, HCHO, HCOOH	39
	*	r-H_2 evol.	
	Po	1 $\underline{M}$ HNO_3	82
	*	e-H^+	282
	*	Photo. exam.; surf. char.	80
	Pt	1 $\underline{M}$ H_2SO_4	121,325
	*	r-oxid. of MeOH, HCHO, HCOOH	39
	Rh	r-oxid. of MeOH, HCHO, HCOOH	39
	Ru	RTM; as $RuNOCl_3$; HCl	205
	Sb	phosphate buff. (8)	224
	*	~ 0.1 $\underline{M}$ Na_2CO_3	232
	*	1 $\underline{M}$ HCl	272
	Sn	T; SRS; 1 $\underline{M}$ $HClO_4$	308
	*	phosphate buff. (8)	224
	*	4 $\underline{M}$ HCl	329,59,330
	*	NaOAc; r-O_2 red.	15
	*	+e	28
	Tl	T; SRS; 1 $\underline{M}$ $HClO_4$	308
	*	T; 0.5 $\underline{M}$ KCl/0.1 m$\underline{M}$ HCl; 0.2 $\underline{M}$ $HClO_4$	332
	*	0.1 $\underline{M}$ Et_4NClO_4/10 m$\underline{M}$ $HClO_4$ in ACN; comp. w/ aqueous UPD	191
	*	1 $\underline{M}$ KF; r-$Ru(NH_3)_6^{2+}$ oxid.	165
	*	T; NaOH; $HClO_4$; NaOH/$HClO_4$; r-O_2 red.	2
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	r-oxid. of MeOH, HCHO, HCOOH	39

Substrate	Adatom(s)	Attributes	Reference(s)
Au	*Tl*	*Continued*	
	*	$HClO_4$; H_2SO_4; HNO_3; HCl	166
	*	SRS; 1 M $NaClO_4$; 0.5 M Na_2SO_4	195
	*	0.5 M Na_2SO_4 (2); 0.5 M $NaClO_4$ (2); a-Cl^-, Br^-, I^-	198
	*	T; $NaClO_4$/$HClO_4$; H_2SO_4	211
	*	0.5 M KCl	59,209,210
	*	phosphate buff. (8)	224
	*	~ 0.1 M Na_2SO_4	232
	*	$HClO_4$; KCl; ΔE_p(0.5 M KCl)=0.46 (cf. 193)	268
	*	NaOAc; r-O_2 red.	15
	*	0.5 M Na_2SO_4; a-Br^-	250
	*	0.5 M KCl/0.1 mM HCl	330
	*	0.5 M Na_2SO_4 (3); ΔE_p=0.68_5	193
	*	NA, isotherms	60
	Zn	phosphate buff. (8)	224
	*	RTM; +e	126
Au-glass	Pb	Au vapor depos.; LEED; RHEED; 0.5 M $NaClO_4$ (2)	349
Au-mc	Cd	Au vapor depos.; r-nitrate red.; $HClO_4$; comment to ref. 345	346
	Pb	Au vapor depos.; LEED; RHEED; 0.5 M $NaClO_4$ (2)	349
Au/X	Hg	surf. char.	148
Au(100)	Bi	0.5 M $HClO_4$; r-O_2 red.; +s	176
	*	DS; 1 M $HClO_4$	286
	Cu	DS; 1 M $HClO_4$	286
	*	1 M $HClO_4$	98
	*	RHEED; as $CuSO_4$; 1 M $HClO_4$	29
	Pb	T; $Ca(ClO_4)_2$/10 mM $HClO_4$	142
	*	1 mM PbF_2/10 mM $HClO_4$; +s	141

Substrate	Adatom(s)	Attributes	Reference(s)
Au(100)	*Pb*	*Continued*	
	*	T; 0.5 $\underline{M}$ $NaClO_4$/1 m$\underline{M}$ $HClO_4$	101,102
	*	as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
	*	SRS; 1 $\underline{M}$ $HClO_4$; cf. 6,280	7
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176
	*	DS; 1 $\underline{M}$ $HClO_4$	286
	*	as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ++ vicinal faces	140
	*	AES; LEED	128,129
	Sb	DS; 1 $\underline{M}$ $HClO_4$	286
	Tl	DS; 1 $\underline{M}$ $HClO_4$	286
Au(110)	Bi	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176
	*	DS; 1 $\underline{M}$ $HClO_4$	286
	Cu	DS; 1 $\underline{M}$ $HClO_4$	286
	*	1 $\underline{M}$ $HClO_4$	98
	Pb	T; $Ca(ClO_4)_2$/10 m$\underline{M}$ $HClO_4$	142
	*	as 1 m$\underline{M}$ PbF_2; 10 m$\underline{M}$ $HClO_4$; +s	141
	*	T; 0.5 $\underline{M}$ $NaClO_4$/1 m$\underline{M}$ $HClO_4$	101,102
	*	as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
	*	SRS; 1 $\underline{M}$ $HClO_4$; see refs. 6,280	7
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176
	*	DS; 1 $\underline{M}$ $HClO_4$	286
	*	AES; LEED	128,129
	Sb	DS; 1 $\underline{M}$ $HClO_4$	286
	Tl	DS; 1 $\underline{M}$ $HClO_4$	286
Au(111)	Bi	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176
	*	DS; 1 $\underline{M}$ $HClO_4$	286
	Cu	AES; LEED; RHEED; 0.1 $\underline{M}$ $HClO_4$	237
	*	DS; 1 $\underline{M}$ $HClO_4$	286
	*	1 $\underline{M}$ $HClO_4$	98
	*	RHEED; as $CuSO_4$; 1 $\underline{M}$ $HClO_4$	29
	Pb	T; $Ca(ClO_4)_2$/10 m$\underline{M}$ $HClO_4$	142
	*	as 1 m$\underline{M}$ PbF_2; 10 m$\underline{M}$ $HClO_4$; ΔE_p=0.28; +s	141

Substrate	Adatom(s)		Attributes	Reference(s)
Au(111)	*Pb*		*Continued*	
		*	T; 0.5 $\underline{M}$ $NaClO_4$/1 m$\underline{M}$ $HClO_4$	101,102
		*	as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
		*	SRS; 1 $\underline{M}$ $HClO_4$; see refs. 6,280	7
		*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.; +s	176
		*	DS; 1 $\underline{M}$ $HClO_4$	286
		*	AES; LEED	128,129
	Sb		DS; 1 $\underline{M}$ $HClO_4$	286
	Tl		DS; 1 $\underline{M}$ $HClO_4$	286
Au(210)	Pb		as 1 m$\underline{M}$ PbF_2; 10 m$\underline{M}$ $HClO_4$; ΔE_p=0.28; +s	141
		*	as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(211)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(221)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(310)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(311)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(320)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(331)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(332)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(410)	Pb		AES; LEED	128,129
Au(511)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(533)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(551)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(554)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au(755)	Pb		as PbF_2; 0.01 $\underline{M}$ $HClO_4$; ΔE_p=f(face); +s	138
Au/m-Ag	Pb		0.5 $\underline{M}$ $NaClO_4$ (2)	301
	Tl		0.5 $\underline{M}$ $NaClO_4$ (2)	301
Au/m-Cu	Pb		0.5 $\underline{M}$ $NaClO_4$ (2)	301
Au/Pt	Pb		1 $\underline{M}$ NaOH; r-ethylene glycol oxid.	31
B/carb	Tl		$HClO_4$; H_2SO_4; HNO_3; HCl	166
Bi	Cd		0.5 $\underline{M}$ NH_4ClO_4/0.5 $\underline{M}$ $HClO_4$; $HClO_4$; KCl	268
	Li		$LiClO_4$ in PPC	32
	Pb		1 $\underline{M}$ HNO_3	82

Substrate	Adatom(s)	Attributes	Reference(s)
Bi	*Pb*	*Continued*	
	*	T; $NaClO_4/HClO_4$; H_2SO_4	211
	Sn	0.5 $\underline{M}$ NH_4ClO_4/0.5 $\underline{M}$ $HClO_4$; $HClO_4$; KCl	268
C:glassy	Ag	1 $\underline{M}$ KNO_3 (3)	99
	Cu/Hg	0.1 $\underline{M}$ KNO_3/10 m$\underline{M}$ HNO_3	179
	H/Hg	0.1 $\underline{M}$ KNO_3/10 m$\underline{M}$ HNO_3	179
	Hg	1 $\underline{M}$ KNO_3 (3)	99
	*	0.1 $\underline{M}$ KNO_3/10 m$\underline{M}$ HNO_3	179
	Hg/Cu	0.1 $\underline{M}$ KNO_3/10 m$\underline{M}$ HNO_3	179
	Hg/H	0.1 $\underline{M}$ KNO_3/10 m$\underline{M}$ HNO_3	179
	K	XRD; LiCl/KCl melt	167
	Li	XRD; LiCl/KCl melt	167
	Pb	0.5 $\underline{M}$ $HClO_4$; r-O_2 red., H_2O_2 red.	220
	Pt	r-H_2 evol.	119
	Ru	r-H_2 evol.	119
C:graph.	Ag	as $AgNO_3$; Na_2SO_4; $NaClO_4$; HCl; $LiClO_4$/ACN	233
	*	HCl	53
	*	0.2 $\underline{M}$ KNO_3	249
	*	RTM; +e	260
	Bi	HNO_3	53
	Cd	as $CdSO_4$; Na_2SO_4; $NaClO_4$; HCl; $LiClO_4$ in ACN	233
	Cu	as $CuSO_4$; Na_2SO_4; $NaClO_4$; HCl; $LiClO_4$ in ACN	233
	*	EM; XRF; 0.1 $\underline{M}$ $KClO_4$/0.1 $\underline{M}$ $HClO_4$	328
	Hg	as $Hg(NO_3)_2$; Na_2SO_4; $NaClO_4$; HCl; $LiClO_4$ in ACN	233
	K	XRD; LiCl/KCl melt	167
	Li	XRD; LiCl/KCl melt	167
	Pb	as $Pb(NO_3)_2$; Na_2SO_4; $NaClO_4$; HCl; $LiClO_4$ in ACN	233

Substrate	Adatom(s)	Attributes	Reference(s)
C:graph.	*Pb*	*Continued*	
	*	HNO_3	53
	Sn	as $SnCl_2$; Na_2SO_4; $NaClO_4$; HCl; $LiClO_4$ in ACN	233
	Tl	$HClO_4$; H_2SO_4; HNO_3; HCl	166
C:py:graph.	K	XRD; LiCl/KCl melt	167
	Li	XRD; LiCl/KCl melt	167
Cd	Zn	RTM; +e	126
CdS	Cd	SRS; 1 $\underline{M}$ KCl	192
Cu	Bi	RTM; 0.25 $\underline{M}$ tartrate; a-0.1 $\underline{M}$ Cl^-	260
	Cd	T; SRS; 1 $\underline{M}$ $HClO_4$	308
	*	RTM; 1 $\underline{M}$ $HClO_4$/24 m$\underline{M}$ H_2SO_4; a-HSO_4^-	158
	*	1 $\underline{M}$ Na_2SO_4; $\Delta E_p=0.22_5$	193
	Li	1 $\underline{M}$ $LiClO_4$ in PPC; $\Delta E_p=1.05$	193
	Pb	Ellip.; 1 $\underline{M}$ $NaClO_4$ (3) ; surf. char.; presence of rhodamine-B dye	105
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.	186
	*	1 $\underline{M}$ HNO_3	82
	*	$HClO_4$; KCl; ΔE_p(0.5 $\underline{M}$ KCl)=0.13 (cf. 193)	268
	*	RTM; comp. w/ Po depos.	81
	Pb/Tl	0.5 $\underline{M}$ KCl	267
	Ru	RTM; as $RuNOCl_3$; HCl	205
	Tl	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.	186
	*	$HClO_4$; KCl; ΔE_p(0.5 $\underline{M}$ KCl)=0.13 (cf. 193)	268
	*	1 $\underline{M}$ Na_2SO_4; $\Delta E_p=0.33_5$	193
	Tl/Pb	0.5 $\underline{M}$ KCl	267
	Zn	RTM; +e	126

Substrate	Adatom(s)	Attributes	Reference(s)
Cu(100)	*Pb*		
Cu(100)	Pb	as Pb(OAc)$_2$; 0.5 $\underline{M}$ NaClO$_4$/1 m$\underline{M}$ HClO$_4$; comp. w/ Ag(100,110,111)-Pb	36
Cu(110)	Pb	as Pb(OAc)$_2$; 0.5 $\underline{M}$ NaClO$_4$/1 m$\underline{M}$ HClO$_4$; comp. w/ Ag(100,110,111)-Pb	36
Cu(111)	Cu/Cd	T; Na$_2$SO$_4$; +e	63
	*	T; 0.19 $\underline{M}$ Na$_2$SO$_4$/0.45 $\underline{M}$ (NH$_4$)$_2$SO$_4$/en	64
	Cd	T; Na$_2$SO$_4$; +e	63
	Cd/Cu	T; Na$_2$SO$_4$; +e	63
	*	T; 0.19 $\underline{M}$ Na$_2$SO$_4$/0.45 $\underline{M}$ (NH$_4$)$_2$SO$_4$/en	64
	Pb	T; Ellip.; 1 $\underline{M}$ NaClO$_4$ (3)	236
	*	as Pb(OAc)$_2$; 0.5 $\underline{M}$ NaClO$_4$/1 m$\underline{M}$ HClO$_4$; comp. w/ Ag(100,110,111)-Pb	36
	*	e-OAc$^-$, en, H$^+$	65
Cu/m-Ag	Pb	0.5 $\underline{M}$ NaClO$_4$ (2)	301
Fe	Mn	5 m$\underline{M}$ H$_2$SO$_4$	24
	Pb	0.5 $\underline{M}$ HClO$_4$; 0.4 $\underline{M}$ NaCl (3); a-Cl$^-$	174
	Sn	5 m$\underline{M}$ H$_2$SO$_4$	24
	Tl	0.5 $\underline{M}$ Na$_2$SO$_4$; a-Cl$^-$	174
	Zn	0.5 $\underline{M}$ (NH$_4$)$_2$SO$_4$/10 m$\underline{M}$ H$_2$SO$_4$	242
	*	5 m$\underline{M}$ H$_2$SO$_4$	24
Hg	Ni	NA	113
	Pt	r-H$_2$ evol.	119
	Ru	r-H$_2$ evol.	119
	*	1 $\underline{M}$ HCl; r-H$_2$ evol.	108
Ir	Ag	1 $\underline{M}$ H$_2$SO$_4$	204
	Cu	0.1 $\underline{M}$ NaClO$_4$; effect of anions, H$^+$	96
	H	H$_2$SO$_4$	54
	Pb	T; 1 $\underline{M}$ HClO$_4$; r-formic acid oxid.	13
Mg	Li	1 $\underline{M}$ LiClO$_4$ in PPC	241
Mo	Po	0.3 $\underline{M}$ HNO$_3$	80
Ni	Fe	0.5 $\underline{M}$ (NH$_4$)$_2$SO$_4$/10 m$\underline{M}$ H$_2$SO$_4$	242

Substrate	**Adatom(s)**		**Attributes**	**Reference(s)**
Ni	*Pb*			
	Pb		1 M HNO_3	82
	Zn		0.5 M $(NH_4)_2SO_4$/10 mM H_2SO_4	242
		*	RTM; +e	127
Pb	Cd		5 M H_2SO_4; r-O_2 red.	76
		*	$NaClO_4$	25
		*	0.5 M NH_4ClO_4/0.5 M $HClO_4$; $HClO_4$; KCl	268
	Ru		RTM; 0.5 M H_2SO_4	136
	Zn		RTM; +e	127
Pd	Ag		0.5 M H_2SO_4; r-formic acid oxid. ΔE_p(Ag on Pd or Pd-Pt)=0.4	200
		*	T; 1 M $HClO_4$; r-formic acid oxid. comp. w/ depos. on Pt & Rh	14
		*	exam.; gen. disc.; 0.1 M $HClO_4$	67,68
		*	RTM; 0.1 M $NaClO_4$; $E_{\frac{1}{2},d}$(0.1 M KNO_3, pH 4)=0.5	258
	Au		0.5 M H_2SO_4; r-MeOH oxid.	339
	Bi		T; SRS; 1 M $HClO_4$	308
		*	T; 1 M $HClO_4$; r-formic acid oxid. comp. w/ depos. on Pt & Rh	14
		*	1 M $HClO_4$	228
		*	XRD; 1 M $HClO_4$	230
	Cd		T; 1 M $HClO_4$; r-formic acid oxid. comp. w/ depos. on Pt & Rh	14
		*	1 M $HClO_4$	228
	Cu		T; 1 M $HClO_4$; r-formic acid oxid. comp. w/ depos. on Pt & Rh	14
		*	0.1 M $NaClO_4$; effect of anions, H^+	96
	Pb		T; 1 M $HClO_4$; r-formic acid oxid. comp. w/ depos. on Pt & Rh	14
		*	T; 1 M $HClO_4$; r-formic acid oxid.	13
		*	1 M $HClO_4$	228

Substrate	Adatom(s)		Attributes	Reference(s)
Pd	*Tl*			
	Tl		T; 1 $\underline{M}$ $HClO_4$; r-formic acid oxid. comp. w/ depos. on Pt & Rh	14
		*	1 $\underline{M}$ $HClO_4$	228
Pd-Pt	Ag		0.5 $\underline{M}$ H_2SO_4; r-formic acid oxid. ΔE_p(Ag on Pd or Pd-Pt)=0.4	200
Pt	Al		$AlCl_3$/BuPyCl	257
	Ag		T, 0.5 $\underline{M}$ $HClO_4$	78
		*	1 $\underline{M}$ $HClO_4$; a-Cl^-, HSO_4^-	160
		*	0.5 $\underline{M}$ $HClO_4$; 0.5 $\underline{M}$ H_2SO_4; 0.1 $\underline{M}$ NaOH; r-hydrazine oxid.	181
		*	T; SRS; 1 $\underline{M}$ $HClO_4$	308
		*	T (2); 1 $\underline{M}$ $HClO_4$	26,262
		*	T (1,2); 0.2 $\underline{M}$ H_2SO_4	296,320,326
		*	T; 0.2 $\underline{M}$ H_2SO_4	317,318
		*	XPS; 0.1 $\underline{M}$ H_2SO_4	143
		*	AES; XPS; 0.1 $\underline{M}$ H_2SO_4	144
		*	0.1 $\underline{M}$ $HClO_4$	40,307
		*	2 $\underline{M}$ $HClO_4$; r-formic acid oxid.	11
		*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
		*	HNO_3/KNO_3; HNO_3/H_3BO_3; H_2SO_4/Na_2SO_4; NaF; KCl	43
		*	exam.; gen. disc.; 0.1 $\underline{M}$ $HClO_4$	67,68
		*	H_2SO_4; $HClO_4$	70
		*	RTM; 1 $\underline{M}$ NaOH; e-H^+	122
		*	SRS; 1 $\underline{M}$ $HClO_4$	222
		*	0.1 $\underline{M}$ HNO_3; 0.1 $\underline{M}$ KCl; 0.1 $\underline{M}$ KNO_3	239
		*	KNO_3; HOAc/NaOAc; $HClO_4$; +e	244
		*	RTM; 0.1 $\underline{M}$ KNO_3 (4); 1 $\underline{M}$ $HClO_4$/0.1 $\underline{M}$ $NaClO_4$; 1 $\underline{M}$ NaOH/0.1 $\underline{M}$ NaCN; 0.1 $\underline{M}$ NH_3; 0.1 $\underline{M}$ NaCN; $E_{½,d}$(0.1 $\underline{M}$ KNO_3, pH 4)=0.6	258
		*	r-H_2 evol.	114

Substrate	Adatom(s)	Attributes	Reference(s)
Pt	*Ag*	*Continued*	
	*	1 $\underline{M}$ H_2SO_4; eff. on H ads.	302
	*	r-HCHO	61
	*	0.2 $\underline{M}$ H_2SO_4; r-O_2 red.	71
	*	LiCl-KCl melt	154
	*	r-O_2 red., H_2 evol. (1)	225,254
	*	1 $\underline{M}$ H_2SO_4	325
	*	0.5 $\underline{M}$ H_2SO_4; $\Delta E_p=0.43_5$	193
	*	1 $\underline{M}$ $LiClO_4$ in ACN; $\Delta E_p=0.44_5$	193
	Ag/Cu	RTM; 1 $\underline{M}$ NaOH; e-H^+	122
	Ag/Pd	RTM; 1 $\underline{M}$ NaOH; e-H^+	122
	Ag/Pt	RTM; 1 $\underline{M}$ NaOH; e-H^+	122
	Au	H_2SO_4; $HClO_4$	70
	*	0.2 $\underline{M}$ H_2SO_4	324,71
	*	0.5 $\underline{M}$ H_2SO_4; r-MeOH oxid.	339
	Bi	0.5 $\underline{M}$ $HClO_4$; increas. revers. of r-hydroquin./p-benzoquin., pyrocatechol/o-benzoquin.	185
	*	0.5 $\underline{M}$ $HClO_4$; 0.5 $\underline{M}$ H_2SO_4; 0.1 $\underline{M}$ NaOH; r-hydrazine oxid.	181
	*	T; SRS; 1 $\underline{M}$ $HClO_4$	308
	*	0.1 $\underline{M}$ $HClO_4$	307,71
	*	0.5 $\underline{M}$ $HClO_4$; r-bezofuroxan/o-benzoquin. dioxime	188
	*	0.5 $\underline{M}$ NaOH; r-NH_3 red., hydroxylamine oxid.	187
	*	0.5 $\underline{M}$ $HClO_4$; r-phenyldinitrometh. red., phenylnitrometh. red.	189
	*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.	186
	*	0.5 $\underline{M}$ $HClO_4$; 0.2 $\underline{M}$ NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl^-	184
	*	1 $\underline{M}$ NaOH; r-ethylene glycol oxid.	177

Substrate	Adatom(s)	Attributes	Reference(s)
Pt	*Bi*	*Continued*	
	*	0.5 M $HClO_4$; r-ethylene glycol oxid.	183
	*	1 M $HClO_4$; r-formic acid oxid.	10
	*	2 M $HClO_4$; r-formic acid oxid.	11
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	0.1 M HCl; ΔE_p=0.56 (cf. 193)	52
	*	1 M HNO_3	82
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of monosacch.; 3^{rd} body effect; a-Cl^-; Temp.	347
	*	RTM; 0.25 M tartrate; a-0.1 M Cl^-	260
	*	RTM; comp. w/ Po depos.	81
	*	r-HCHO	61
	*	$HClO_4$	229
	*	XRD; 1 M $HClO_4$	231
	*	NA	84
	*	0.12 M $HClO_4$; ΔE_p=0.49	72,193
	Cd	0.5 M $HClO_4$; 0.5 M H_2SO_4; 0.1 M NaOH; r-hydrazine oxid.	181
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl^-	184
	*	1 M NaOH; r-ethylene glycol oxid.	177
	*	0.5 M $HClO_4$; r-ethylene glycol oxid.	183
	*	1 M $HClO_4$; r-formic acid oxid.	10
	*	2 M $HClO_4$; r-formic acid oxid.	11
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	H_2SO_4	111
	*	0.5 M KOH	120
	*	RTM; 1 M $HClO_4$; a-Cl^-, HSO_4^-	155
	*	50 mM H_2SO_4	214
	*	0.5 M H_2SO_4	348
	*	$HClO_4$	229

Substrate	Adatom(s)	Attributes	Reference(s)
Pt	*Cd/Tl*		
	Cd/Tl	0.1 M HCl	49
	Cs	ClO_4^- or I^- salts; mono. red. sep. bulk	110
	Cu	FIM; 0.5 M H_2SO_4	103
	*	0.5 M $HClO_4$; 0.5 M H_2SO_4; 0.1 M NaOH; r-hydrazine oxid.	181
	*	T; SRS; 1 M $HClO_4$	308
	*	XPS; 0.1 M H_2SO_4	143
	*	AES; XPS; 0.1 M H_2SO_4	144
	*	0.1 M $HClO_4$	307
	*	0.5 M HCl	69,71,238
	*	HCl; ΔE_p(0.1 M HCl)=0.24_5 (cf. 193)	51
	*	0.5 M $HClO_4$; r-O_2 red.	186
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl^-	184
	*	1 M NaOH; r-ethylene glycol oxid.	177
	*	0.5 M $HClO_4$; r-ethylene glycol oxid.	183
	*	2 M $HClO_4$; r-formic acid oxid.	11
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	0.5 M H_2SO_4; 1 M $HClO_4$	55
	*	H_2SO_4; $HClO_4$	70
	*	T; 1 M H_2SO_4	112
	*	T; 0.5 M H_2SO_4; surf. char.	116
	*	T; RTM; 1 M $HClO_4$; a-HSO_4^-	157
	*	RTM; 1 M $HClO_4$; a-Cl^-	156
	*	SRS (1); 0.5 M H_2SO_4	197,56
	*	0.5 M H_2SO_4; r-ethylene red.	235
	*	0.1 M HNO_3; 0.1 M KCl; 0.1 M KNO_3	239
	*	KNO_3; HOAc/NaOAc; $HClO_4$; +e	244
	*	0.5 M H_2SO_4	283
	*	0.2 M H_2SO_4	315-319,324
	*	0.1 M $NaClO_4$; effect of anions, H^+	96

Substrate	Adatom(s)	Attributes	Reference(s)
Pt	*Cu*	*Continued*	
	*	0.1 $\underline{M}$ $NaClO_4$; mech. of depos.	41
	*	SRS; 1 $\underline{M}$ $HClO_4$	338
	*	1 $\underline{M}$ H_2SO_4; eff. on H ads.	302
	*	r-HCHO	61
	*	0.2 $\underline{M}$ H_2SO_4; r-O_2 red.	71
	*	SRS	196
	*	96% H_3PO_4	221
	*	HCl; H_2SO_4	243
	*	0.5 $\underline{M}$ H_2SO_4; ΔE_p=0.41	193
	Cu/Ag	RTM; 1 $\underline{M}$ NaOH; e-H^+	122
	Cu/Ru	surf. char. by Cu depos.	253
	Cu/Tl	0.1 $\underline{M}$ HCl	49
	Cs	2 m$\underline{M}$ Cs^+ in PPC; ΔE_p=~1.7	110,193
	Fe/Ni	10 m$\underline{M}$ H_2SO_4	242
	Ge	0.5 $\underline{M}$ $HClO_4$; 0.2 $\underline{M}$ NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl^-	184
	*	0.5 $\underline{M}$ H_2SO_4; r-oxid. of CO, MeOH, HCHO HCOOH	343
	H	H_2SO_4	54
	*	T; 1 $\underline{M}$ H_2SO_4	112
	*	SRS; 1 $\underline{M}$ $HClO_4$	33
	Hg	0.5 $\underline{M}$ H_2SO_4; r-formic acid oxid.	23
	*	1 $\underline{M}$ $HClO_4$	58,146
	*	0.5 $\underline{M}$ H_2SO_4; r-ethylene red.	235
	*	XRD; 1 $\underline{M}$ $HClO_4$	256
	*	surf. char. (1)	148
	*	anal. use	93,57
	*	$HClO_4$	145
	*	NA	337
	*	0.5 $\underline{M}$ H_2SO_4; ΔE_p=0.47	193
	Hg/Bi	0.1 $\underline{M}$ HNO_3	216

Substrate	**Adatom(s)**	**Attributes**	**Reference(s)**
Pt	*Hg/Cd*		
	Hg/Cd	0.1 M HNO_3	216
	Hg/Cu	0.1 M HNO_3	216
	Hg/Pb	0.1 M HNO_3	216
	Hg/Tl	0.1 M HNO_3	216
	In	$HClO_4$	229
	K	ClO_4^- or I^- salts; mono. red. sep. bulk	110
	*	20 mM K^+ in PPC; ΔE_p=~1.3	110,193
	Li	ClO_4^- or I^- salts; mono. red. sep. bulk	110
	*	20 mM Li^+ in PPC; ΔE_p=1.30	110,193
	Na	ClO_4^- or I^- salts; mono. red. sep. bulk	110
	*	10 mM Na^+ in PPC; ΔE_p=~1.1	110,193
	Ni	0.1 M KSCN; 0.1 M KNO_3	240
	*	LiCl-KCl melt	154
	Ni/Fe	10 mM H_2SO_4	242
	Pb	0.5 M $HClO_4$; increas. revers. of r-hydroquin./p-benzoquin., pyrocatechol/o-benzoquin.	185
	*	0.5 M $HClO_4$; 0.5 M H_2SO_4; 0.1 M NaOH; r-hydrazine oxid.	181
	*	T; SRS; 1 M $HClO_4$	308
	*	T; 1 M $HClO_4$; r-formic acid oxid.	13
	*	1 M $HClO_4$; r-formic acid oxid.	10
	*	2 M $HClO_4$; r-formic acid oxid.	11
	*	0.5 M $HClO_4$; r-benzofuroxan/o-benzoquin. dioxime	188
	*	1 M $HClO_4$; r-formic acid oxid.; comp. w/ other Pt catal.	74
	*	as $Pb(ClO_4)_2$; 1 M KF; r-$Ru(NH_3)_6^{2+}$ oxid.	165
	*	0.5 M NaOH; r- NH_3 red., hydroxylamine oxid.	187

Substrate	Adatom(s)	Attributes	Reference(s)
Pt	*Pb*	*Continued*	
	*	0.5 M $HClO_4$; r-phenyldinitrometh. red., phenylnitrometh. red.	189
	*	0.5 M $HClO_4$; r-O_2 red.	186
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl^-	184
	*	1 M NaOH; r-ethylene glycol oxid.	177
	*	0.1 M $(C_2H_5)_4NClO_4$ in ACN; r-oxid. of hydraz., methylhydraz., 1,1-dimethylhydraz.	168
	*	0.5 M $HClO_4$; r-ethylene glycol oxid.	183
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	HNO_3	53
	*	H_2SO_4 (1); $HClO_4$	70,229
	*	1 M HNO_3	82
	*	T; $NaClO_4/HClO_4$; H_2SO_4	211
	*	0.1 M HNO_3; 0.1 M KCl; 0.1 M KNO_3	239
	*	KNO_3; HOAc/NaOAc; $HClO_4$; +e	244
	*	0.5 M KCl; 0.5 M NaCl; ΔE_p(0.5 M NaCl)=0.65 (cf. 193)	277
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of monosacch.; 3rd body effect; a-Cl^-; Temp.	347
	*	SRS; r-HCOOH oxid.	12
	*	RTM; comp. w/ Po depos.	81
	*	0.5 M H_2SO_4; r-MeOH oxid.	30
	*	r-HCHO	61
	*	0.2 M H_2SO_4	71
	Pd/Ag	RTM; 1 M NaOH; e-H^+	122
	Po	1 M HNO_3	82
	Pt/Ag	RTM; 1 M NaOH; e-H^+	122
	Rb	ClO_4^- or I^- salts; mono. red. sep. bulk	110

Substrate	Adatom(s)		Attributes	Reference(s)
Pt	*Re*			
	Re		1 $\underline{M}$ NaOH; r-ethylene glycol oxid.	177
		*	0.5 $\underline{M}$ H_2SO_4; r-MeOH oxid.	30
	Ru		1 $\underline{M}$ NaOH; r-ethylene glycol oxid.	177
		*	0.5 $\underline{M}$ H_2SO_4; r-CO oxid.	341
		*	0.5 $\underline{M}$ H_2SO_4; r-MeOH oxid.	340
		*	RTM; as $RuNOCl_3$; HCl	205
		*	0.5 $\underline{M}$ H_2SO_4; r-MeOH oxid.	30
		*	RTM; 0.5 $\underline{M}$ H_2SO_4	136
	Se		0.5 $\underline{M}$ H_2SO_4; r-ethylene red.	235
	Sn		Moss.; acidic solns.	50
		*	0.5 $\underline{M}$ H_2SO_4	299
		*	0.5 $\underline{M}$ H_2SO_4; r-oxid. of CO, MeOH, HCHO HCOOH	343
		*	r-MeOH oxid.	170
		*	H_2SO_4; a-CO_2	227
		*	0.5 $\underline{M}$ H_2SO_4; r-MeOH oxid.	30
		*	0.1 $\underline{M}$ H^+; ΔE_p=~0.53	193
	Tc		RTM; H_2SO_4; search of formal pot.	107
	Tl		0.5 $\underline{M}$ $HClO_4$; increas. revers. of r-hydroquin./p-benzoquin., pyrocatechol/o-benzoquin.	185
		*	0.5 $\underline{M}$ $HClO_4$; 0.5 $\underline{M}$ H_2SO_4; 0.1 $\underline{M}$ NaOH; r-hydrazine oxid.	181
		*	0.5 $\underline{M}$ $HClO_4$; r-benzofuroxan/o-benzoquin. dioxime	188
		*	1 $\underline{M}$ KF; r-$Ru(NH_3)_6^{2+}$ oxid.	165
		*	0.5 $\underline{M}$ NaOH; r-NH_3 red., hydroxylamine oxid.	187
		*	0.5 $\underline{M}$ $HClO_4$; r-phenyldinitrometh. red., phenylnitrometh. red.	189
		*	0.5 $\underline{M}$ $HClO_4$; r-O_2 red.	186

Substrate	Adatom(s)	Attributes	Reference(s)
Pt	*Tl*	*Continued*	
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl^-	184
	*	1 M NaOH; r-ethylene glycol oxid.	177
	*	0.1 M $(C_2H_5)_4NClO_4$ in ACN; r-oxid. of hydraz., methylhydraz., 1,1-dimethylhydraz.	168
	*	0.5 M $HClO_4$; r-ethylene glycol oxid.	183
	*	1 M $HClO_4$; r-formic acid oxid.	10
	*	2 M $HClO_4$; r-formic acid oxid.	11
	*	$HClO_4$; H_2SO_4; r-O_2 red., H_2O_2 red.	9
	*	RTM; 0.1 M HCl	48
	*	0.1 M HCl	49
	*	$HClO_4$; H_2SO_4; HNO_3; HCl	166
	*	50 mM H_2SO_4	214
	*	RTM; 0.05 M H_2SO_4	215
	*	0.5 M $HClO_4$; 0.2 M NaOH; r-oxid. of monosacch.; 3rd body effect; a-Cl^-; Temp.	347
	*	0.5 M H_2SO_4	348
	*	r-HCHO	61
	*	$HClO_4$	229
	Tl/Cu	0.1 M HCl	49
	Tl/Cd	0.1 M HCl	49
	Zn	0.5 M H_2SO_4	348
	*	RTM; +e	126
	*	$HClO_4$	229
Pt(100)	Ag	AES; 1 M H_2SO_4; ΔE_p=f(face); +s	100
	Cu	AES; LEED; 0.3 M HF; UHV single cryst. trans. to Ar electrochem.	22
	*	0.5 M H_2SO_4; for ver. of third strip. peak for H UPD	291

Substrate	Adatom(s)		Attributes	Reference(s)
Pt(100)	*Cu*		*Continued*	
		*	0.5 M H_2SO_4; 0.01 M $HClO_4$; surf. char.	290
		*	0.5 M H_2SO_4; 1 M HCl; 0.1 M $HClO_4$; $\Delta E_p(Cu,100,H_2SO_4)=0.0$; comp. w/ 311 and poly.	288
	H		0.5 M H_2SO_4; for ver. of third strip. peak by Cu codepos.	291
		*	0.5 M H_2SO_4; 0.01 M $HClO_4$; surf. char.	290
		*	0.5 M H_2SO_4; 1 M HCl; 0.1 M $HClO_4$; comp. w/ 311 and poly.	288
		*	4 M H_2SO_4; Temp.	344
Pt(110)	Ag		AES; 1 M H_2SO_4; $\Delta E_p=f(face)$; +s	100
	Cu		AES; LEED; 0.3 M HF; UHV single cryst. trans. to Ar electrochem.	22
		*	0.5 M H_2SO_4; for ver. of third strip. peak for H UPD	291
		*	0.5 M H_2SO_4; 0.1 M $HClO_4$; 0.1 M NaOH; 0.1 M $NaHCO_3$ (8.5); a,c-sup.; $\Delta E_p(Cu,110,H_2SO_4)=0.27$	289
	H		0.5 M H_2SO_4; for ver. of third strip. peak by Cu codepos.	291
		*	0.5 M H_2SO_4; 0.1 M $HClO_4$; 0.1 M NaOH; 0.1 M $NaHCO_3$ (8.5); a,c-sup.;	289
		*	4 M H_2SO_4; T	344
Pt(111)	Ag		AES; 1 M H_2SO_4; $\Delta E_p=f(face)$; +s	100
	Cu		AES; LEED; 0.3 M HF; UHV single cryst. trans. to Ar electrochem.	22
		*	-I; AES; LEED; 1 M $NaClO_4$; surf. char.	300

Substrate	Adatom(s)	Attributes	Reference(s)
Pt(111)	*Cu*	*Continued*	
	*	0.5 $\underline{M}$ H_2SO_4; for ver. of third strip. peak for H UPD	291
	*	0.5 $\underline{M}$ H_2SO_4; 0.01 $\underline{M}$ $HClO_4$; surf. char.	290
	*	0.5 $\underline{M}$ H_2SO_4; 0.1 $\underline{M}$ $HClO_4$; 0.1 $\underline{M}$ NaOH; 0.1 $\underline{M}$ $NaHCO_3$ (8.5); a,c-sup.; $\Delta E_p(Cu,111,H_2SO_4)=0.0$	289
	H	0.5 $\underline{M}$ H_2SO_4; for ver. of third strip. peak by Cu codepos.	291
	*	0.5 $\underline{M}$ H_2SO_4; 0.01 $\underline{M}$ $HClO_4$; surf. char.	290
	*	0.5 $\underline{M}$ H_2SO_4; 0.1 $\underline{M}$ $HClO_4$; 0.1 $\underline{M}$ NaOH; 0.1 $\underline{M}$ $NaHCO_3$ (8.5); a,c-sup.;	289
	*	4 $\underline{M}$ H_2SO_4; Temp.	344
Pt(311)	Cu	0.5 $\underline{M}$ H_2SO_4; for ver. of third strip. peak for H UPD	291
	H	0.5 $\underline{M}$ H_2SO_4; for ver. of third strip. peak by Cu codepos.	291
Pt(331)	Cu	0.5 $\underline{M}$ H_2SO_4; for ver. of third strip. peak for H UPD	291
	H	0.5 $\underline{M}$ H_2SO_4; for ver. of third strip. peak by Cu codepos.	291
Pt(S)-I	Ag	AES; LEED; 1 $\underline{M}$ $HClO_4$; 3 UPD reg.	297
Pt/Au	Pb	1 $\underline{M}$ NaOH; r-ethylene glycol oxid.	31
Pt-C	Pb	1 $\underline{M}$ $HClO_4$; r-formic acid oxid.; comp. w/ other Pt catal.	74
Pt/Hg	Bi	anal. use	93
	*	HNO_3; $HClO_4$	145
	Cd	anal. use	93
	*		152
	Co	anal. use	93

Substrate	Adatom(s)	Attributes	Reference(s)
Pt/Hg	*Cu*		
	Cu	anal. use	93
	Pb	anal. use	93
	*		152
	Sn	anal. use	93
	Tl	anal. use	93
	*		152
	Zn		152
Rh	Ag	RTM; 0.1 M $NaClO_4$; $E_{½,d}$(0.1 M KNO_3, pH 4)=-0.1	258
	Bi	1 M $HClO_4$; r-formic acid oxid.; comp. w/ rxns. at Pt	97
	Cd	1 M $HClO_4$; r-formic acid oxid.; comp. w/ rxns. at Pt	97
	Cu	1 M H_2SO_4	92
	*	0.1 M $NaClO_4$; effect of anions, H^+	96
	H	H_2SO_4	54
	Pb	T; 1 M $HClO_4$; r-formic acid oxid.	13
	*	1 M $HClO_4$; r-formic acid oxid.; comp. w/ rxns. at Pt	97
	Ru	RTM; as $RuNOCl_3$; HCl	205
	Tl	1 M $HClO_4$; r-formic acid oxid.; comp. w/ rxns. at Pt	97
Ru	H	NA	125
Ru-Pt	Cu	0.5 M H_2SO_4; surf. char. by Cu depos.	252
Sb	Li	$LiClO_4$ in PPC	32
Sn	Cd	0.5 M NH_4ClO_4/0.5 M $HClO_4$; $HClO_4$; KCl	268,193
	Hg	+e	28
	Tl	0.5 M NH_4ClO_4/0.5 M $HClO_4$; $HClO_4$; KCl	268,193
	Zn	RTM; +e	126

Substrate	Adatom(s)	Attributes	Reference(s)
Ta	*Ag*		
Ta	Ag	RTM; 0.1 $\underline{M}$ $NaClO_4$; $E_{\frac{1}{2},d}$(0.1 $\underline{M}$ KNO_3, pH 4)=-0.45	258
	Bi	1 $\underline{M}$ HNO_3	82
	*	RTM; comp. w/ Po depos.	81
	Pb	1 $\underline{M}$ HNO_3	82
	*	RTM; comp. w/ Po depos.	81
	Po	1 $\underline{M}$ HNO_3	82
	*	0.3 $\underline{M}$ HNO_3	80
W	Ag	RTM; 0.1 $\underline{M}$ $NaClO_4$; $E_{\frac{1}{2},d}$(0.1 $\underline{M}$ KNO_3, pH 4)=0.2	258
	Al	$AlCl_3$/BuPyCl	257
	Po	1 $\underline{M}$ HNO_3	82
	*	0.3 $\underline{M}$ HNO_3	80
ZnO	Zn	SRS; 1 $\underline{M}$ KCl	192

V. OVERVIEW OF INSTRUMENTATION

A. Foreword

This chapter is included to describe some of the components used in the electrochemical experiments; however, it is an overview and the exact instrumentation utilized for a specific analysis or detection scheme is discussed in the appropriate chapter. One can expect to find an in depth discussion of the computer controlled waveform generator, but their exists no discussion of the exact waveforms which have been produced. In addition, some of the instrumentation, such as commercially available potentiostats, rotators, etc., may not be discussed in this section, and the reader is encouraged to seek out this information in the appropriate chapter.

B. Potentiostats

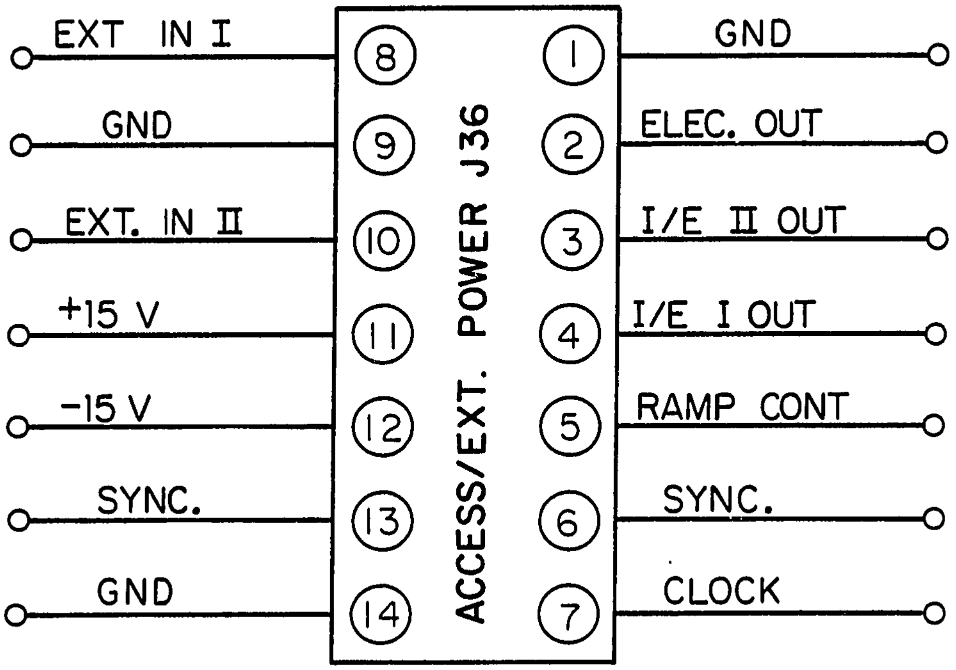
1. *Computer-controlled PAR 174A*

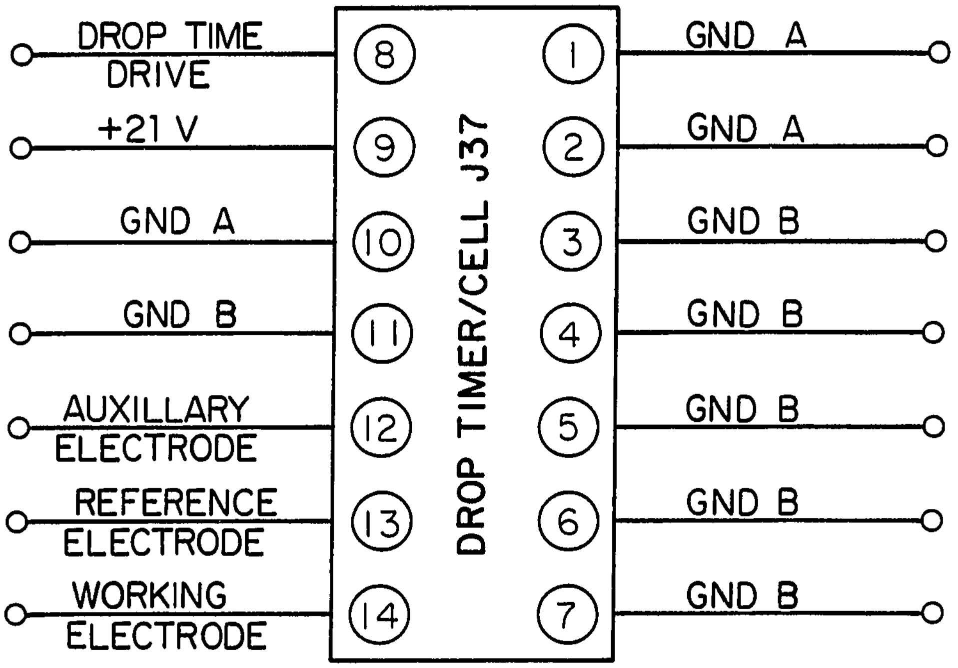
A majority of the experiments were centered around the use of a PAR 174A potentiostat (EG&G Princeton Applied Research, Princeton, NJ). However, in order to construct a universal computer system it was necessary to alter some of the existing circuitry and to override others. For example, of great use were the circuits for application of the selected potential to the three electrode cell and current measurement off the working electrode. However, for all experiments the circuitry for applied potential variation to the working electrode was overridden and controlled by the computer system with the use of a D/AC. Some circuits were used only in special cases, such as droptime actuation in polarographic experiments utilizing a DME.

Application of the selected potential to the three-electrode cell was accomplished with existing circuitry within the potentiostat. The initial design of the PAR 174A potentiostat allowed for this simple condition by including a summing circuit with the bias potential junction (EXT. IN. II) extended to the J36 connector on the back of the instrument (see Fig. V-1). To allow for exact applied potential control instead of a simple voltage offset all switches related to selection of initial potential on the face of the PAR 174A potentiostat were dialed to 0.000V. In addition, the instrument was switched into its "initial" state to prevent any potential ramping circuitry from being added at the same summing junction. With the instrument in its initial state, all switches related to the "scan rate" are not active and will have no affect on any experiment performed while under computer control.

Potential output, representative of the current passed at the working electrode, was obtained from two points: 1) directly off the output of the I/E converter, and 2) directly off the output of the S/H circuitry. The former output allowed for obtaining transient responses in chronoamperometric and chronocoulometric experiments. The latter output

Figure V-1. Schematic diagram of the external connectors of the PAR 174A potentiostat


ACCESS/EXT. POWER J36
8 EXT IN I
9 GND
10 EXT. IN II
11 +15 V
12 −15 V
13 SYNC.
14 GND
1 GND
2 ELEC. OUT
3 I/E II OUT
4 I/E I OUT
5 RAMP CONT
6 SYNC.
7 CLOCK


DROP TIMER/CELL J37
8 DROP TIME DRIVE
9 +21 V
10 GND A
11 GND B
12 AUXILLARY ELECTRODE
13 REFERENCE ELECTRODE
14 WORKING ELECTRODE
1 GND A
2 GND A
3 GND B
4 GND B
5 GND B
6 GND B
7 GND B

was used to take advantage of the low noise 16.67 ms S/H circuitry for use with pulsed amperometric methods. The points for measurement of these two potentials are shown in Figs. V-2 and V-3. To control the S/H operation it was necessary to alter the original circuit. This was accomplished by introducing a short TTL pulse (i.e., a 30 μs, 0 to 5 V transition) to the input stage of the timing monostable (Fig. V-4). To eliminate triggering also by the PAR 174A potentiostat, the input of capacitor C217 was disconnected from the circuit board. Selection of the type of output from the potentiostat was not under computer control, and required switching on the back of the potentiostat and on the front of the interface in accordance with the experiments being performed.

Provisions were also made for controlling a manual drop knocker for use with polarographic methods. All circuitry was kept intact with the exception of the triggering pulse for drop knocker actuation which was supplied by the computer system and not the potentiostat. The pulse was supplied to the input of the timing monostable, as shown in Fig. V-5, and to prevent triggering by the potentiostat the input of capacitor C220 and the output of resistor R279 were disconnected from the circuit board. As a result of only replacing the actuating pulse of the drop knocker driver, any drop knocker can be used that was originally intended for use with the PAR 174A potentiostat.

Figure V-2. Schematic diagram of PAR 174A circuit for cell current measurement. The point of measurement (test point 108), after conversion from cell current to a corresponding voltage by the I/E converter, is enclosed in the dotted oval

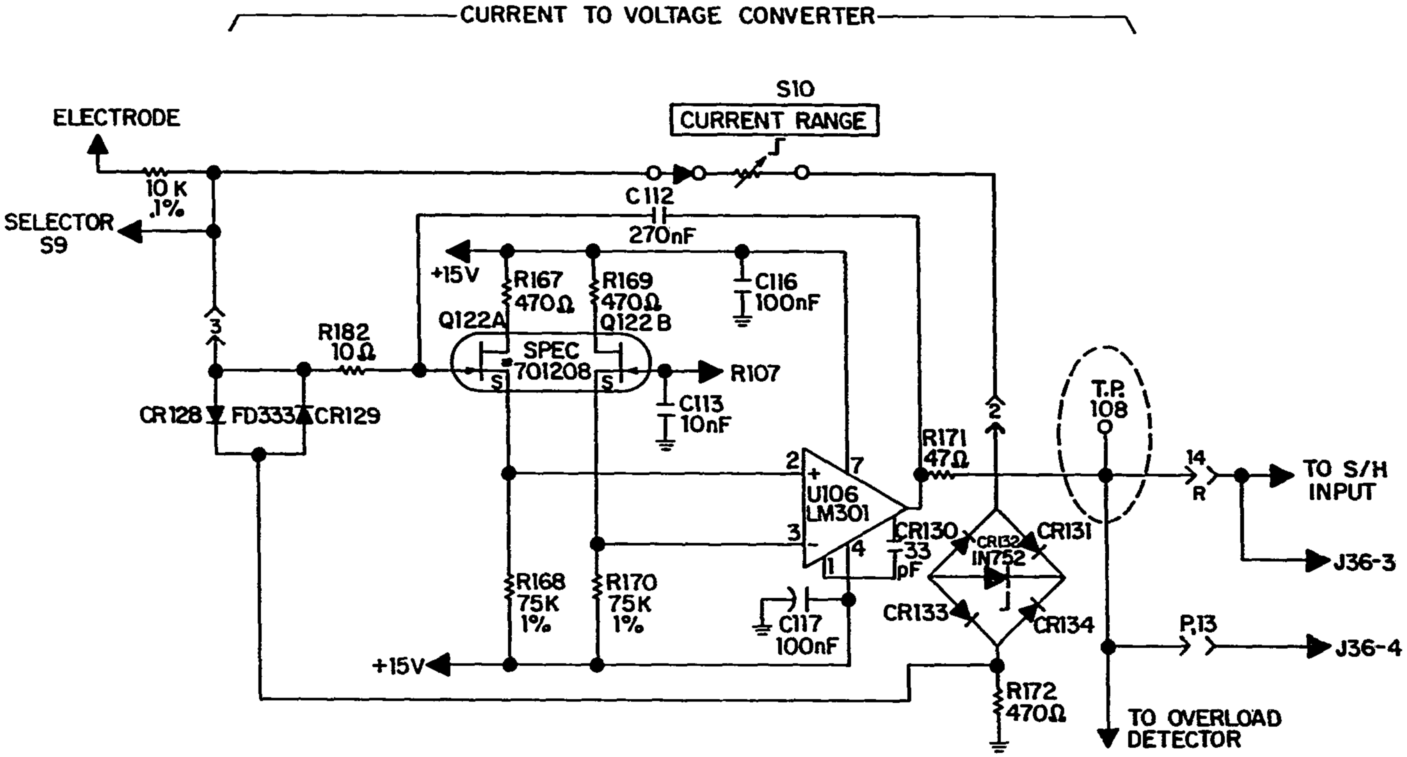

CURRENT TO VOLTAGE CONVERTER
ELECTRODE
S10
CURRENT RANGE
10 K
.1%
SELECTOR
S9
C112
270nF
+15V
R167
470Ω
R169
470Ω
C116
100nF
Q122A
Q122B
SPEC
701208
S
S
R107
R182
10Ω
3
C113
10nF
CR128
FD333
CR129
2
R171
47Ω
T.P.
108
2
7
+
U106
LM301
3
-
4
1
CR130
33
pF
CR132
IN752
CR131
14
R
TO S/H
INPUT
J36-3
R168
75K
1%
R170
75K
1%
C117
100nF
CR133
CR134
P13
J36-4
+15V
R172
470Ω
TO OVERLOAD
DETECTOR

Figure V-3. Schematic diagram of PAR 174A sample-and-hold circuit. The point of signal measurement (test point 201) is enclosed in the dotted circle

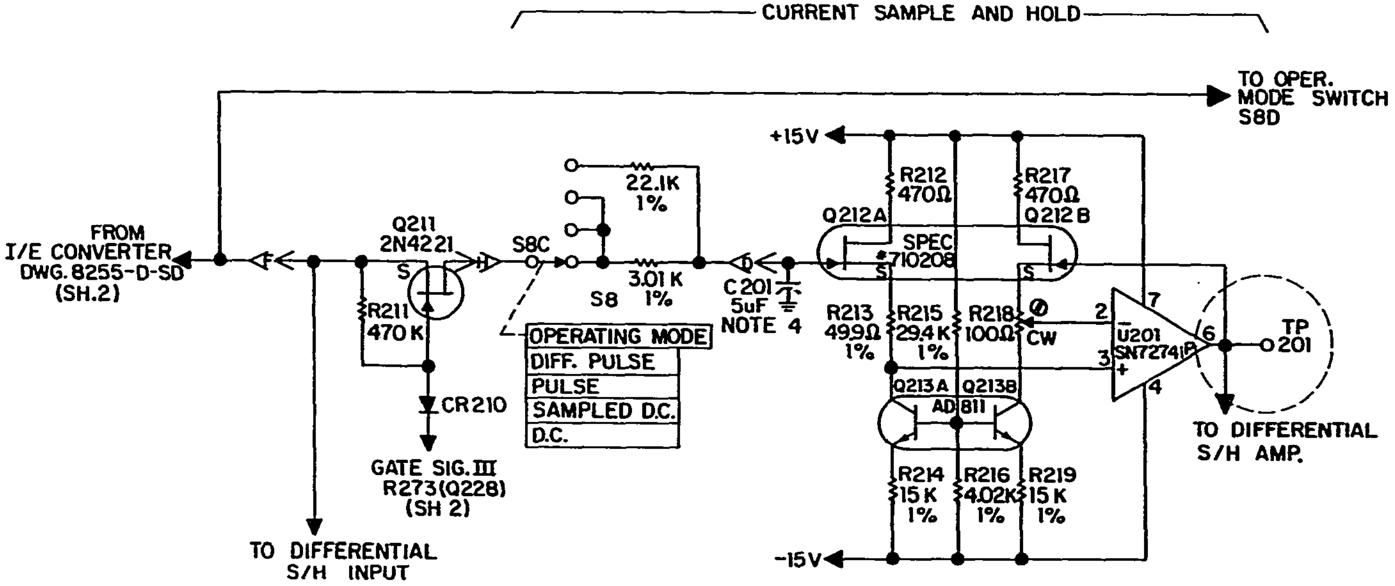

CURRENT SAMPLE AND HOLD
TO OPER. MODE SWITCH S8D
+15V
-15V
FROM I/E CONVERTER DWG. 8255-D-SD (SH.2)
F
Q211 2N4221
S
R211 470 K
CR210
GATE SIG. III R273 (Q228) (SH 2)
TO DIFFERENTIAL S/H INPUT
H
S8C
S8
22.1K 1%
3.01 K 1%
OPERATING MODE
DIFF. PULSE
PULSE
SAMPLED D.C.
D.C.
D
C201 5uF NOTE 4
R212 470Ω
R217 470Ω
Q212A
Q212 B
SPEC #710208
S
S
R213 49.9Ω 1%
R215 29.4 K 1%
R218 100Ω
CW
Q213A
Q213B
AD 811
R214 15 K 1%
R216 4.02K 1%
R219 15 K 1%
2
3
7
4
6
U201 SN72741P
TP 201
TO DIFFERENTIAL S/H AMP.

Figure V-4. Schematic diagram of the modified PAR 174A sample-and-hold timing monostable circuit. The external connection for the TTL triggering pulse is shown in the dotted circle

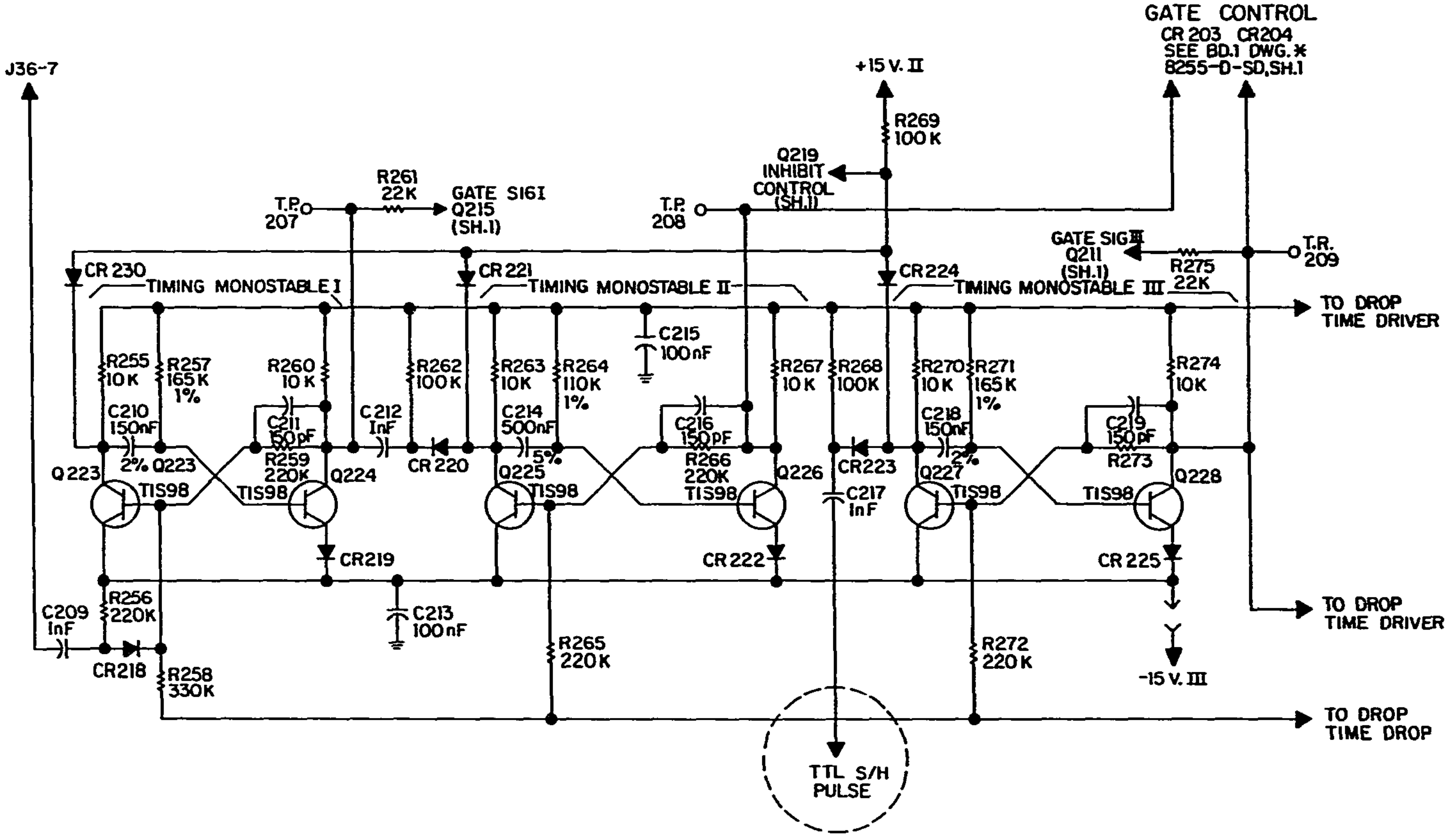

GATE CONTROL
CR203 CR204
SEE BD.1 DWG.*
8255-D-SD,SH.1
J36-7
+15 V. II
R269
100 K
Q219
INHIBIT
CONTROL
(SH.1)
R261
22K
GATE SIGI
Q215
(SH.1)
T.P.
207
T.P.
208
GATE SIG III
Q211
(SH.1)
R275
22K
T.R.
209
CR230
TIMING MONOSTABLE I
CR221
TIMING MONOSTABLE II
CR224
TIMING MONOSTABLE III
TO DROP
TIME DRIVER
C215
100 nF
R255
10 K
R257
165 K
1%
R260
10 K
R262
100 K
R263
10K
R264
110K
1%
R267
10 K
R268
100K
R270
10 K
R271
165 K
1%
R274
10K
C210
150nF
2%
C211
150pF
R259
220K
C212
InF
C214
500nF
5%
C216
150pF
R266
220K
C218
150nF
2%
C219
150pF
R273
Q223
Q224
CR220
Q225
Q226
CR223
Q227
Q228
TIS98
C217
InF
CR219
CR222
CR225
C213
100 nF
R256
220K
C209
InF
CR218
R258
330K
R265
220K
R272
220 K
-15 V. III
TO DROP
TIME DRIVER
TO DROP
TIME DROP
TTL S/H
PULSE

Figure V-5. Schematic diagram of the drop timer driver of the PAR 174A potentiostat. The connection for the external TTL activating pulse is shown in the dotted circle

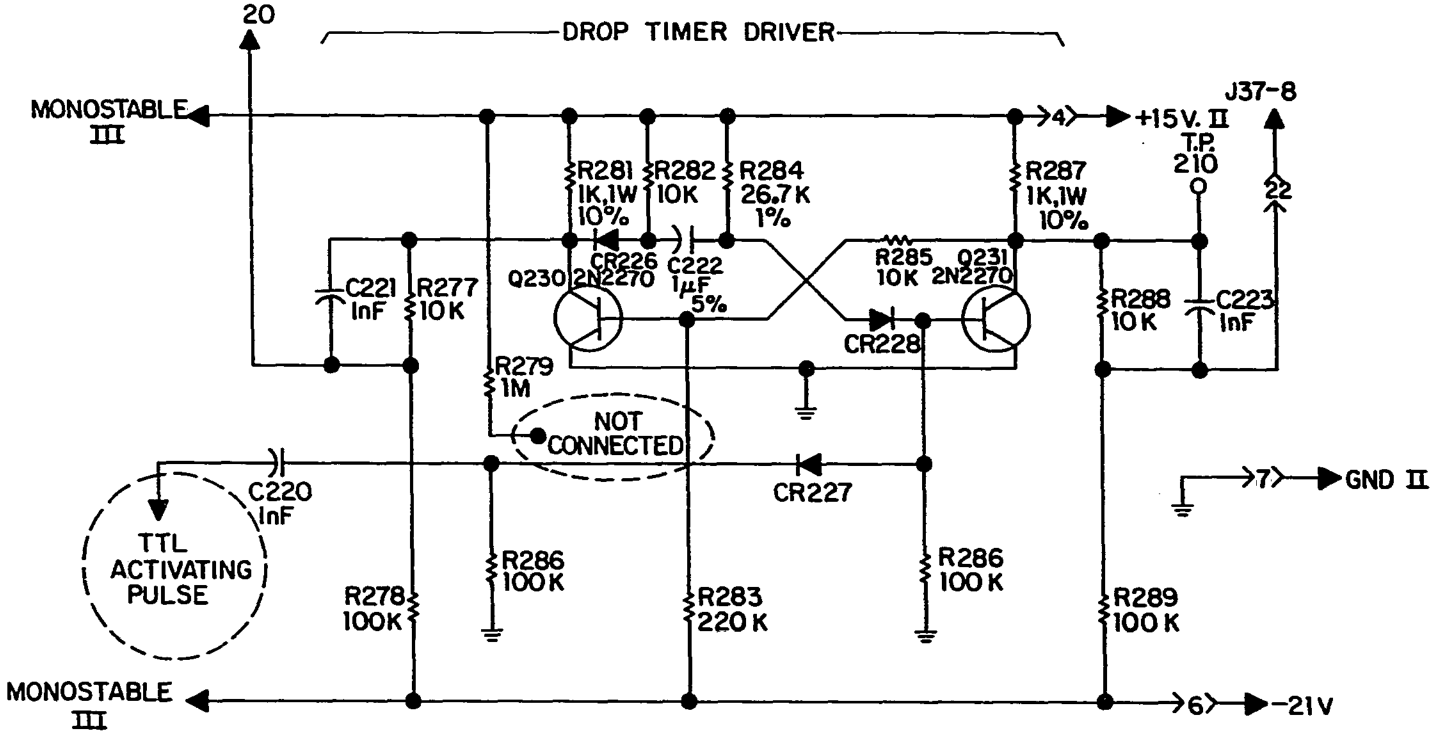
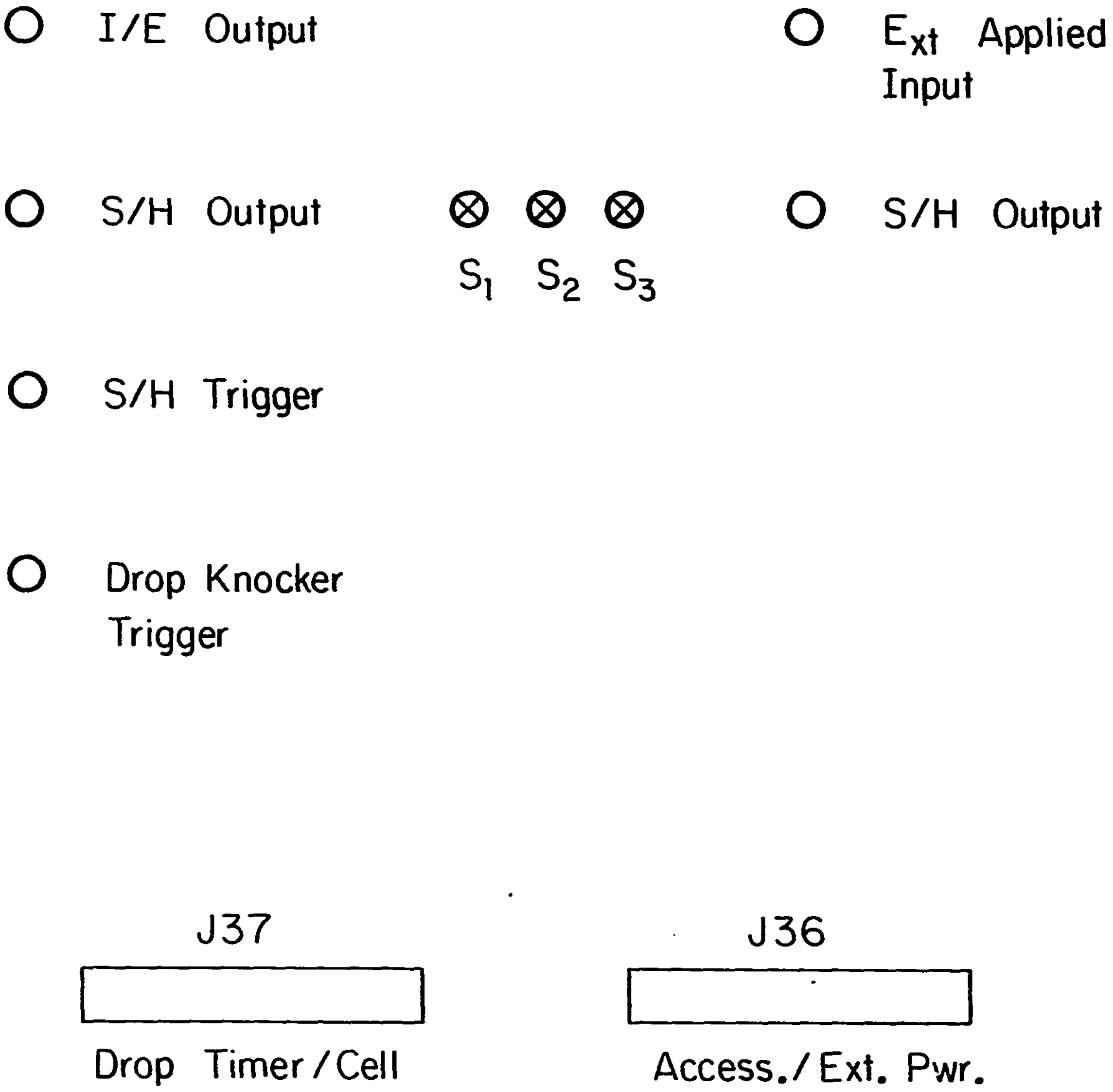

DROP TIMER DRIVER
20
MONOSTABLE III
MONOSTABLE III
4
+15V. II
J37-8
T.P. 210
22
R281 1K,1W 10%
R282 10K
R284 26.7K 1%
R287 1K,1W 10%
CR226
C222 1μF 5%
Q230 2N2270
R285 10K
Q231 2N2270
C221 1nF
R277 10K
CR228
R288 10K
C223 1nF
R279 1M
NOT CONNECTED
C220 1nF
CR227
7
GND II
TTL ACTIVATING PULSE
R286 100K
R286 100K
R278 100K
R283 220K
R289 100K
6
-21V

Figure V-6. Schematic diagram of the rear panel of the PAR 174A potentiostat showing external connections for computer control


I/E Output
E_{xt} Applied Input
S/H Output
S_1 S_2 S_3
S/H Output
S/H Trigger
Drop Knocker Trigger
J37
Drop Timer/Cell
J36
Access./Ext. Pwr.

All inputs and outputs to and from the 174A potentiostat have connections on the rear panel of the instrument. A schematic diagram of the rear panel of the potentiostat is shown in Fig. V-6. Provisions were also made for switching the instrument back to its original format. This was accomplished by throwing all toggle switches (S_1-S_3) in the downward most position.

2. *Stand-alone PAR 174A for two-step waveforms*

An additional PAR 174A potentiostat was modified for experiments utilizing a two-step waveform. These modifications resulted in the substitution of a resistor and a capacitor to lengthen the pulse time at the final potential, i.e., the potential where the current is sampled. A more thorough discussion of this modification can be found in the experimental section of Chapter VIII.

3. *Dionex UEM*

a. Hardware modifications A microprocessor controlled Dionex UEM potentiostat was used for the PCD of metals at a gold electrode (Chapter XI); however, in order to perform the desired waveform some of the existing hardware and software had to be modified. The hardware modifications are shown in Figs. V-7 and V-8, and are discussed below.

Due to the relatively long integration times needed for PCD experiments, additional provisions were made for time constant variation via a rotary switch mounted on a plug-in card within the potentiostat (slot 16). This increased the

Figure V-7. Schematic diagram of the hardware modifications for the Dionex UEM potentiostat allowing for increased integration periods and greater offset compensation

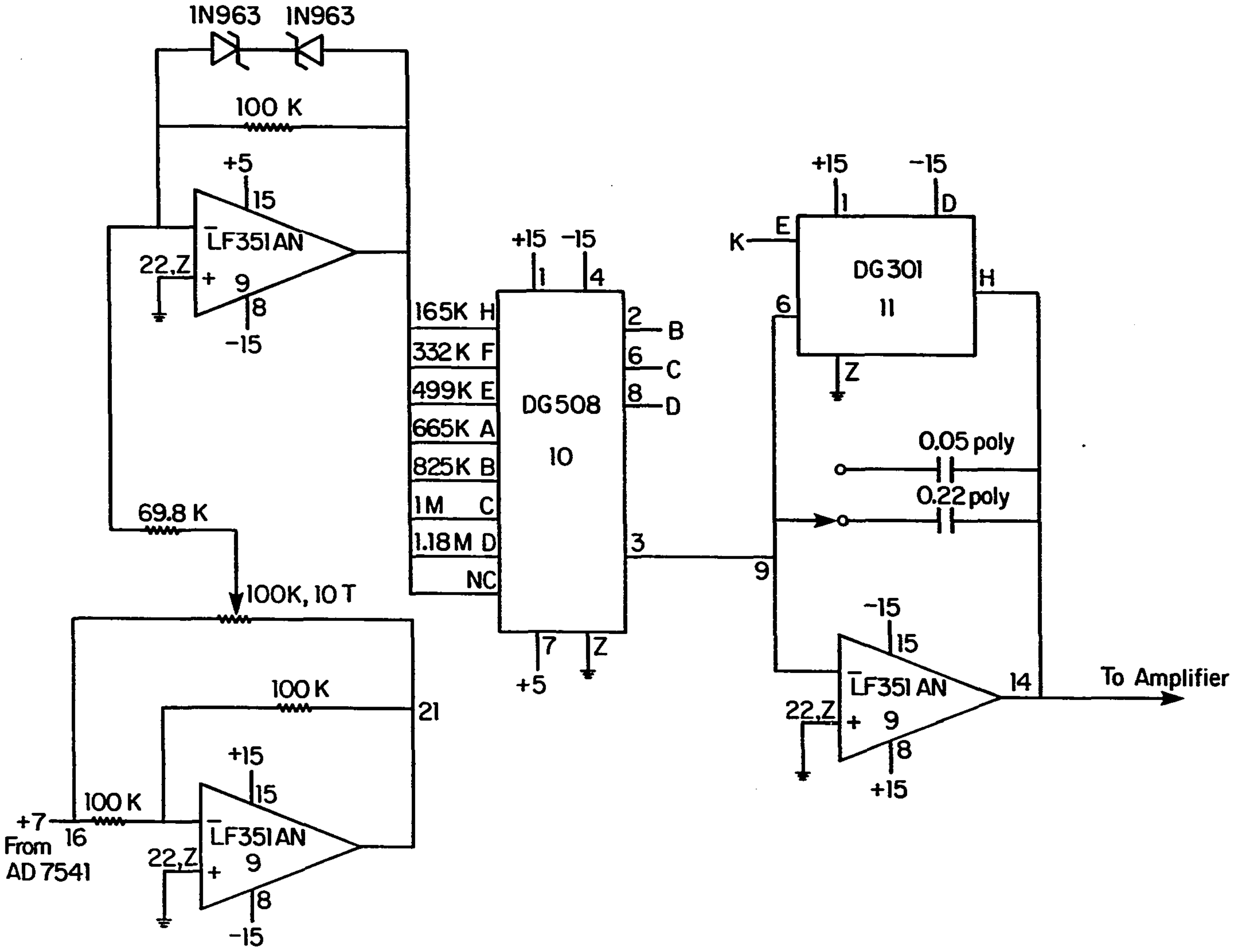
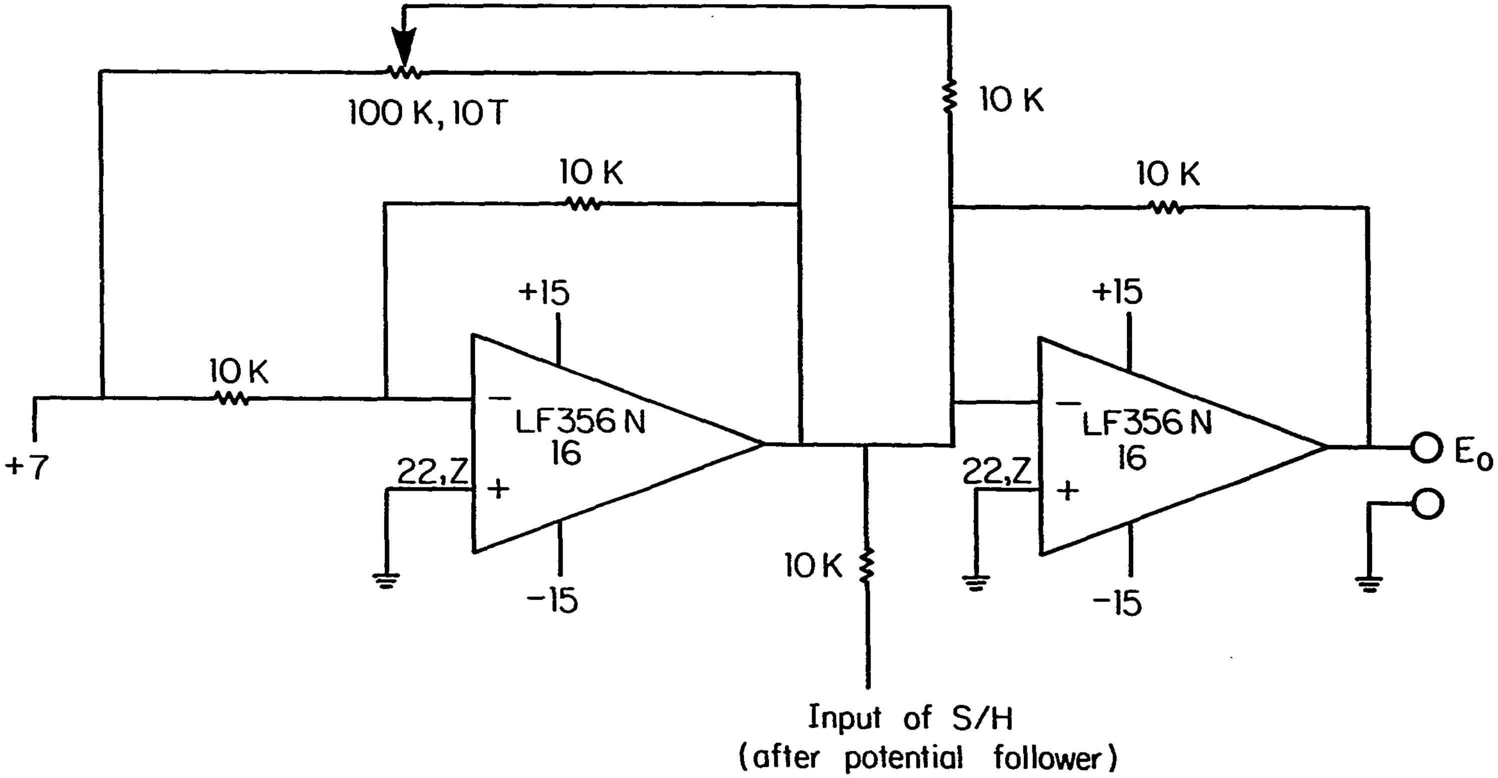

1N963
1N963
100 K
+5
15
LF351 AN
22,Z
+
9
8
-15
69.8 K
100K, 10 T
100 K
21
+15
15
+7
From
AD 7541
16
100 K
22,Z
LF351 AN
9
8
-15
165K H
332 K F
499K E
665K A
825K B
1M C
1.18 M D
NC
+15
-15
1
4
DG 508
10
2 B
6 C
8 D
3
7
+5
Z
+15
-15
1
D
K
E
DG 301
11
H
6
Z
0.05 poly
0.22 poly
9
-15
15
LF351 AN
22,Z
+
9
8
+15
14
To Amplifier

Figure V-8. Schematic diagram of the hardware modifications for the Dionex UEM potentiostat allowing for additional offset compensation



100 K, 10 T
10 K
10 K
10 K
10 K
+15
+15
−
−
LF356 N
16
LF356 N
16
22,Z
22,Z
+
+
+7
−15
−15
10 K
E$_0$
Input of S/H
(after potential follower)

number of allowable time constants for all experiments and did not override any of the existing indirect user-selected values; that is, upon selection of an integration time and amplification value via the potentiostat keypad, the internal programs automatically select the correct resistance values for both amplification stages (see the discussion of software modifications below).

Additional changes were needed in the offset circuitry because of the large backgrounds which can be observed. The existing offset circuitry, summed at the input of the I/E converter was enhanced to allow for greatly increased positive and negative voltage offsets. However, if the compensation is too great at one potential, it may cause saturation at another. To eliminate, or at least reduce this effect, an additional voltage offset was added after the amplification stage of the potentiostat (mounted on a plug-in card within the potentiostat, slot 16). This latter stage would not be necessary if the recording device, such as a strip chart recorder, had sufficient offset compensation.

Because of the adverse effects which can be seen with improper usage of an RC filter, an additional set of banana-plug connectors was added from which the direct output of the amplification stage can be measured. This resulted in high frequency background noise which can be easily removed with digital filtering techniques.

b. Software modifications To allow for long integration times, the software, as shipped from Dionex Corp. on UV EPROMS, had to be modified. The programs were read from the EPROMS, modified and the new programs were burned onto new EPROMS. The modifications resulted in the allowance of longer integration times with a maximum set at 254 x 16.67 + 16.67 ms with 16.67 ms increments. The added 16.67 ms results from software timing errors which are not easily corrected in the assembled version of the program. This results simply in the minimum integration time of 33.3 ms. The input resistance of the integration circuit is automatically selected with the user-selected integration time; however, for long integration times (i.e., > 7 x 16.67 + 16.67 ms) this would result in the selection of a infinite input resistance since there is no resistor connected between the output of the I/E converter and the input of line 8 of the digital switch (see Fig. V-8). To allow for larger integration times the series of resistances was repeated with each eight-fold increase in the integration time. However, no output signal will be seen for user-selected integration times of positive integer multiples of eight for the same reason as stated above (see Table V-1). To the user, the instrument will operate as a normal UEM detector with the exception of longer allowable integration times. Because of internal timing sequences for switching, the delay time before current measurement could not be reduced from its original value of 4 ms.

Table V-1. Switching sequence of the Dionex UEM potentiostat for analog integration

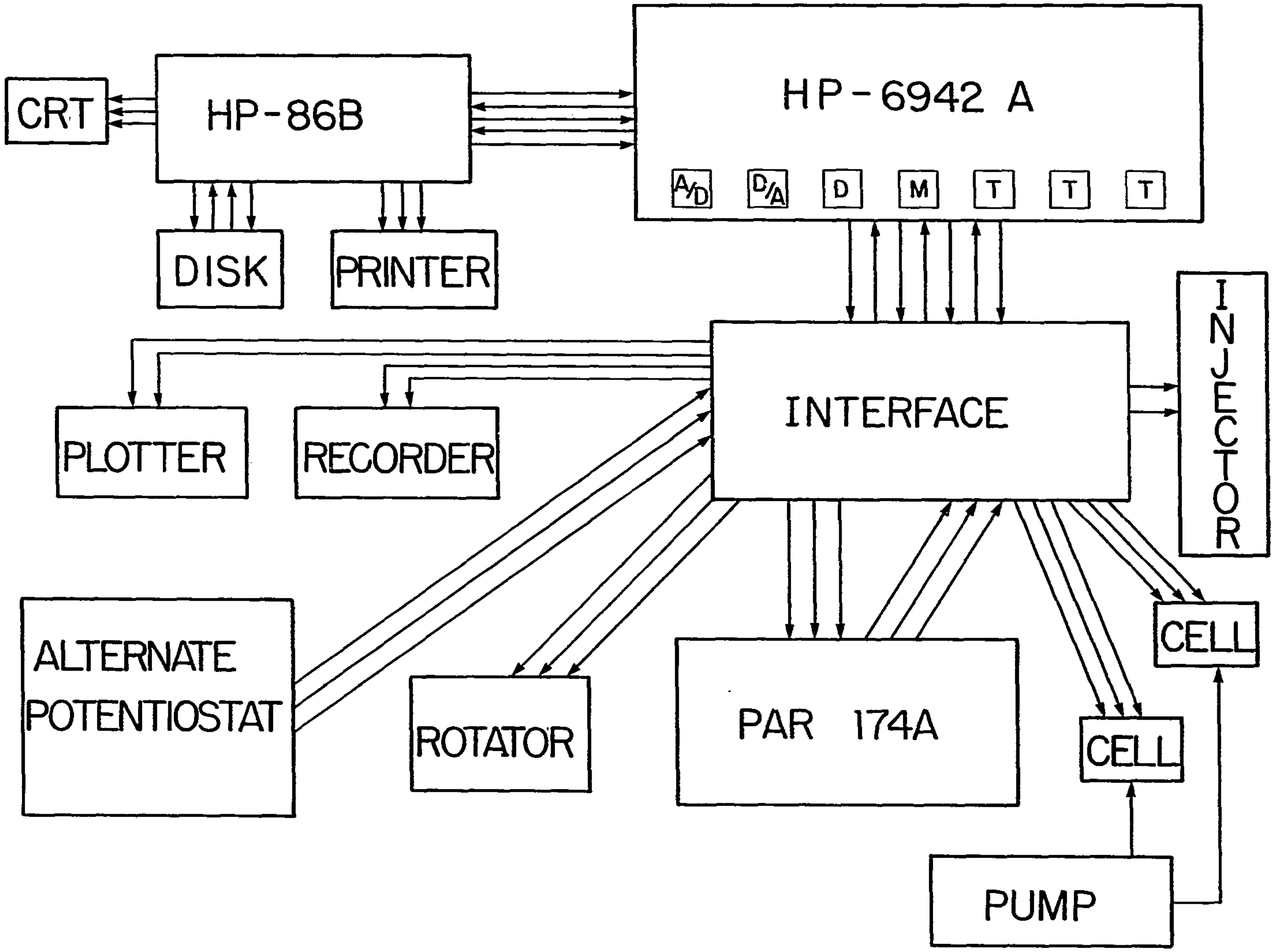
Integration number	Line 10-2[a]	Line 10-6	Line 10-8[b]
1	L	L	H
2	L	H	L
3	L	H	H
4	H	L	L
5	H	L	H
6	H	H	L
7	H	H	H
8[c]	L	L	L
9	L	L	H
10	L	H	L
11	L	H	H
12	H	L	L
13	H	L	H
14	H	H	L
15	H	H	H
16[c]	L	L	L
17	L	L	H
18	L	H	L
19	L	H	H
20	H	L	L
etc.			

[a] Most significant bit.
[b] Least significant bit.
[c] Integration sequence inactive.

C. Computer System

The computer system consisted of two Hewlett Packard computers (Palo Alto, CA) connected in series via the HP-IB interface bus (an IEEE-488 standard parallel bus). The entire computer controlled experimental apparatus is shown schematically in Fig. V-9. Programs were written in BASIC on the HP-

Figure V-9. Block diagram of the computer controlled electrochemical apparatus


CRT
HP-86B
HP-6942 A
A/D
D/A
D
M
T
T
T
DISK
PRINTER
INTERFACE
INJECTOR
PLOTTER
RECORDER
ALTERNATE POTENTIOSTAT
ROTATOR
PAR 174A
CELL
CELL
PUMP

86B microcomputer to control experimental waveform parameters, and for data acquisition and manipulation (see Appendix B). Waveform definition statements were sent from the HP-86B microcomputer to the dedicated mainframe HP-6942A multiprogrammer where they were processed and output to the computer interface. The multiprogrammer itself contains several plug-in cards which perform various tasks, such as analog-to-digital conversion (HP-69751A), digital-to-analog conversion (HP-69720A), single or multiple pulse timer control (HP-69736A), and digital I/O control (HP-69731B). The actual communication time for a statement from the microcomputer to the multiprogrammer is on the order of tens to hundreds of ms and depends upon the frequency of statements sent to the mainframe owing to its minimal memory capacity (4k RAM). However, once received these statements are processed rapidly, within μs. With careful programming, it is possible to eliminate any delays due to transferring information over the interface bus, and this has been accomplished for many of the waveforms, such as those used for staircase voltammetry, pulse amperometric and static-potential pulsed coulometric detection. Inefficient programming, although unavoidable in some instances, results in bogging down the interface bus, and causes the times selected for potential application within a waveform to be longer than anticipated. For example, the waveform described in Chapter X for PS-PCD of carbohydrates executes at a much slower frequency than selected via the input menus and the results can be misleading if the actual times are not measured.

Reference should also be made to the specific cards within the multiprogrammer. Programming of the plug-in cards is performed in normal engineering units; for example, the timing cards are programmed directly in units of ms, and the D/AC is programmed in units of volts. This minimizes errors due to improper conversion or scaling.

Voltage inputs and outputs are executed via 12-bit A/D and D/A convertors, respectively. D/AC output requires ca. 1 μs, whereas A/DC requires a maximum of ca. 40 μs. The 12-bit A/DC resolution is sufficient for all experiments so long as the proper scaling (i.e., amplification or deamplification) is performed before digitization. For experiments which require rapid A/DC, i.e., experiments which cannot be performed if data are transferred directly from the mainframe to the HP-86B microcomputer, there exists a set of memory cards which are coupled to the A/DC via a direct memory bus. These memory cards will hold a maximum of 4096 12-bit words. Memory storage and recall, as opposed to direct input, is employed for all experiments with the exception of staircase voltammetry.

Timing control is accomplished via three programmable timing or pacing cards. Each is capable of being programmed for a single TTL pulse, or for a burst output, where a symmetric square-wave is output until deactivated by the user (or program).

Electronic switching is accomplished with either the timing or digital output cards. This latter card contains 16 digital output TTL drivers capable of supplying several hundred μA output current in its 5 V true state. The digital output lines are used for rotation speed control and for switching the sample-and-hold circuitry contained within the computer interface.

D. Computer Interface

The computer interface served three purposes: 1) to link the computer system to the electrochemical instruments, 2) to increase the total number of possible electrochemical experiments, providing for such modes as pulsed coulometric detection, and for the allowance of computer controlled functions, such as electrode rotation speed control, by the addition of extended electronic circuitry, and 3) as a traffic-controller, allowing for multiple analog inputs from various potentiostats, such as those capable of cyclic voltammetry, and multiple outputs to a variety of recording devices. All of the extended electronic functions (e.g., amplification, integration, etc.) are contained within the interface on plug-in cards for ease of inspection and modification. The interface and its plug-in function cards were built in-house by this author. All connections to the interface were external and are shown schematically in Figs. V-10 an V-11.

Figure V-10. Schematic diagram of the front panel of the computer interface/traffic controller. See Table V-2 for an explanation of terms

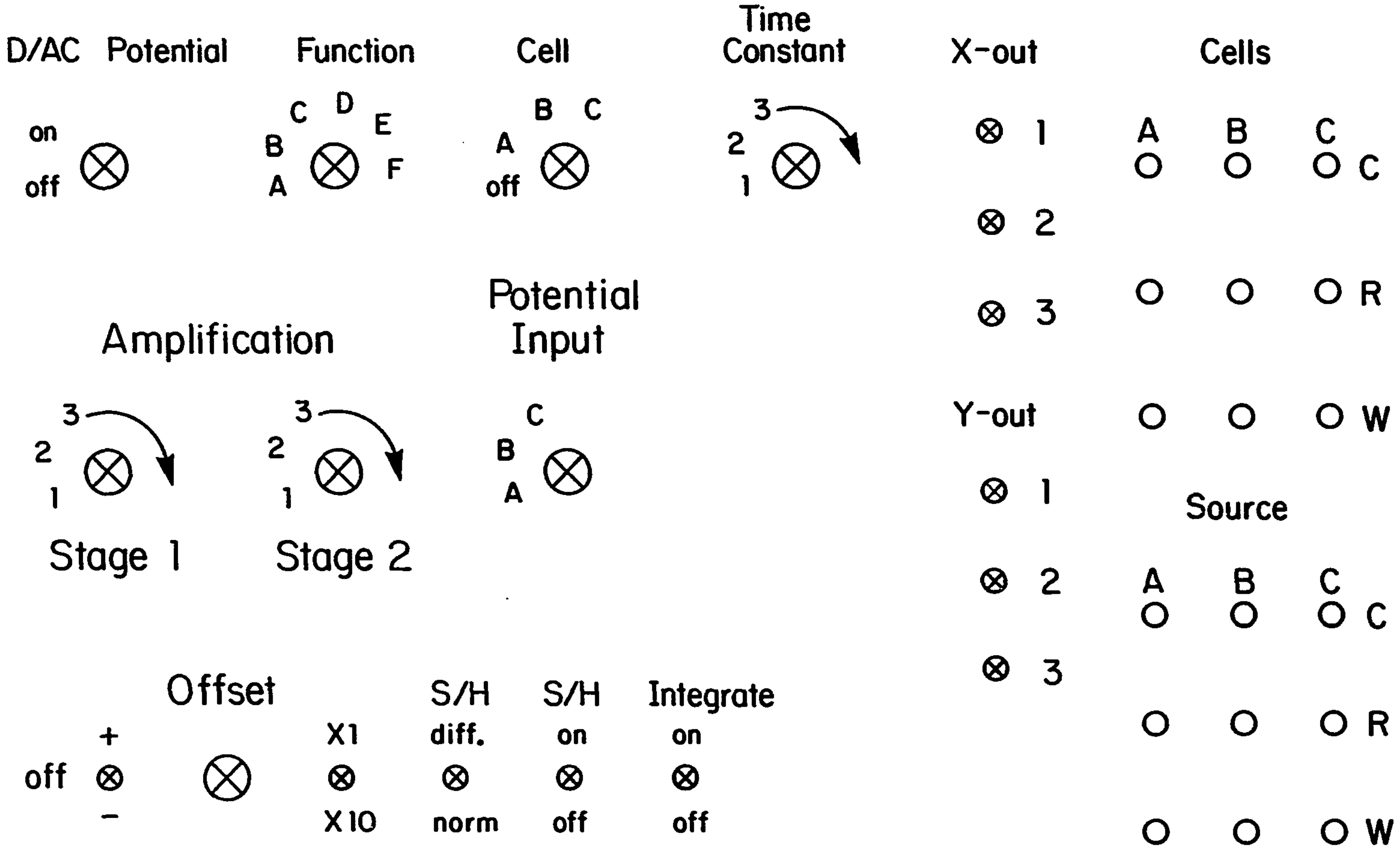
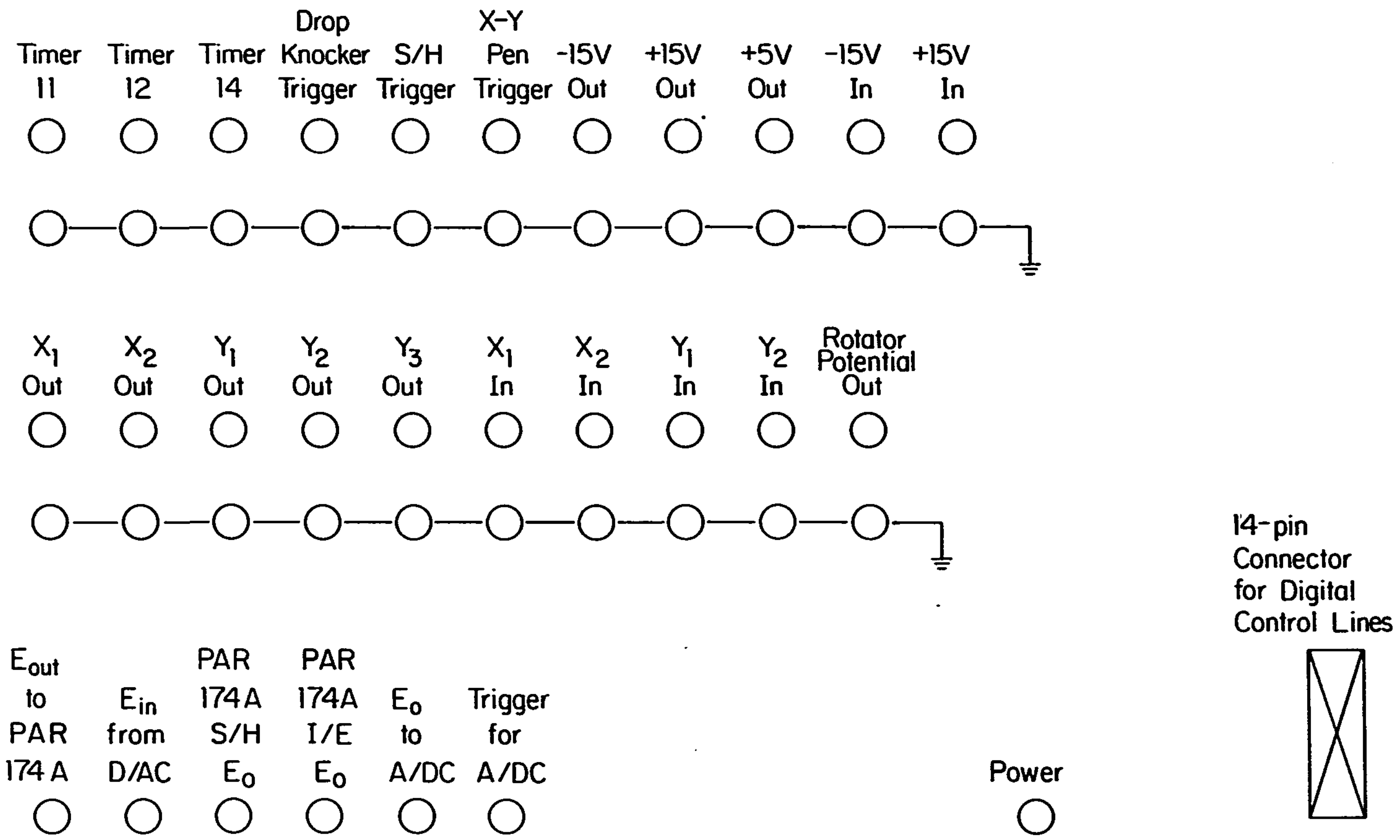

D/AC Potential
on
off
Function
A
B
C
D
E
F
Cell
off
A
B
C
Time Constant
1
2
3
X-out
1
2
3
Cells
A
B
C
C
R
W
Amplification
3
2
1
Stage 1
3
2
1
Stage 2
Potential Input
C
B
A
Y-out
1
2
3
Source
A
B
C
C
R
W
Offset
off
+
−
X1
X10
S/H
diff.
norm
S/H
on
off
Integrate
on
off

Figure V-11. Schematic diagram of the rear panel of the computer interface/traffic controller. Note, the majority of the electronic circuits contained within this interface derive their power from the PAR 174A potentiostat; power is supplied as -15 V and +15 V inputs. An internal power supply has been added to drive the electrode rotation speed control circuits


Timer 11
Timer 12
Timer 14
Drop Knocker Trigger
S/H Trigger
X-Y Pen Trigger
-15V Out
+15V Out
+5V Out
-15V In
+15V In
X_1 Out
X_2 Out
Y_1 Out
Y_2 Out
Y_3 Out
X_1 In
X_2 In
Y_1 In
Y_2 In
Rotator Potential Out
E_{out} to PAR 174 A
E_{in} from D/AC
PAR 174A S/H E_o
PAR 174A I/E E_o
E_o to A/DC
Trigger for A/DC
Power
14-pin Connector for Digital Control Lines

Additionally, parameters which were not controlled via the computer system were manually switched on the front panel of the interface (Fig. V-10). For a discussion of the interface switch settings and the various connections on the face of the interface see Table V-2. Following will be a discussion of the design an operation of the interface with respect to communication with various components of the experimental apparatus.

Table V-2. Switch settings and interface connections on the face of the computer interface/traffic controller

D/AC Potential	Switch for disconnecting the D/AC output from the interface (e.g., the electrochemical cell).
Function	Type of "experiment" performed [A] Polarographic experiments [B] Experiments employing the S/H circuit of the PAR 174A [C] Experiments for direct current measurement, the S/H circuits of the PAR 174A are not used [D] Digital plotting on X-Y recorder [E] Alternate potentiostat inputs for electrochemical experiments [F] Same as [E]

Table V-2. Continued

Cell	Selection of the electrochemical cell used, C, R, W denote the counter, reference and working electrode connections, respectively.
Time Constant	The time constant of the analog integrator used for PCD experiments.
X-out, Y-out	External switching of signal outputs to recording devices.
Amplification	Selection of the magnitude of amplification to be employed for each of the two stages.
Potential Input	Switching for control of the analog voltage input source. Connections are made at the appropriate source inputs, where C, R, W denote the counter, reference and working electrode connections, respectively. Normally the inputs are taken from the modified PAR 174A potentiostat, but any alternate source input may be used.
Offset	Offset circuitry may be used for any of the electrochemical experiments. In the X1 position the offset is 0.15 V turn^{-1}.
S/H	This circuit is used in conjunction with the integration circuitry. The diff. (differential) mode is no longer active, and this switch must stay in the norm. position.
Integrate	This switch is used to activate the analog integration circuitry for PCD experiments. The S/H circuit of the interface must be used for PCD experiments.

1. Potentiostat

a. Amperometric methods The major service of the interface was to act as a link between the computer system and the PAR 174A potentiostat. For methods of PAD and staircase voltammetry the S/H circuitry of the potentiostat was utilized. This greatly reduced the observed noise for both experiments over comparable integration circuits within the interface.

In staircase and PAD experiments the applied potential is routed from the D/AC to the potential input of the PAR 174A potentiostat. The output of the PAR 174A S/H circuit is routed through the amplification/offset circuitry (Figs. V-12 and V-13) to the A/DC input. Triggering of this S/H circuit is accomplished by pacer board 14 (see Fig. V-4). The sensitivity control on the potentiostat is still active and the knowledge of its position is pertinent to accurate current conversion within the data acquisition programs.

b. Coulometric methods An analog integrator (Figs. V-14 and V-15) may be switched onto the back-end of the amplification circuitry to allow for coulometric measurements. In these experiments the time constant may be varied for the desired integration time, with a minimum and maximum time constants of 50 and 2000 ms, respectively. Amplification is performed before the integration step (see Figs. V-12 and V-13); however, the offset circuitry acts on the output of the integrator and not the amplifier. The offset circuitry output

Figure V-12. Schematic diagram of the amplification/offset circuitry contained within the computer interface. Values of resistances for both amplification stages are tabulated in Fig. V-13

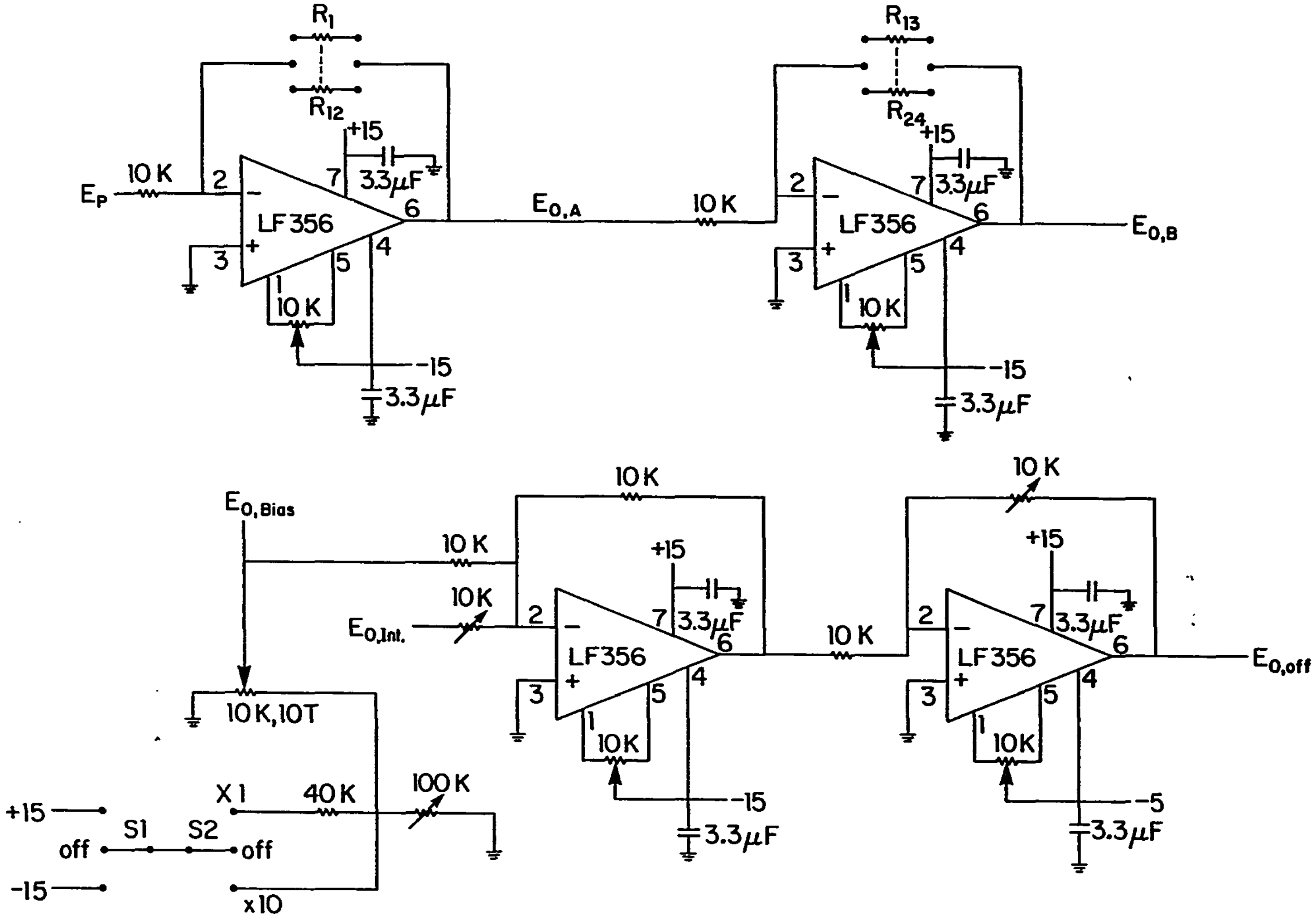

R1
R12
R13
R24
EP
10 K
2
3
7
6
4
5
1
LF356
+15
3.3μF
-15
E0,A
E0,B
E0,Bias
E0,Int.
E0,off
10K,10T
-5
+15
off
-15
S1
S2
X1
off
x10
40K
100K

Figure V-13. Diagram of the card edge connector for the amplification/offset circuitry of Fig. V-12. Resistances for both amplification stages are also shown

Resistances (±1%)

Stage A index	Stage A $R_i(\Omega)$	Stage B index	Stage B $R_i(\Omega)$
1	10 K	13	10 K
2	15 K	14	15 K
3	20 K	15	20 K
4	34.8 K	16	34.8 K
5	49.9 K	17	49.9 K
6	69.8 K	18	69.8 K
7	90.9 K	19	90.9 K
8	100 K	20	100 K
9	150 K	21	150 K
10	200 K	22	200 K
11	348 K	23	348 K
12	499 K	24	499 K

Edge Connector

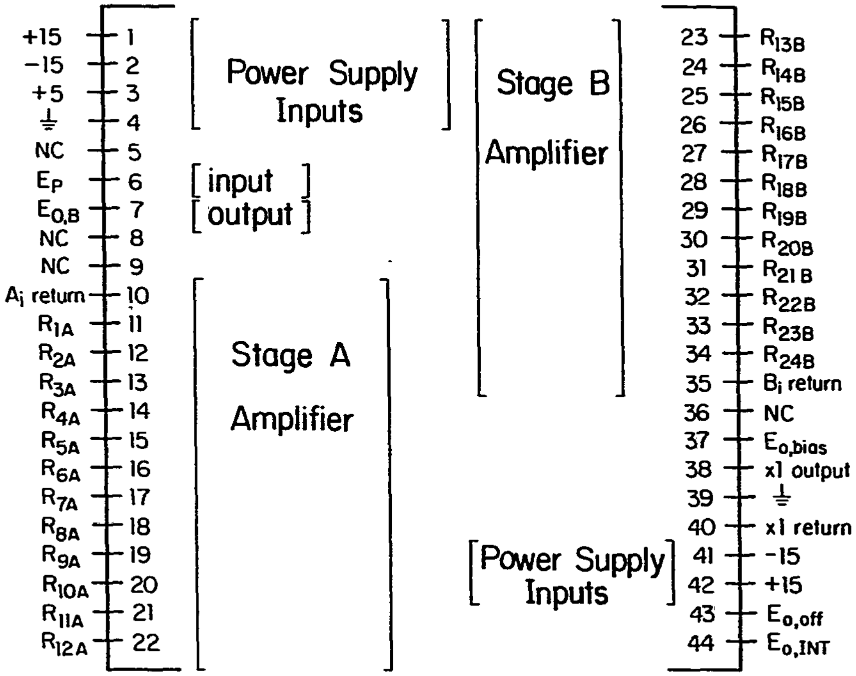


Figure V-14. Schematic diagram of the analog integration circuitry contained within the computer interface. The values of resistances, denoted as R_i, are tabulated in Fig. V-15

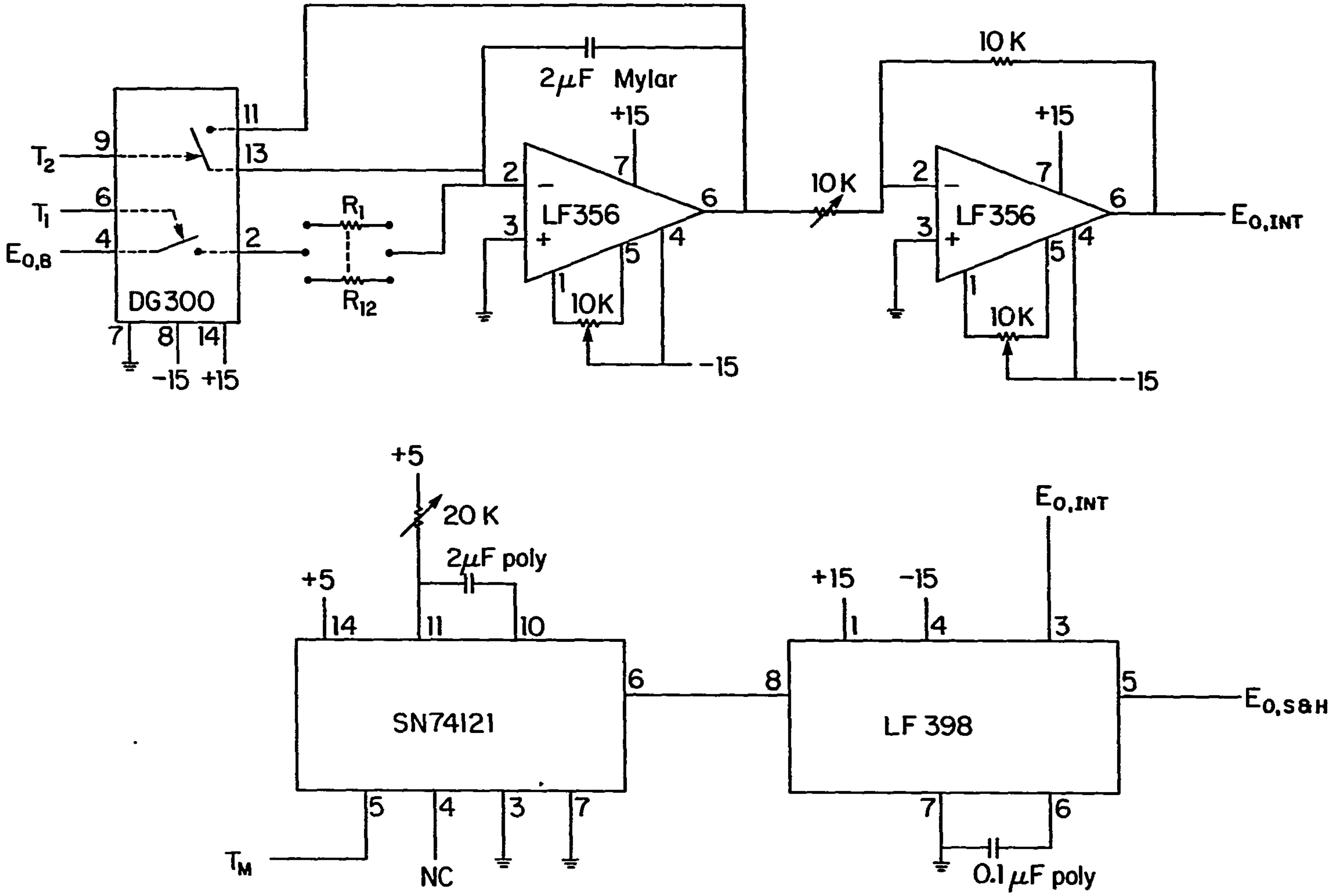
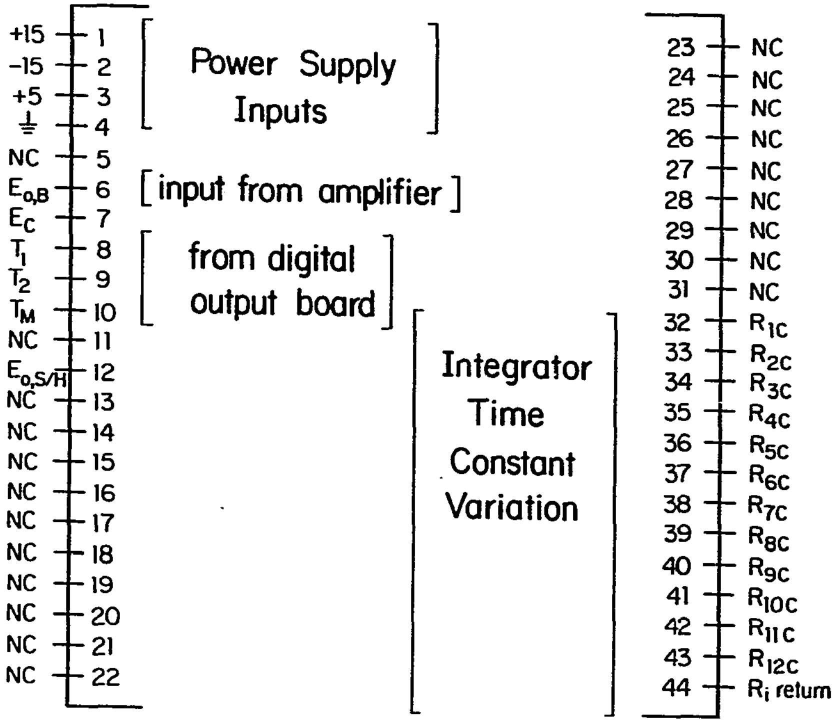

T2
T1
E0,8
9
6
4
11
13
2
DG300
7
8
14
−15
+15
R1
R12
2μF Mylar
+15
2
3
7
6
5
4
1
LF356
10K
−15
10K
10 K
+15
2
3
7
6
5
4
1
LF356
10K
−15
E0,INT
+5
20 K
2μF poly
+5
14
11
10
6
5
4
3
7
SN74121
TM
NC
E0,INT
+15
−15
1
4
3
8
5
7
6
LF 398
E0,S&H
0.1μF poly

Figure V-15. Diagram of the card edge connector for the analog integration circuitry of Fig. V-14. The allowable time constants τ for the analog integrator are also shown

Time Constants

$R_i (\Omega)$	τ (ms)
5 K	10
25 K	50
50 K	100
125 K	250
200K	400
250 K	500
300 K	600
400 K	800
500 K	1000
625 K	1250
750 K	1500
1 M	2000

Edge Connector



is directed to the A/DC. To determine if the integrator is functioning properly, it is possible to switch the interface S/H circuitry off, with the appropriate toggle switch on the front panel of the interface, and monitor the output of the integrator directly (i.e., a saw-tooth wave should be observed for a PCD experiment).

c. Polarographic methods In the initial design of the interface, provisions were made for the application of pulsed polarographic experiments and have been kept with later designs. The switching and circuitry is the same for the **amperometric methods** described above with the exception of a timing pulse for triggering the drop-knocker monostable of the PAR 174A potentiostat (see Fig. V-5). This is accomplished with pacer card 12 utilizing a triggering time of ca. 30 μs.

d. Noise considerations In the development of the PAR 174A potentiostat interface, several precautions were taken to minimize the observed noise (e.g., shielding of voltage inputs and outputs, and capacitive decoupling of power inputs); however, the noise level of the system is still far greater than desired. Contributions to the observed noise are believed to be from several sources, including, improper switching sequences for integration, digital logic input feed-through to the interface S/H output, and most importantly ground current loops. Of these, the latter deserves additional attention.

Difficulties will be observed when several instruments are joined if serious consideration is not given to the methods of coupling. It is necessary that the proper grounds from each instrument (up to five isolated grounds may exist with these instruments) be properly connected to insure that no ground current loops are formed. However, in the case of the HP-6942A and its multiple plug-in cards, there exists several different isolated grounds which at some point must converge; however, if not performed correctly the noise level becomes excessively high. The challenge, of course, is connecting all of these instruments with no observed ground current loops. Few individuals--I have yet to meet or speak with such a person--are totally knowledgeable of such methods. Use of only earth ground for all connections can result in the destruction of any coupled circuits due to large floating voltages. Isolation of any of these instruments may reduce the observed noise, but again at the risk of destroying present circuitry. In the end, the large background noise still persists, and its existence is known, signifying the necessary development of a single instrument capable of similar waveform programming.

2. *Digital Plotter*

An X-Y recorder may be used as a digital plotter so long as arrangements are made for triggering of the pen-lift solenoid with TTL drivers. The circuitry for pen-lift control of a PAR RE0074 X-Y recorder, as designed by Houston Instruments, is shown in Fig. V-16. To control the pen position

Figure V-16. Schematic diagram of the TTL driven pen-lift circuitry as designed by Houston Instruments. The TTL input is connected to pin 1 of the barrier strip and is referenced to a common ground. Contact closure actuation may also be performed between barrier strip contacts 2 and 3. The external pen-lift switch, with this circuit in place, is still active

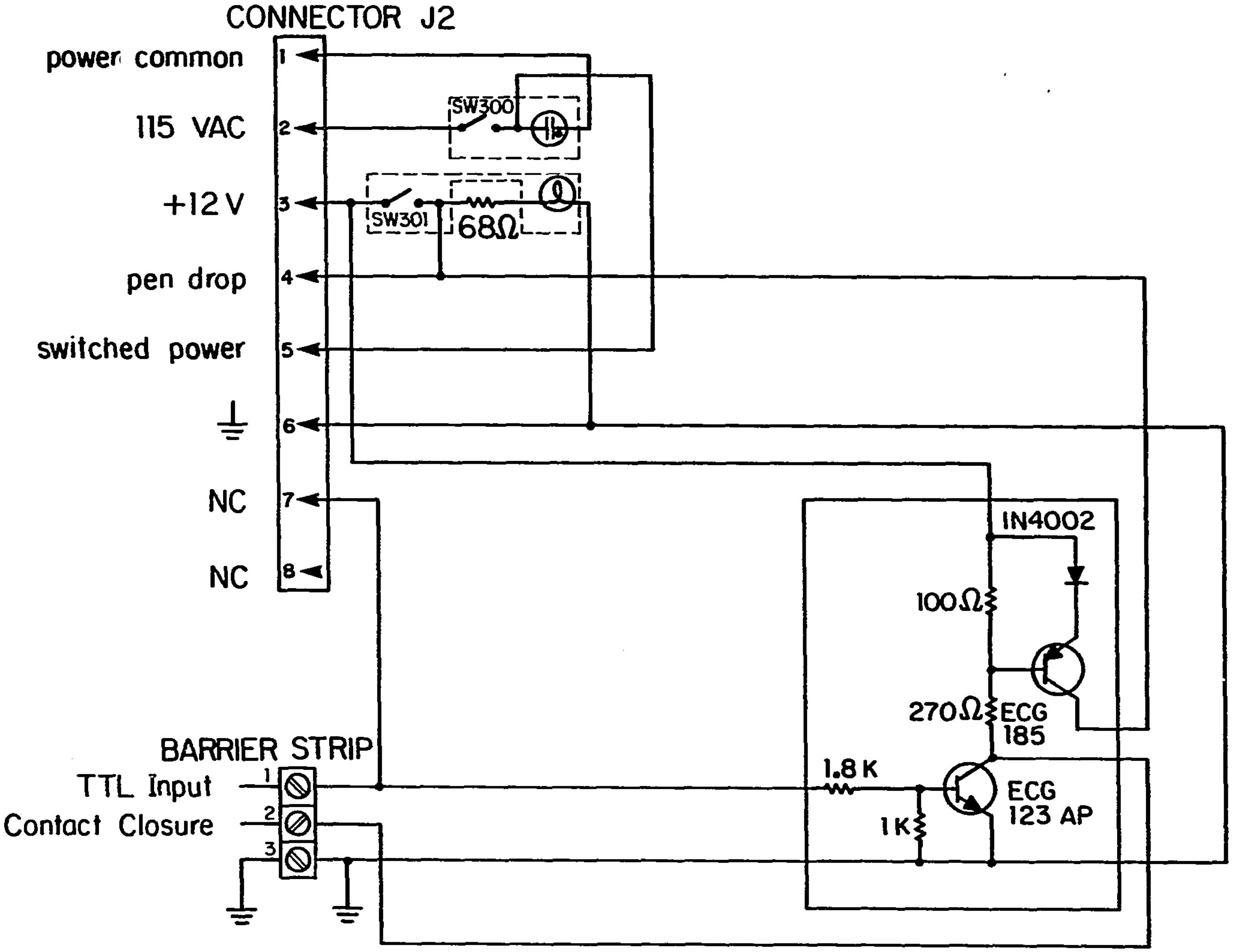
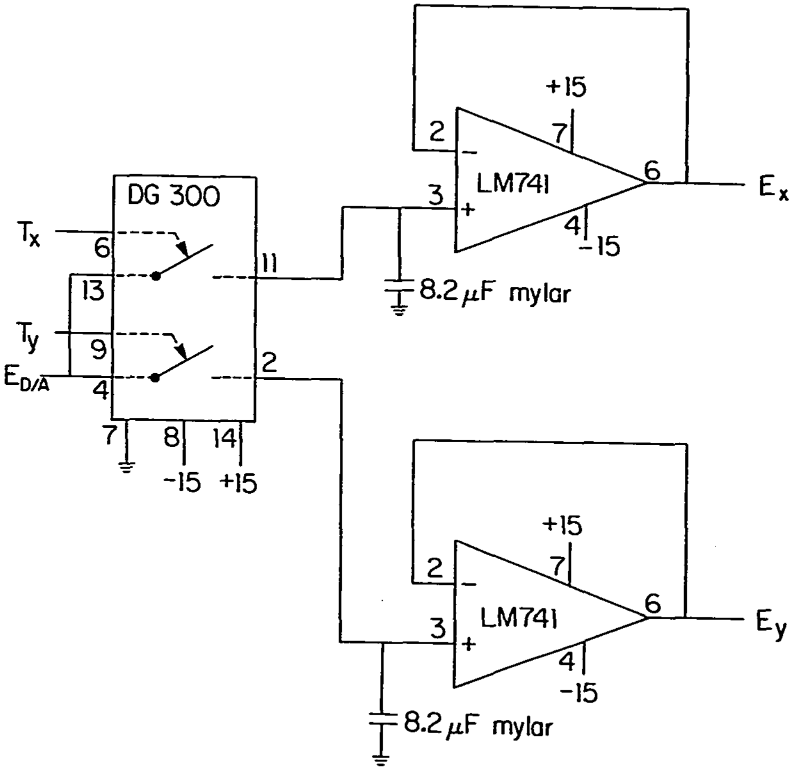
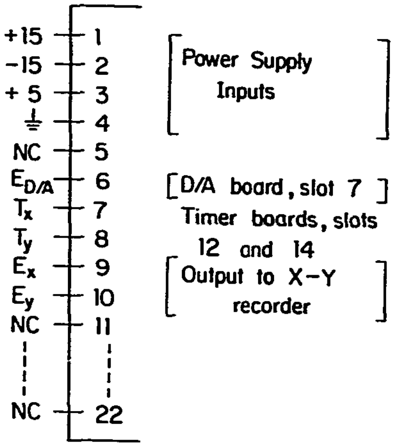

CONNECTOR J2
power common
115 VAC
+12 V
pen drop
switched power
NC
NC
1
2
3
4
5
6
7
8
SW300
SW301
68Ω
IN4002
100Ω
270Ω
ECG
185
1.8 K
1 K
ECG
123 AP
BARRIER STRIP
TTL Input
Contact Closure
1
2
3

Figure V-17. Schematic diagram and card edge connector for sample-and-hold circuitry for digital plotting with an X-Y recorder



Edge Connector



(i.e., x and y coordinates) a simple S/H circuit was designed with the aid of a double-pole digital switch (Fig. V-17). Stored ordered pairs of applied potential and measured current are converted to representative voltages within an 10 V by 8 V grid (x by y) with minimum steps of 0.005 V, and are alternately output through the D/AC and stored in their respective S/H circuits (Fig. V-17). Once both capacitors of the S/H circuits have been charged the pen is dropped to mark the point on the graph. This process is repeated until all points have been plotted.

3. *Electrode rotator*

Electrode rotation speed variation for RDE and RRDE was accomplished by computer controlled alteration of the voltage input to the MSR rotator (Pine Instruments Co., Grove City, PA). Although the circuits were designed with the MSR rotator in mind the circuitry is compatible with any rotator which utilizes a voltage/rotation-speed input. The circuits for potential variation and its corresponding card edge connector are shown in Figs. V-18 and V-19, respectively. Seven identical stages were built with the voltage output of each stage tuned to correspond to the rotation speed desired. Since the potential input of the MSR rotator control is calibrated to 1000 rpm/V the voltage output of the interface drivers were calibrated in integer multiples of 10 $\text{rpm}^{1/2}$, corresponding to rotation speeds of 100 to 4900 rpm. If an alternate rotator is used where the output rotation speed to voltage input ratio differs from that of the MSR rotator control (i.e., 1000 rpm/V) the output voltages of the individual drivers may be altered by changing the variable input resistances (see stage outputs of Fig. V-19). The drivers were controlled, through software, by the digital I/O lines available within the multiprogrammer (see stage digital access numbers of Fig. V-19). Since the output of all drivers is summed before being output to the rotator control, individual drivers may be activated in any combination yielding a greater number of available rotation speeds which can be automatically selected. All data acquisition programs were capable of utilizing automatic rotation speed control.

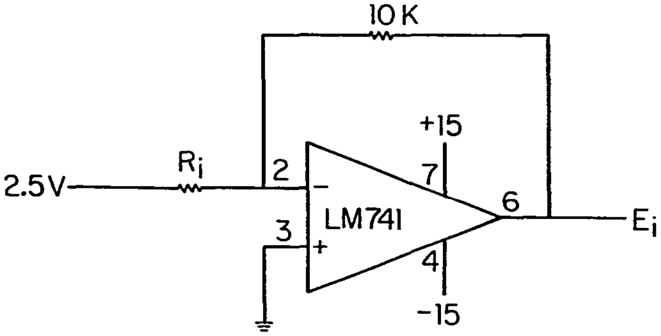
4. External Inputs

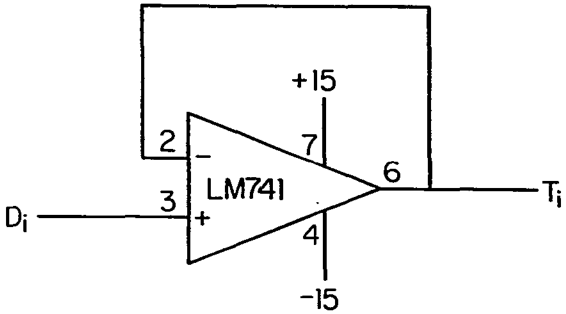
The interface could also act as a traffic-controller, allowing inputs from sources other than the multiprogrammer while taking advantage of some of the features of the computer system, such as rotation speed variation. This reduced the need for multiple cabling of several instruments and reduced the switching time between the various electrochemical cells. Additionally, it is possible to digitize the analog signal for future use. Two additional potentiostat inputs were added and may be selected via a switch on the front panel of the interface (see Fig. V-10 and Table V-2).

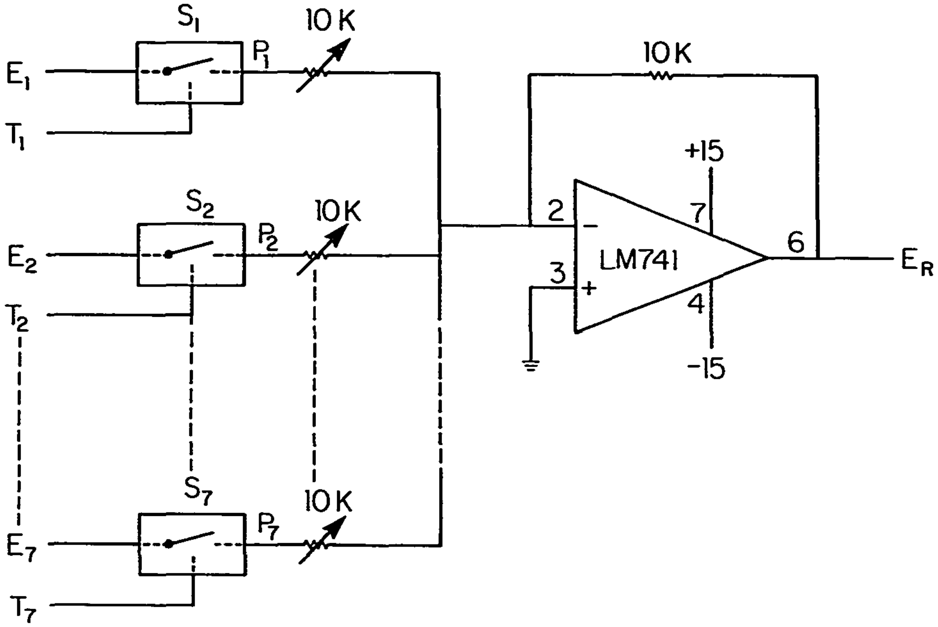
5. Display Outputs

Irrespective of the experiment being performed the option always exists for displaying the electrochemical output to a

Figure V-18. Schematic diagram of the electrode rotation speed control circuitry as designed for Pine Instruments Model MSR rotators. Values of resistances, output stage voltages and their corresponding rotation speeds (rpm) are tabulated in Fig. V-19


10 K
+15
R_i
2.5V
2
7
6
E_i
LM741
3
+
−
4
−15


+15
2
7
−
LM741
6
T_i
D_i
3
+
4
−15


S_1
10 K
E_1
P_1
T_1
10 K
S_2
10 K
E_2
P_2
T_2
+15
2
7
−
LM741
6
E_R
3
+
4
−15
S_7
10 K
E_7
P_7
T_7

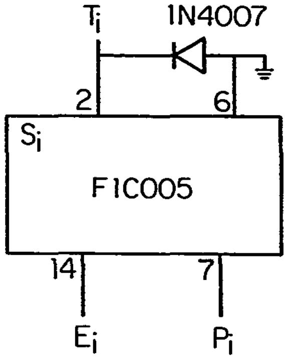

T_i
1N4007
2
6
S_i
F1C005
14
7
E_i
P_i

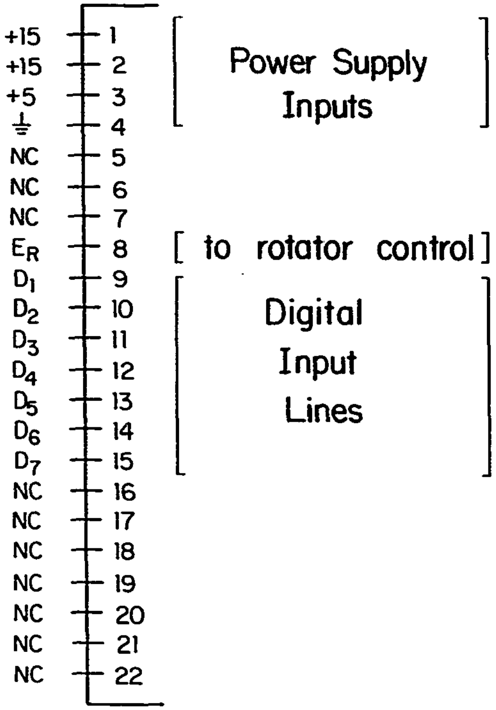
Figure V-19. Diagram of the card edge connector for electrode rotation speed control as shown schematically in Fig. V-18. Tabulated values for output stage resistances, potentials, and corresponding rotation rates, and, the digital access number for activation of each stage, are also shown

Stage Outputs

Stage	R_i (Ω)	E_i(V)	w_i(rpm)
1	250 K	0.100	100
2	62.5 K	0.400	400
3	27.78 K	0.900	900
4	15.63 K	1.600	1600
5	10 K	2.500	2500
6	6.94 K	3.600	3600
7	5.10 K	4.900	4900

Stage	Digital Access Number
1	16
2	32
3	64
4	128
5	256
6	512
7	1024

Edge Connector



variety of recording devices, such as a strip-chart or an X-Y recorder. Two X-axis outputs and three Y-axis outputs were provided with simple toggle switch controls (see Fig. V-10). The same outputs are used for digital plotting on an X-Y recorder as described previously.

D. Electrodes

RDE and RRDE (Pine Instrument Co., Grove City, PA) were used for all batch experiments. The specific types and sizes of electrodes are described in the experimental sections of the following chapters.

Three flow-through detectors were used for all FIA experiments. For CPPP, a perpendicular flow-cell detector was used (Fig. V-20) mounted on the end of a DME glass capillary. For these experiments, the SCE reference and Pt counter electrodes were placed in the vicinity of the indicating electrode, and all electrodes were placed within a glass receptacle.

For all other FIA work, two types of electrochemical cells were used. Initially, a thin-layer cell (Dionex Corporation, Sunnyvale, CA) was used in which were mounted the Au or Pt indicating (0.005 cm^2), glassy carbon counter, and Ag/AgCl reference electrodes (Fig. V-21). Because of leakage problems at the Nafion membrane junction of the reference electrode in this cell, latter experiments were performed with the Ag/AgCl reference electrode replaced with a SCE mounted in a Kel-F cylindrical block (see Fig. V-21). When a SCE reference electrode was used the Nafion membrane was removed to minimize the iR drop through the reference electrode channel.

The second cell used for FIA experiments was of a wall-jet design (Oxford Electrodes, United Kingdom; see Fig. V-22). The Au working electrode (0.005 cm^2) was mounted within an inert plastic block, and the whole indicating electrode assembly could be moved laterally from the entrance stream orifice. Initial usage of this cell, demonstrated that iR drops across the Ag/AgCl reference electrode were to severe and the whole assembly was replaced by an SCE reference electrode mounted in a Kel-F cylindrical block (see Fig. 22). To minimize iR drops no external membrane existed between the reference electrode and the working electrode.

F. Flow-Injection Apparatus

The flow-injection apparatus was centered around the use of a Minipuls-2 peristaltic pump (Gilson Medical Electronics, Inc., Middletown, WI) for many of the experiments; however, a system was designed using a reciprocating piston pump (LDC Milton Roy) and all stainless steel plumbing for studies which required removal of dissolved oxygen from the carrier and samples. The exact apparatus used for each experiment is described in the appropriate chapter.

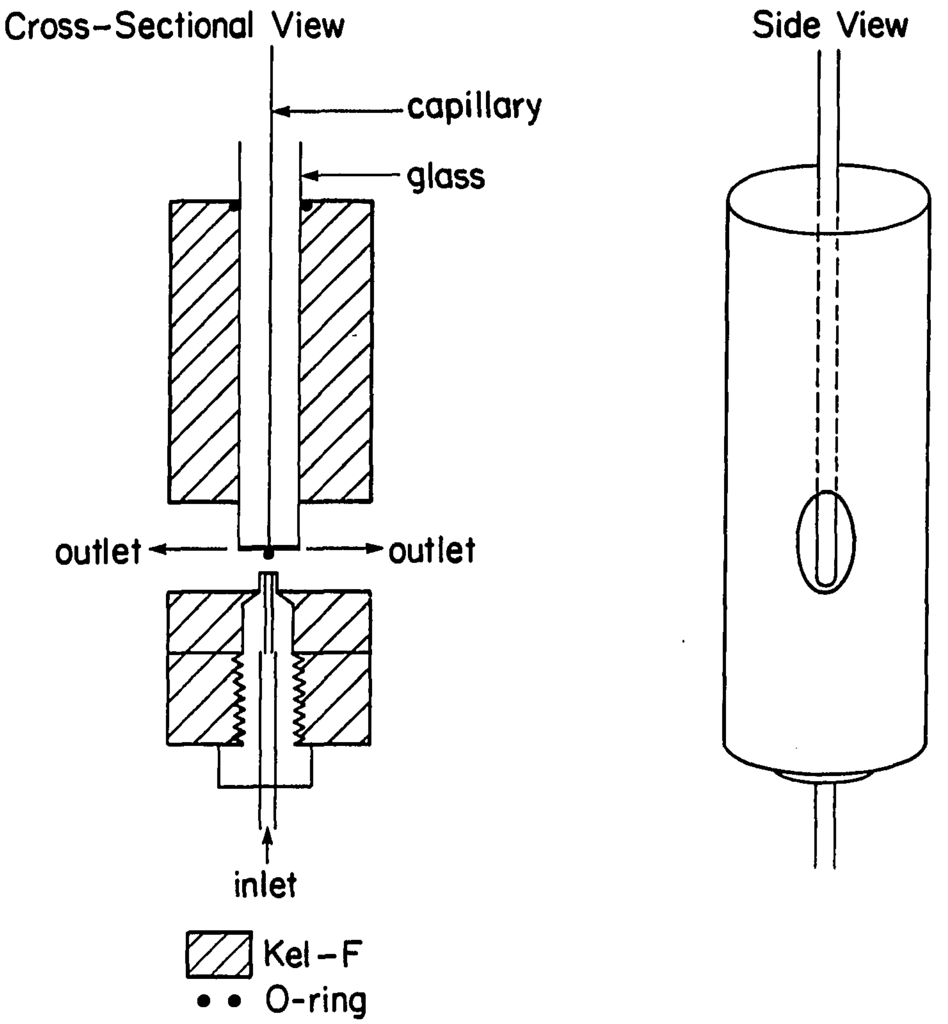


Figure V-20. Diagrams of the perpendicular flow-cell detector used for CPPP studies

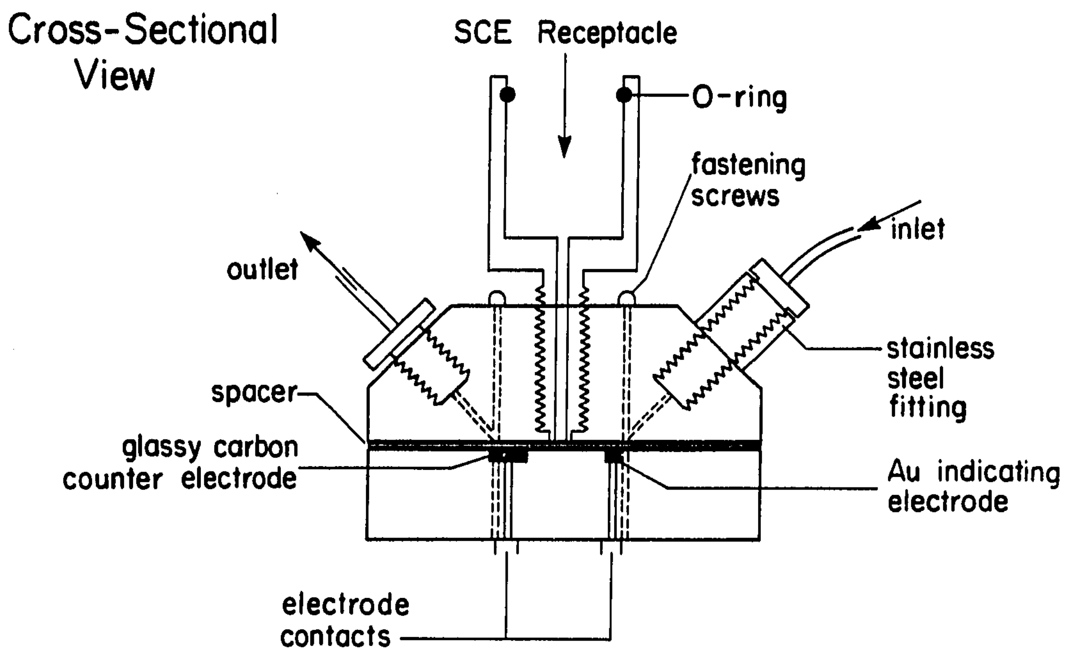


Figure V-21. Cross-sectional diagram of the Dionex thin-layer flow cell

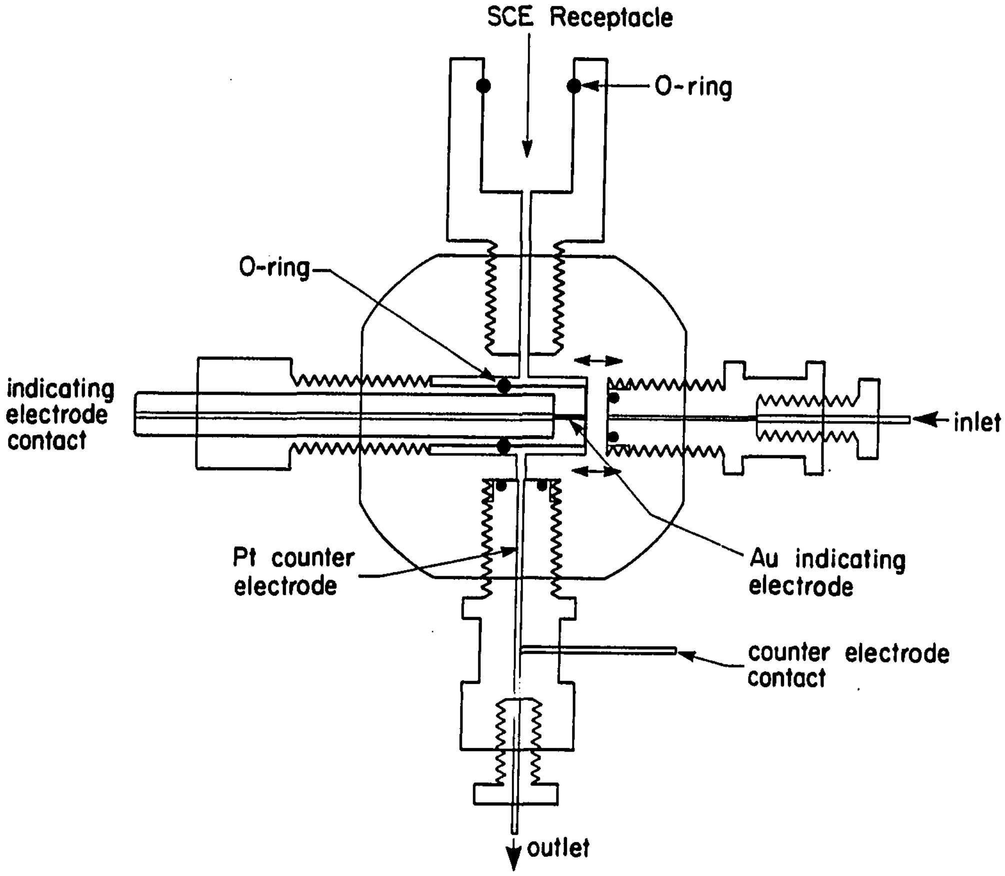


Figure V-22. Cross-sectional diagram of the Oxford Electrodes wall-jet flow cell

VI. CONSTANT POTENTIAL PULSE POLAROGRAPHIC DETECTION IN FLOW INJECTION ANALYSIS WITHOUT DEAERATION OF SOLVENT OR SAMPLE

A. Abstract

A constant potential pulse waveform is applicable for the polarographic analysis of buffered solutions (pH << 7) of cathodically active metal ions without voltammetric interference from dissolved oxygen. The technique is demonstrated at a dropping mercury electrode for detection of lead(II) and cadmium(II) in a conventional cell (ca. 75 mL) as well as for small samples (2 mL) in a flow-injection system. The flow-injection polarographic technique is recommended for higher sample throughput than conventional polarography and is demonstrated for an electroless copper plating solution containing about 1.5 X 10^{-2} M copper(II).

B. Introduction

The necessity of thorough deaeration of solutions prior to polarographic analysis to eliminate faradaic interference from reduction of dissolved oxygen is well known.[1,2] Oxygen is reduced to H_2O_2 (n=2) with $E_{1/2}$ = ca. 0.0 V vs. SCE and H_2O_2 is reduced to H_2O (n=4 for $O_2 \rightarrow H_2O$) with $E_{1/2}$ = ca. -1.2 V. This electroactivity of oxygen over ca. 80% of the accessible potential range at mercury electrodes has been a major deterrent to their application for cathodic detections in flow-injection (FI) and liquid chromatographic (LC) systems.[3,4] Various approaches have been described for elimination of dissolved oxygen in flow systems[3,5] including placement of the entire apparatus in a drybox purged with inert gas.[6] Here, the use of constant potential pulse (CPP) polarography is demonstrated for eliminating interference from dissolved oxygen in polarographic determinations of reducible metal ions. The significance of the CPP waveform (E-t) is made apparent by comparison to the more familiar normal pulse (NP) and reverse pulse (RP) polarographic methods.

NP polarography is well known for increased sensitivity ($\mu A\ M^{-1}$) in comparison to linear-sweep (DC) polarography. The NP waveform, as depicted in Fig. VI-1A for a reducible analyte, utilizes a value of initial potential more positive than the half-wave potential of the analyte ($E_i >> E_{1/2}$) with a negative scan of ΔE. The ratio of the limiting currents for NP and DC polarography at a dropping mercury electrode (DME) is given by

$$\frac{i_{NP}}{i_{DC}} = \left[\frac{3\tau}{7t_p}\right]^{1/2} \qquad [1]$$

where τ is the drop lifetime, t_p is the pulse period and $\tau = t_i + t_p$.[7] The value of i_{DC} is given by

$$i_{DC} = nFAC^b \left[\frac{7D}{3\pi\tau}\right]^{1/2} \qquad [2]$$

where n, F, A and C^b have their usual electrochemical significance.

Oldham and Parry[8] described scan-reversal polarography in which the NPP waveform is applied but with polarities reversed, i.e., $E_i << E_{1/2}$ and ΔE is scanned in a positive direction. Osteryoung and Kirowa-Eisner[9] reviewed the theory and assigned the preferred name of reverse pulse polarography (RPP). In RPP, applied for a reducible analyte, the product of the cathodic reaction at E_i can be detected anodically for $E_d >> E_{1/2}$, where $E_d = E_i + \Delta E$, and the i-E response curve contains both the cathodic and anodic components characteristic of the redox couple. Oldham and Parry[8] recommended this technique for study of electrochemical reversibility and this application has been pursued by others.[10,11]

In RPP at a DME, the limiting cathodic current detected at $E_d << E_{1/2}$ is equal to i_{DC} (Eqn. 2). The limiting anodic current (i_{RP}) for $E_d >> E_{1/2}$ is related to i_{DC} by

$$-\frac{i_{RP}}{i_{DC}} = \frac{n_{red}}{n_{ox}} \left[\frac{3\tau}{7t_p}\right]^{1/2} - \left[\frac{3\tau}{3\tau + 4t_p}\right]^{1/2} \qquad [3]$$

where n_{red} and n_{ox} are the numbers of electrons for the reductive and oxidative processes, respectively.[8,9] For $t_p << \tau$, Eqn. 3 simplifies to

$$-\frac{i_{RP}}{i_{DC}} = \frac{n_{red}}{n_{ox}} \left[\frac{3\tau}{7t_p}\right]^{1/2} - 1 \qquad [4]$$

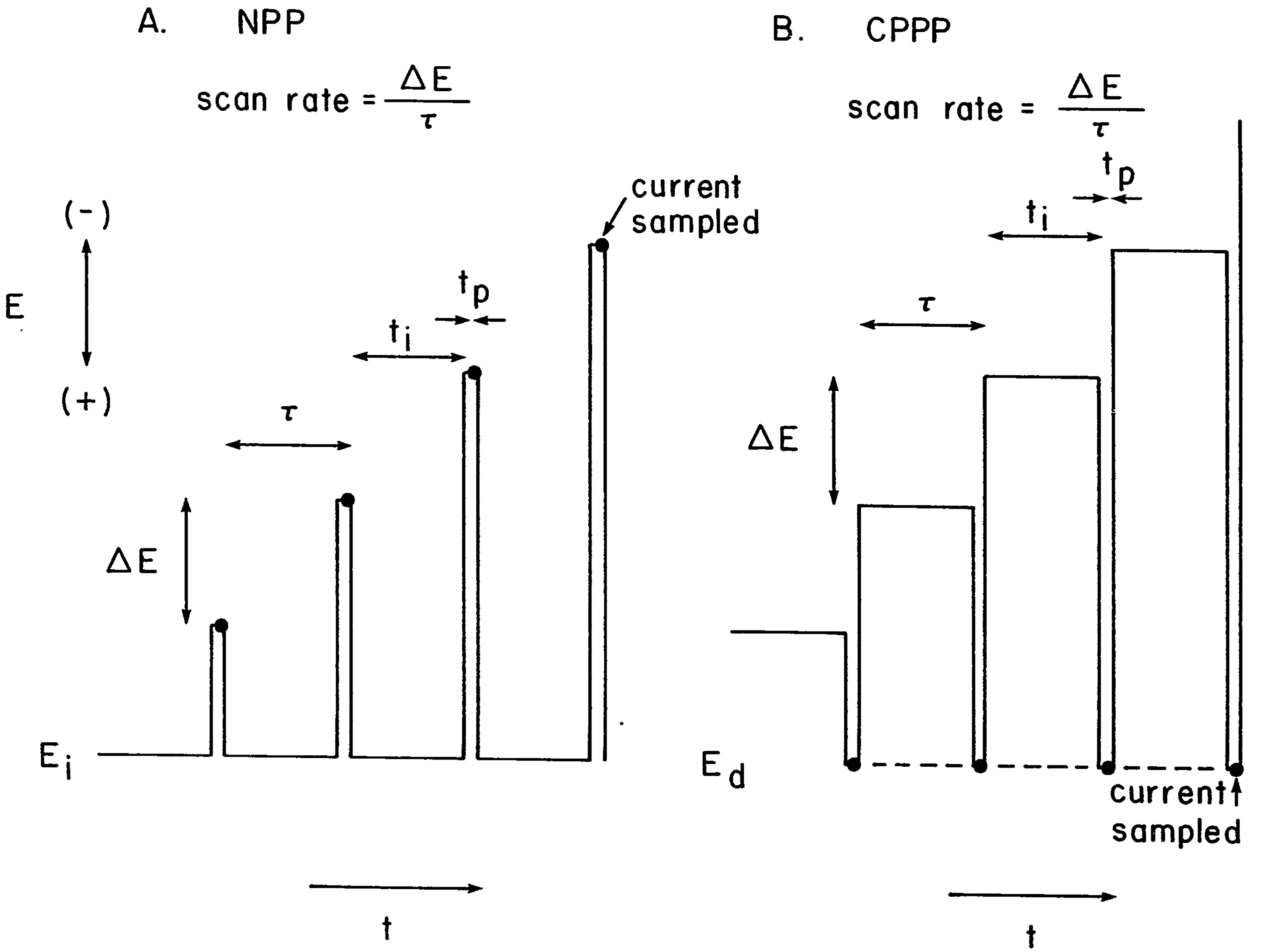
and in the limit for $\tau/t_p \rightarrow \infty$, Eqn. 4 becomes identical to Eqn. 1 for $n_{red} = n_{ox}$. If the product of the reaction at E_i undergoes an irreversible homogeneous conversion to an electro-inactive product, i_{RP} is less than predicted by Eqn. 3[9] and the deviation can be applied for kinetic studies of following chemical reactions coupled to the electron-transfer processes.[12]

Maitoza and Johnson[13] recognized that when RPP is used, dissolved oxygen is not detected for E_d >> ca. 0.0 V vs. SCE, because of the irreversibility of oxygen at mercury. They demonstrated the amperometric form of RPP (i.e., constant ΔE) can be used for detection of reducible metal ions without interference from oxygen in flow-injection and liquid chromatographic analyses using a flow-through detector based on a DME. Hsi and Johnson[14] recently applied this technique for the ion chromatographic determination of Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} and Fe^{2+} using a low capacity cation-exchange column with a tartrate buffer (pH 3.5-4.5) containing Mg^{2+} as the mobile phase. Representative detection limits for 100 μL samples were 1.3 ng Zn^{+2} and 6.4 ng Cu^{+2}. The detection limits were lowered 100-fold using a 10-mL sample with on-line preconcentration on a high-capacity precolumn.

Christie et al.[15] introduced constant potential pulse polarography (CPPP) (see waveform B in Fig. VI-1). Their study emphasized the comparison of faradaic and capacitive responses of CPPP with NPP and differential pulse polarography

Figure VI-1. Pulse waveforms for reducible analyte

A. Normal pulse polarography (NPP).
B. Constant potential pulse polarography (CPPP).


A. NPP
scan rate = ΔE / τ
(-)
E
(+)
ΔE
τ
t_i
t_p
current sampled
E_i
t
B. CPPP
scan rate = ΔE / τ
t_p
t_i
τ
ΔE
E_d
current sampled
t

(DPP). In CPPP, E_i is scanned with current sampling at a constant detection potential, E_d, and the current measured at E_d is plotted vs. E_i. The i-E response curve obtained for a reducible analyte with $E_d << E_{1/2}$, in the absence of dissolved oxygen, will show only an anodic wave with a limiting current (i_{CPP}) equal to i_{RP} (see Eqns. 1-3). Hara and Nomura[16,17] applied CPPP for the determination of Ba(II) and alkali metal cations in solutions of low pH. The reduction waves for these species are hidden by the large current for reduction of H^+ at the mercury electrode. The applicability of RPP for the study of waves unresolved from solvent breakdown had been recognized earlier by J. Osteryoung and Kirowa-Eisner.[9]

Hara and Nomura noted for CPPP[16,17] in agreement with Maitoza and Johnson[13] for RPP, that dissolved oxygen is not detected for $E_d >>$ ca. 0.0 V. It should be noted that the waveforms for the amperometric versions of RPP and CPPP are identical (ΔE is constant). Here CPPP is applied in the analysis of solutions of reducible metal ions in conventional polarographic cells and in a flow-injection system without interference from dissolved oxygen. The use of FI/CPPP without deaeration is recommended to increase significantly the sample throughput of polarographic analysis.

C. Experimental

1. Instrumentation

A Model 264A Polarographic Analyzer (EG&G Princeton Applied Research Corporation, Princeton, NJ) was used. The analyzer was modified by EG&G PARC to conform to the technique of CPPP. A mechanical drop-timer assembly (Model 174/70, EG&G PARC) was used with the DME and a lifetime of 1.0 s was chosen for all work. A natural lifetime of ca. 10 s was selected to minimize noise due to mechanical vibrations of the drop. Polarograms were recorded on an X-Y recorder (Model RE0074, EG&G PARC) or a strip chart recorder (Model 250-1B, Curken Instrument Co., Hawleyville, CT). All potentials are reported versus the SCE.

The flow-injection system consisted of a Gilson Minipuls-2 peristaltic pump (Gilson Medical Electronics, Inc., Middletown, WI) in line with two inverted T-shaped pulse dampeners, a 10-foot coil of 0.5-mm i.d. Teflon tubing, a manual injection valve (Model CV-6-uHPa-N60, Valco Instrument Co., Houston, TX), and finally a perpendicular flow-cell detector mounted on the end of the DME capillary in the style of the PARC Model 310 LC detector. The 2 mL sample loop was constructed from 1.0-mm Teflon tubing and had a volume of 2.0 mL. The retention volume of the system from injector to detector was ca. 0.25 mL.

2. Reagents

All solutions were prepared from analytical reagent grade chemicals (Fisher Scientific certified A.C.S. grade) and triply distilled water. Mercury was triply distilled. When applicable, solutions were deaerated by purging with reagent grade argon (99.99%) for ten minutes. The supporting electrolyte was 0.1$\underline{M}$ KNO_3/0.01$\underline{M}$ HNO_3 in all cases.

D. Results and Discussion

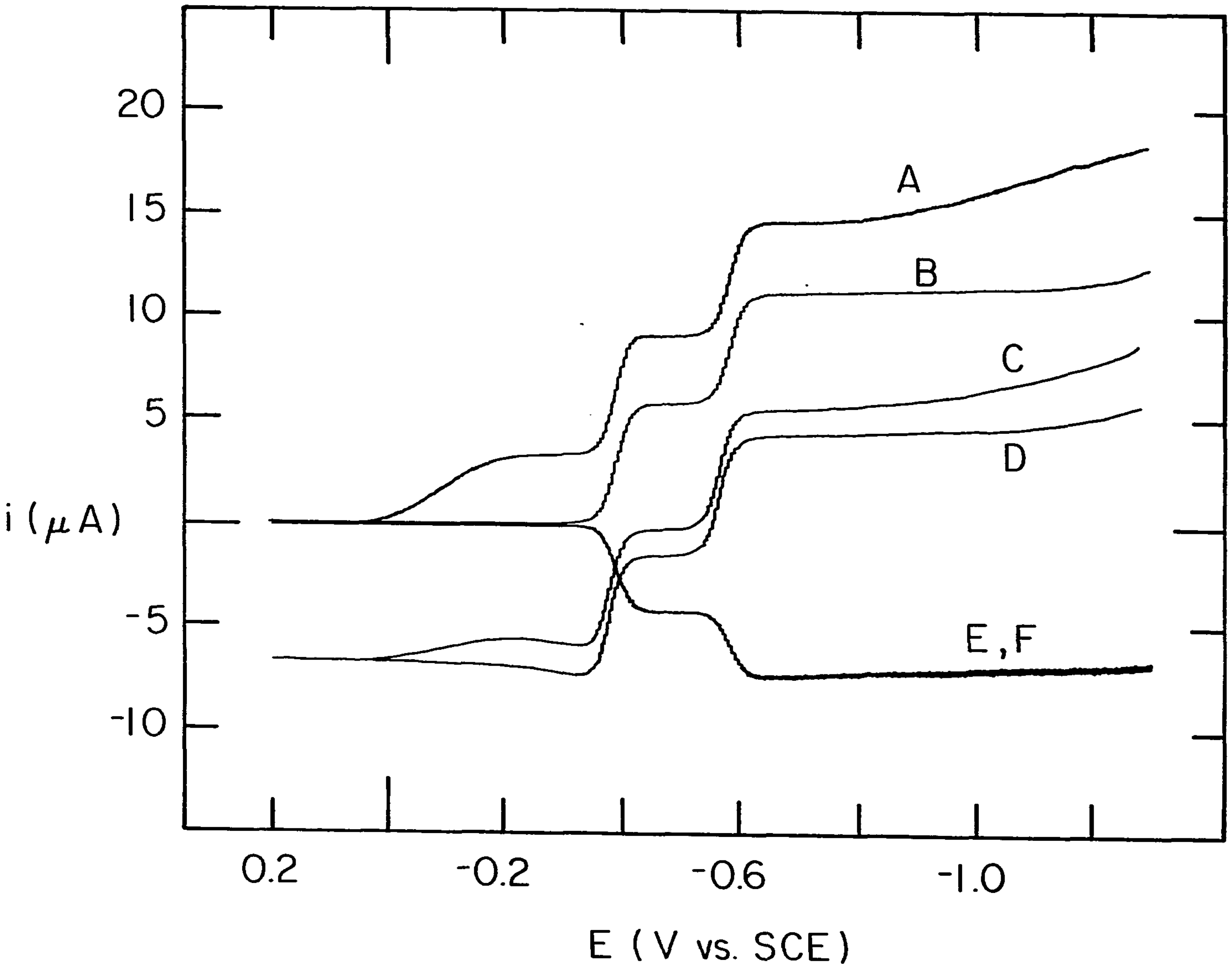
1. Comparison of polarographic methods

Current-potential (i-E) curves obtained by RPP, NPP and CPPP are compared in Fig. VI-2 for 0.5m$\underline{M}$ Pb(II) and Cd(II) in 0.1$\underline{M}$ KNO_3/0.01$\underline{M}$ HNO_3 with and without oxygen present. The reductions of Pb(II) and Cd(II) to their corresponding metal amalgams are reversible with $E_{½}$ values of ca. -0.4 V and -0.6 V, respectively. As observed by Maitoza and Johnson[13], the total anodic current in RPP for $E_d >> 0.0$ V is not affected by the presence of dissolved oxygen and RP amperometry is useful without deaeration; RPP (with the sweep of E_d) is not particularly useful in the presence of oxygen. Only for CPPP, with constant $E_d >> 0.0$ V, is the i-E response identical over the entire potential range whether or not oxygen is present. The ratio of the total anodic current for CPPP to the cathodic current for NPP (with oxygen absent) at -0.7 V is 0.67. This compares favorably with the predicted ratio of 0.65 for t_p = 50 ms and τ = 1 s, on the basis of Eqns. 1-3 using the

Figure VI-2. Current-potential curves for 0.5m$\underline{M}$ Pb(II) + 0.5 m$\underline{M}$ Cd(II) in 0.1 $\underline{M}$ KNO_3/0.01 $\underline{M}$ HNO_3

Conditions: ΔE = 5 mV, τ = 1.0 s.

Curves:
[A] NPP, air sat'd, E_i = 0.2 V;
[B] NPP, Ar sat'd, E_i = 0.2 V;
[C] RPP, air sat'd, E_i = -1.3 V;
[D] RPP, Ar sat'd, E_i = -1.3 V;
[E] CPPP, air sat'd, E_d = 0.2 V;
[F] CPPP, Ar sat'd, E_d = 0.2 V.


20
15
10
5
i (μA)
-5
-10
0.2
-0.2
-0.6
-1.0
E (V vs. SCE)
A
B
C
D
E, F

equality $i_{CPP} = i_{RP}$.

The major advantage of all pulse polarographic techniques is the increased signal-to-noise ratio, hence, better detectability is obtained in comparison to that for DC polarography. Because i_{CPP} is nearly 70% the value of i_{NP}, for this case (τ and t_p values), low detection limits are also expected for CPPP in addition to the advantage gained by elimination of oxygen interference. Polarographic curves are shown in Fig. VI-3 for Pb(II) and Cd(II) in the range 5-20 μ<u>M</u> with and without deaeration. The thickness of the pen tracing results from instrumental noise originating within the potentiostat, apparently associated with switching in the sample-hold circuit.

Interference from dissolved oxygen is observed in CPPP in unbuffered solutions, as illustrated in Fig. VI-4 for 0.1<u>M</u> KNO_3. This is caused by the increase in pH at the electrode surface resulting from reduction of O_2 (Eqns. 5 and 6) with subsequent anodic detection of OH^- (Eqn. 7).

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^- \quad (0.0\ V > E_i > -1.2\ V) \quad [5]$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad (-1.2\ V > E_i) \quad [6]$$

$$2OH^- + Hg \rightarrow Hg(OH)_2 + 2e \quad (E_d > -0.1\ V) \quad [7]$$

The detection of OH^- produced by the cathodic reaction at E_i is observed also in RPP and was applied by Brestovisky et al.[18] in a study of the reduction of H_2O_2. Because of the

Figure VI-3. Current-potential curves by CPPP for Pb(II) and Cd(II) in 0.1 M KNO_3/0.01 M HNO_3

Conditions: $\Delta E = 5$ mV, $\tau = 1.0$ s.

Concentrations:
[A] Blank;
[B] 5.0)M Pb(II), 5.0 µM Cd(II);
[C] 10.0 µM Pb(II), 10.0 µM Cd(II);
[D] 15.0 µM Pb(II), 15.0 µM Cd(II);
[E] 20.0 µM Pb(II), 20.0 µM Cd(II).

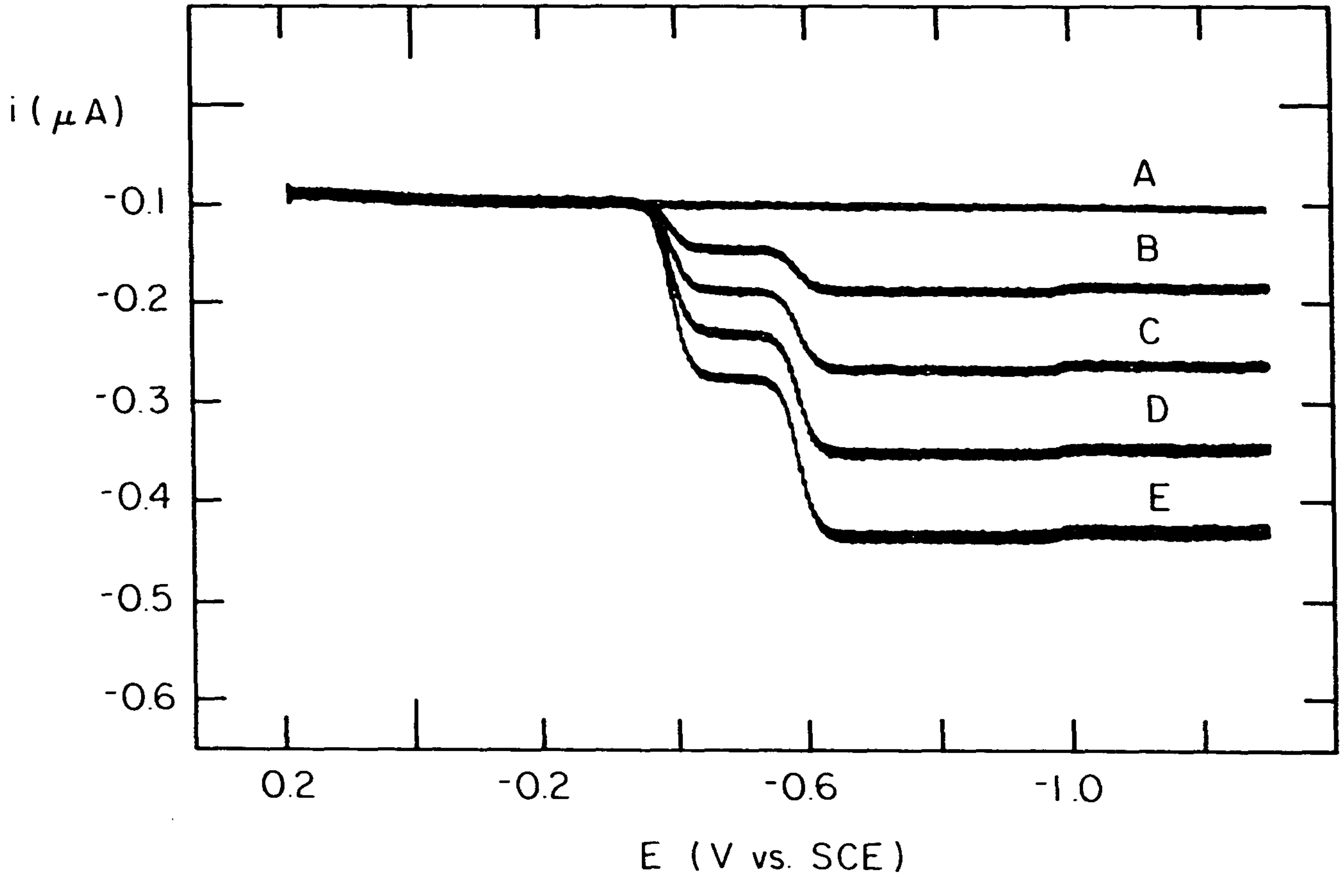
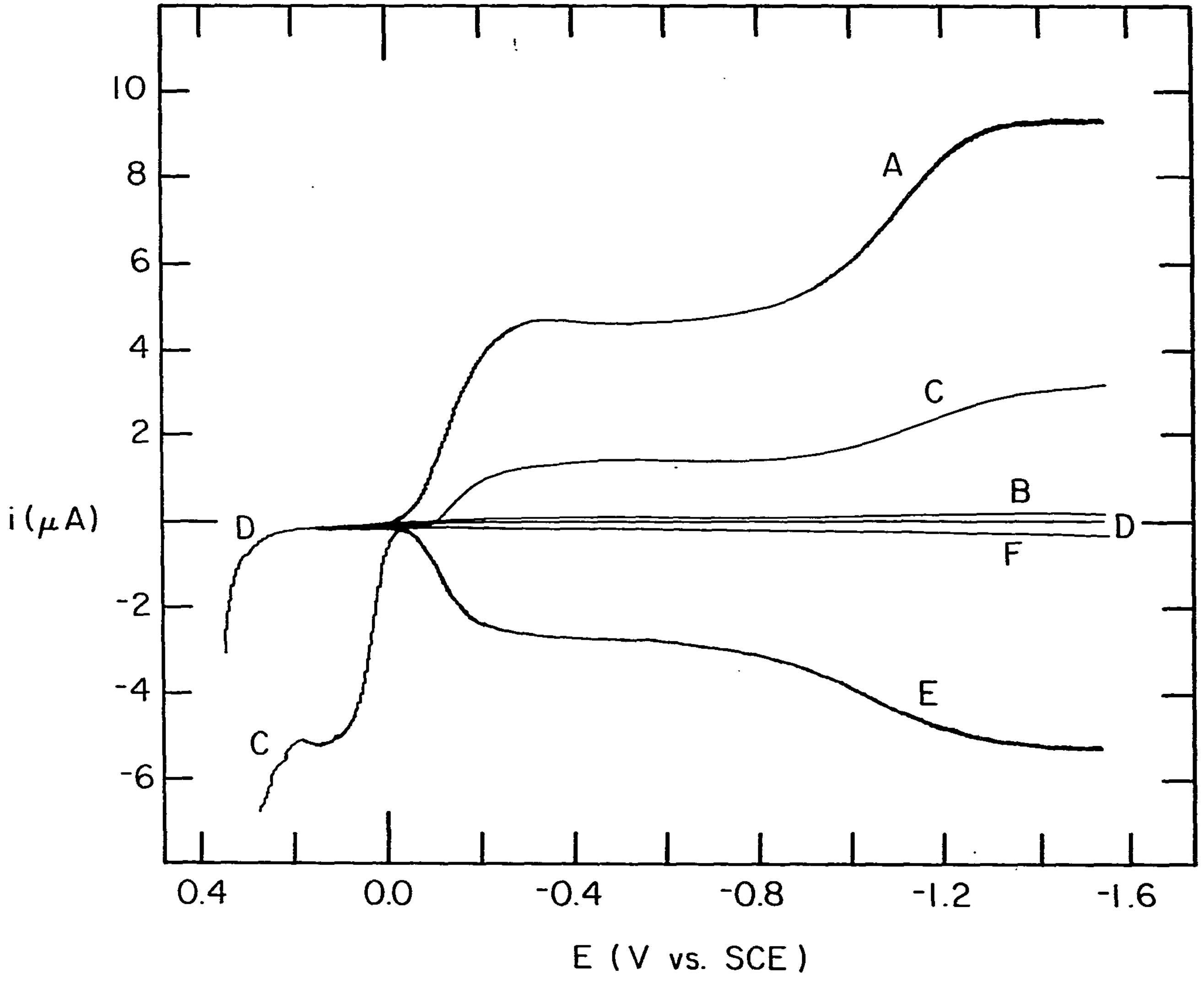

i (μA)
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
0.2
-0.2
-0.6
-1.0
E (V vs. SCE)
A
B
C
D
E

Figure VI-4. Current-potential curves for unbuffered 0.1 M KNO_3

Conditions: ΔE = 5 mV, τ = 1.0 s,
natural pH = 4.8.

Curves:
[A] NPP, air sat'd, E_i = 0.2V;
[B] NPP, Ar sat'd, E_i = 0.2 V;
[C] RPP, air sat'd, E_i = -1.5 V;
[D] RPP, Ar sat'd, E_i = -1.5 V;
[E] CPPP, air sat'd, E_d = 0.2 V;
[F] CPPP, Ar sat'd, E_d = 0.2 V.


i (μA)
10
8
6
4
2
-2
-4
-6
0.4
0.0
-0.4
-0.8
-1.2
-1.6
E (V vs. SCE)
A
C
B
D
D
F
E
C

response to OH^-, CPPP cannot be applied in alkaline solutions for $E_d > -0.1$ V. When $E_d < -0.1$ V, removal of dissolved oxygen is required.

Interesting results are obtained when the CPPP waveform depicted in Fig. VI-1B is applied for analytes which yield anodic waves by stabilizing the product of Hg oxidation (e.g., halides and chelate-forming anions). This application of the waveform should be known as reverse CPPP and is related to CPPP in the same manner as RPP is related to NPP. Polarographic curves are shown for I^- by reverse CPPP in Fig. VI-5 (curves A-E). The electrode reaction for E >> ca. -0.1 V is

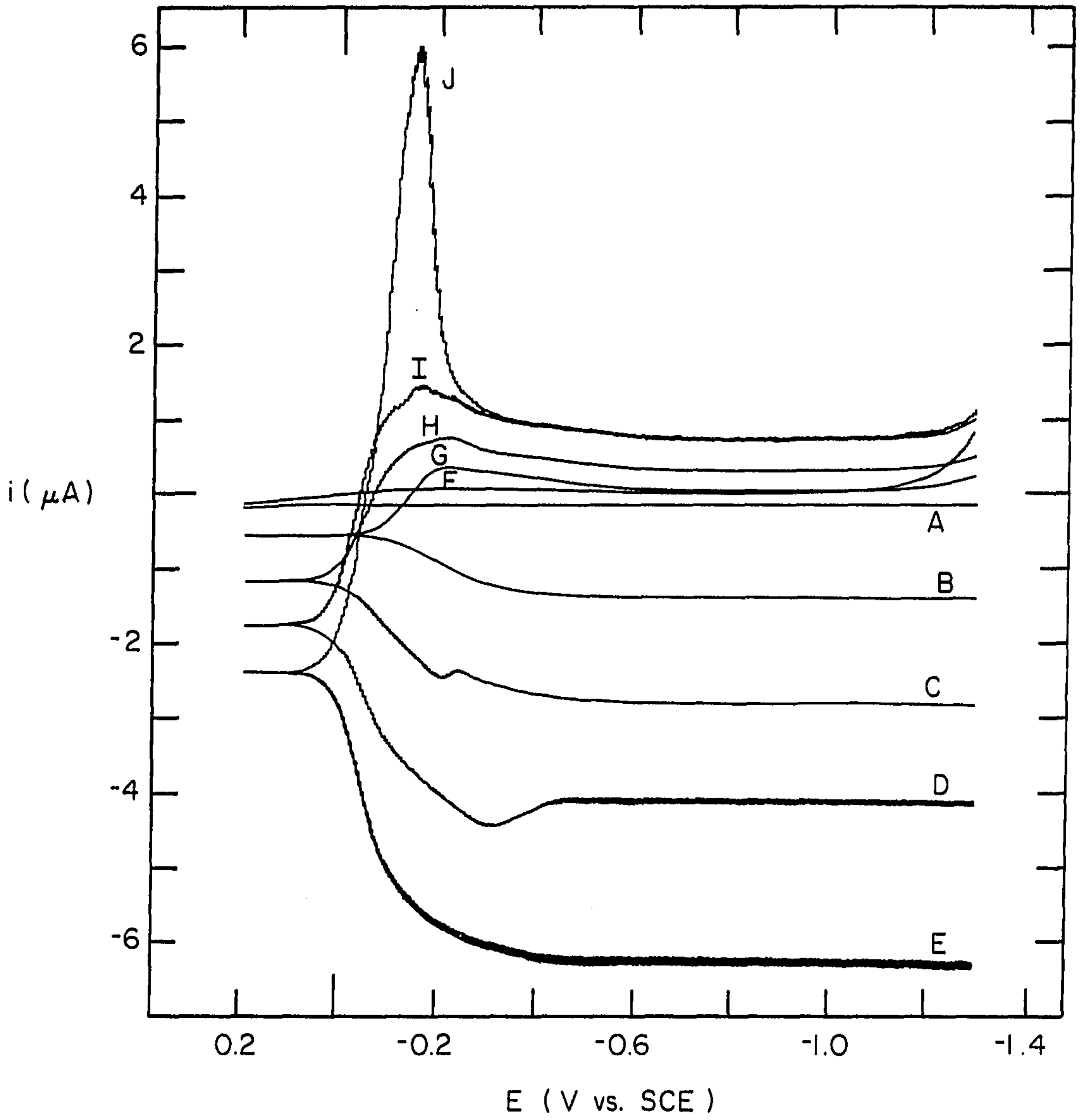
$$2I^- + Hg \rightarrow Hg_2I_2(s) + 2e \qquad [8]$$

For $E_i >>$ ca. -0.1 V, the anodic current corresponds to i_{DC} for I^-. When $E_i <<$ ca. -0.1 V, the anodic current equals that of i_{NP} for I^-. The i-E response of reverse CPPP is more complicated that for NPP because of the two-step wave, although the advantage is retained regarding tolerance of dissolved oxygen. The slight incongruities in the otherwise smooth i-E curves for reverse CPPP are attributed to the diffusion barrier offered by the surface film of insoluble Hg_2I_2. Shown for comparison in Fig. VI-5 (curves F-J) are polarographic curves for I^- obtained by RPP (E_i = 0.2 V) taken in the absence of dissolved oxygen.

Figure VI-5. Current-potential curves for I^- in 0.1 M KNO_3/0.01 M HNO_3

Conditions: ΔE = 5 mV, τ = 1.0 s.
CPPP (A-E), E_d = 0.2 V;
RPP (F-J), E_i = 0.2 V.

Concentrations I^- (mM):
(A,F) blank;
(B,G) 0.20;
(C,H) 0.40;
(D,I) 0.60;
(E,J) 0.80.


6
4
2
-2
-4
-6
i (μA)
0.2
-0.2
-0.6
-1.0
-1.4
E (V vs. SCE)
J
I
H
G
F
A
B
C
D
E

2. Application in flow-injection systems

Elimination of the necessity for oxygen removal in CPPP renders this technique suitable for polarographic analysis in automated flow-injection systems. Accordingly, In FI/CPPP, sample volumes (V_s) of ca. 1-2 mL are injected into a flow system having a low retention volume (V_r) between the injection valve and detector. When $V_s >> V_r$, the system is characterized as having a very low dispersion and a significant time period exists during which the concentration profile (C-t) at the detector is in a steady-state condition ($dC/dt = 0$) with a plateau concentration equal to the analytical concentration of the sample injected. The i-t response is shown in Fig. VI-6 for injection of 2.0 mL of 2.0 m$\underline{M}$ Cd(II) and Pb(II) into the FI system with V_r = ca. 0.25 mL and v_f = 0.50 mL min^{-1}. For ΔE = 10 mV and τ = 1.0 s, completion of a 1.2-V potential sweep was achieved in 2 min. For this system, an injection interval of ca. 6 min allowed for complete washout of the system between samples and the sample throughput of the system was ca. 10 per hour. This throughput could be easily doubled or tripled using smaller V_s and V_r with faster scan rates and shorter τ. Application of FI/CPPP for analysis of the solution of Cd(II) and Pb(II) is shown in Fig. VI-7A. Application for an electroless copper plating bath is shown in Fig. VI-7B; the equation of the line obtained for the standard additions plot was $-i = 1.40 + 1.04 \times 10^4$ Cu(II) and the concentration of copper(II) in the original plating bath

Figure VI-6. Current-time profile for pulse amperometric detection in the flow-injection system

Carrier solution: air sat'd 0.1 $\underline{M}$ KNO_3/0.01 $\underline{M}$ HNO_3. ν_f = 0.50 mL min^{-1}.

Sample: 2.0 m$\underline{M}$ Pb(II) + 2.0 m$\underline{M}$ Cd(II) in 0.1 $\underline{M}$ KNO_3/0.01 $\underline{M}$ HNO_3;

V_s = 2.0 mL.

Detection: E_i = -1.0 V, E_d = 0.2 V, τ = 1.0 s.

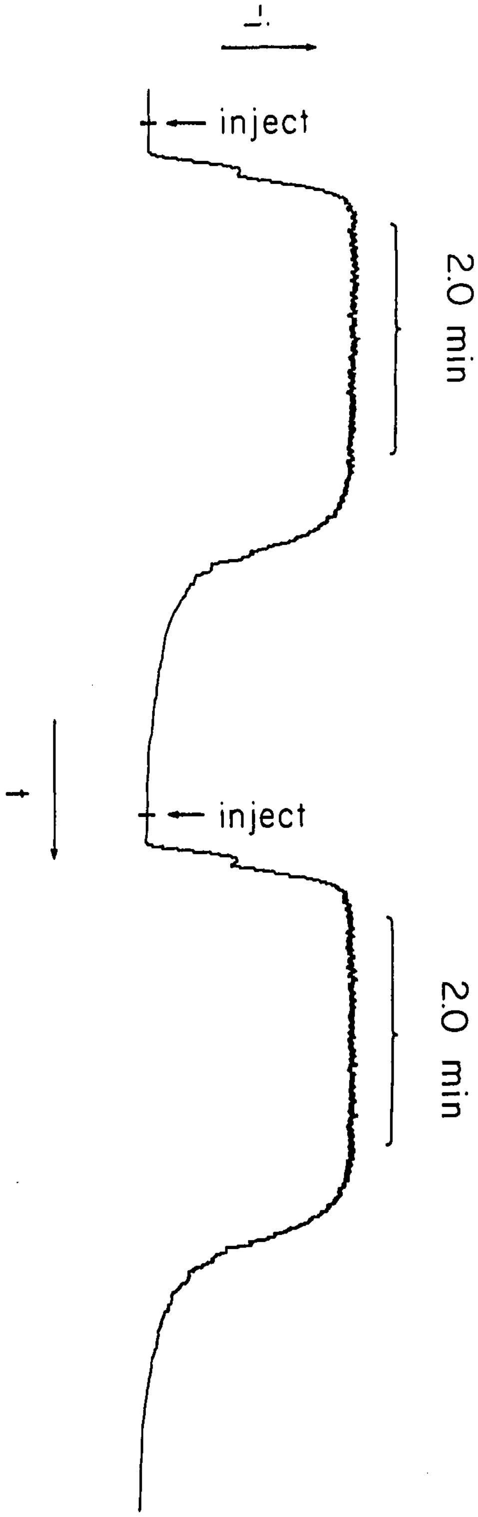

inject
2.0 min
inject
2.0 min

Figure VI-7. Flow-injection polarographic analyses

Detection: CPPP, $E_d = 0.2$ V, $\Delta E = 10$ mV, $\tau = 1.0$ s.

FI system: $V_s = 2.0$ mL, $\nu_f = 0.50$ mL min^{-1}.

A. Pb(II) + Cd(II) in 0.1 M KNO_3/0.01 M HNO_3.

Concentrations (mM each):
[A] blank;
[B] 0.20;
[C] 0.40;
[D] 0.60.

B. 100X dilution of Cu plating bath in 0.035 F HOAc/0.23 F HCOOH/0.1 M KNO_3.

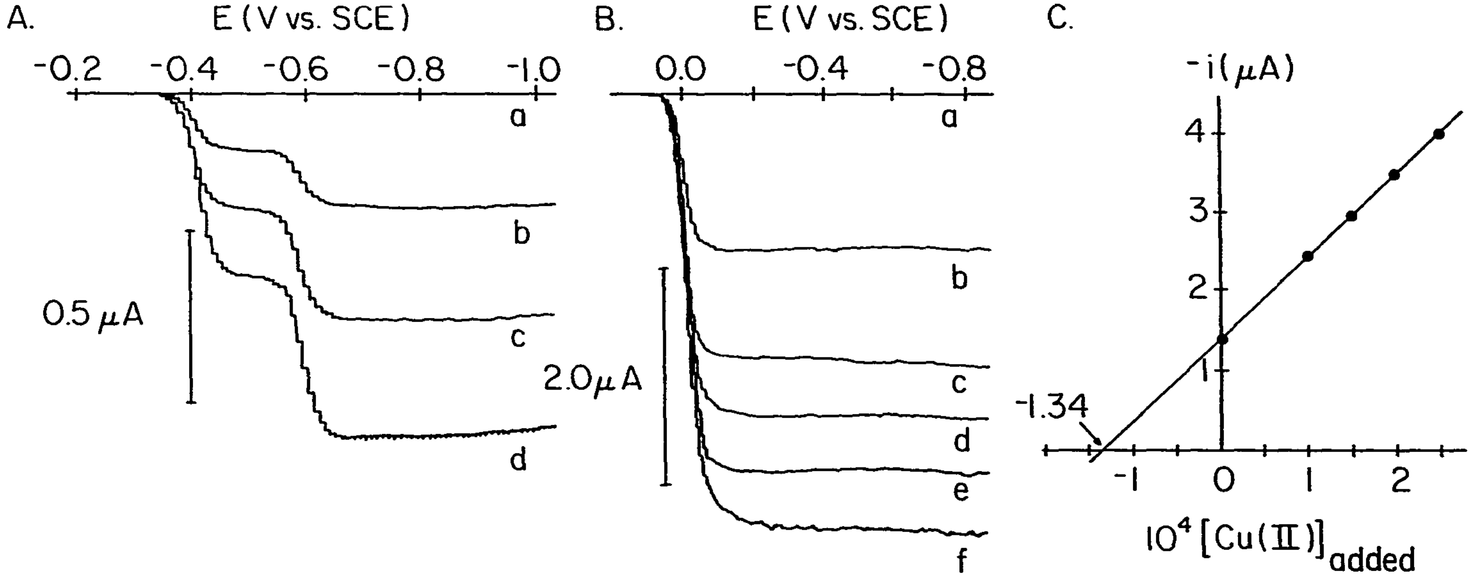
Curves:
[A] blank;
[B] plating bath;
[C-F] standard additions of Cu(II) to diluted plating bath.

Concentration Cu(II) added (mM):
[C] 0.05;
[D] 0.10;
[E] 0.15;
[F] 0.20.

C. Standard additions plot for data in B.

Equation of line: $-i = 1.40 + 1.04 \times 10^4 C^b$

Result: concentration of Cu(II) in original plating bath calculated to be 1.34×10^{-2} M.


A.
E (V vs. SCE)
-0.2
-0.4
-0.6
-0.8
-1.0
a
b
c
d
0.5 μA
B.
E (V vs. SCE)
0.0
-0.4
-0.8
a
b
c
d
e
f
2.0μA
C.
-i(μA)
4
3
2
1
-1.34
-1
0
1
2
10^4 [Cu(II)]added

was calculated as 1.34 X 10^{-2} M. In both cases, no attempt was made to remove dissolved oxygen in samples or the carrier solution.

E. Summary

We have demonstrated that CPPP is suitable for analysis of metal solutions buffered at moderate to low pH in conventional polarographic cells and in flow systems with no adverse effects due to dissolved oxygen. The application to flow injection analysis offers exciting possibilities for automated polarographic analysis with reasonably high sample throughput.

Future developments related to CPPP will include alternate-drop differential CPPP for higher resolving power in complex mixtures similar to DPP. Development is expected also of rapid-scan CPPP and differential CPPP at a single mercury-drop electrode.

F. Acknowledgements

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VII. COMPARISON OF THE PULSED AMPEROMETRIC DETECTION OF CARBOHYDRATES AT GOLD AND PLATINUM ELECTRODES FOR FLOW INJECTION AND LIQUID CHROMATOGRAPHIC SYSTEMS

A. Abstract

Detection limits for PAD at Au electrodes for several carbohydrates in alkaline solutions are ca. 5X lower than for Pt electrodes. Interference from dissolved oxygen is also less at Au than Pt electrodes.

B. Results and Discussion

Since 1981 our laboratory has been successfully developing pulsed amperometric detection (PAD) at Pt electrodes for compounds considered to be electroinactive under conditions of dc detection. The intended application of the PAD technique is for detection in high performance liquid chromatography (LC-PAD). However, application to one-component samples in flow-injection systems (FI-PAD) is immediately obvious and is, in fact, used to test the reliability of the detector technology. We have focused our attention on classes of organic compounds without extensive π-bonding for which UV-visible photometric detection in LC and FI systems does not offer sufficient sensitivity. Applications of LC-PAD with Pt electrodes in our laboratory have included amino acids[1], aminoglycosides[2], carbohydrates[3-5], and recently, sulfur containing compounds.[6,7] The highest sensitivity for carbohydrate PAD is observed in alkaline media and robust chromatographic columns are preferred which utilize the alkaline supporting electrolyte as the mobile chromatographic phase. Instrumentation for LC-PAD is now commercially available based on separator columns designed for inorganic ion chromatography.[8,9] In the commercialized version, a Au detector has been recommended over a Pt detector.[10,11] General comparisons of electrode materials for amperometric detection in LC have appeared;[12] however, no specific comparison has emerged related to the use of PAD for carbohydrates at Au and Pt electrodes. Here we describe briefly some results for glucose and fructose, taken to be representative of simple carbohydrates, and conclude that PAD at Au electrodes has the advantages of high sensitivity and lower detection limits in comparison to Pt electrodes.

The triple-step potential waveform described previously for detection of carbohydrates at Pt electrodes[3] is based on a detection potential corresponding to the surface-controlled anodic oxidation of adsorbed carbohydrate in a potential region where dissolved O_2 can be cathodically reduced (e.g., -0.2 to -0.8V vs. SCE in 0.2M NaOH, see Fig. VII-1). This can lead to serious analytical interferences in FI-PAD if the presence of O_2 results in larger baseline signals with an expected decrease in the signal-to-noise ratio (S/N). Deaeration of the mobile phase in LC-PAD improves the situa-

Figure VII-1. Pulsed voltammograms for glucose obtained at a Pt rotated disk electrode (0.16 cm^2; 900 rev min^{-1}) using a three-step potential waveform

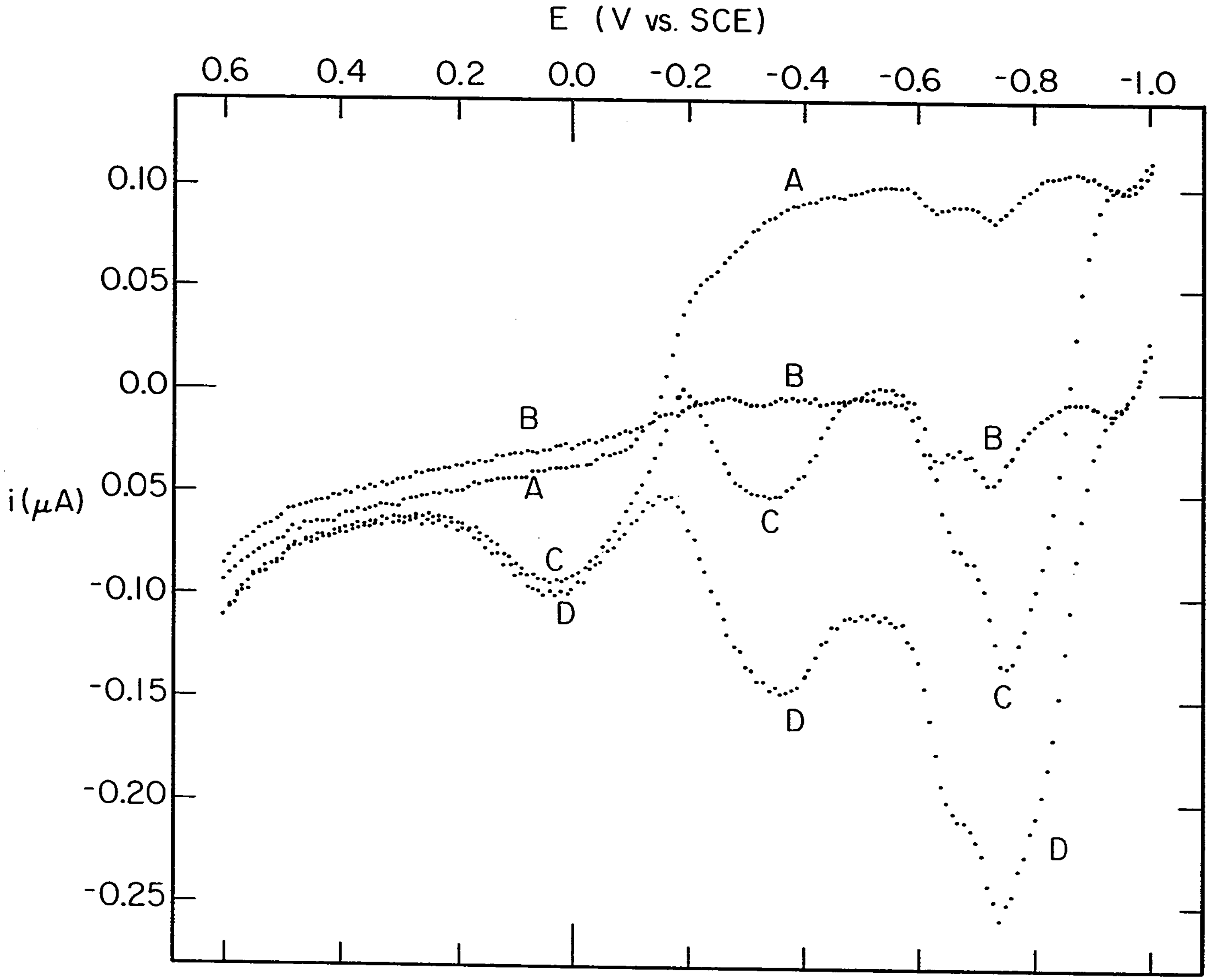
Waveform:
E_1 = varied (200 ms);
E_2 = 0.60 V (200 ms);
E_3 = −1.0 V (600 ms).

Curves:
[A] air sat'd 0.20 $\underline{M}$ NaOH;

[B] N_2 sat'd 0.20 $\underline{M}$ NaOH;

[C] air sat'd 2.0 m$\underline{M}$ glucose and 0.20 $\underline{M}$ NaOH;

[D] N_2 sat'd 2.0 m$\underline{M}$ glucose and 0.20 $\underline{M}$ NaOH.


E (V vs. SCE)
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
i (μA)
0.10
0.05
0.0
0.05
-0.10
-0.15
-0.20
-0.25
A
B
B
A
C
D
C
D
B
C
D

tion; however, since the chromatographic systems commonly used in ion chromatography are constructed with O_2-permeable plastic tubing, complete elimination of dissolved oxygen from the effluent stream is not practical. Detection of carbohydrates at Pt electrodes can be achieved without O_2 interference using a detection potential in the waveform which is more positive than recommended above (e.g., 0.00V vs. SCE in 0.20M NaOH). This corresponds to the potential region where the anodic formation of surface oxide is rapid at the Pt electrode and the resulting increase in baseline signal (and noise) more than eliminates any advantage expected from removal of O_2 interference.

Carbohydrates can be detected anodically at Au electrodes in a potential region where O_2 reduction does not occur and the formation of surface oxide is not significant (e.g., 0.00 to 0.20V vs. SCE in 0.2M NaOH, see Fig. VII-2). The resulting increase in the signal-to-noise ratio for LC-PAD at Au as compared to Pt electrodes has been verified with detection limits decreased by ca. 5X, for glucose, fructose, sorbitol, and sucrose. The linear region of the calibration curve (i-C) is also more extensive for Au as compared to Pt.

A comparison of the observed signals obtained utilizing the best waveforms for Au and Pt is shown in Fig. VII-3 for 1.0 mM fructose. In addition, the peak signals are also shown which are obtained by dc detection. The baseline currents (μA) for each set of peaks are given in parentheses. Selec-

Figure VII-2. Pulsed voltammograms for glucose obtained at a Au rotated disk electrode (0.005 cm^2; 900 rev min^{-1}) using a three-step potential waveform

Waveform: E_1 = varied (200 ms);
E_2 = 1.0 V (200 ms);
E_3 = -1.0 V (600 ms).

Curves: [A] air sat'd 0.20 M NaOH;

[B] N_2 sat'd 0.20 M NaOH;

[C] air sat'd 2.0 mM glucose and 0.20 M NaOH;

[D] N_2 sat'd 2.0 mM glucose and 0.20 M NaOH.

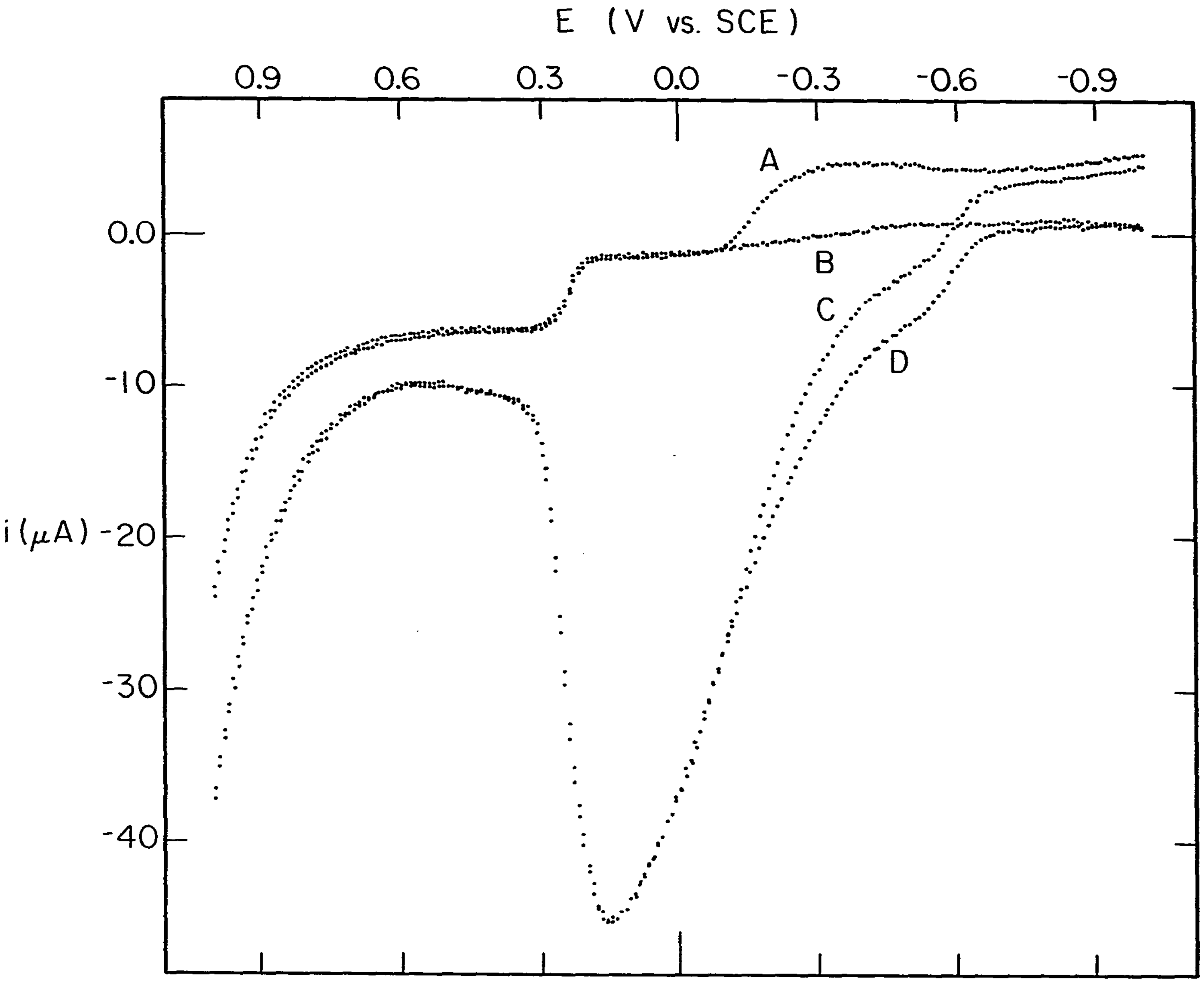

E (V vs. SCE)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
i (μA)
0.0
-10
-20
-30
-40
A
B
C
D

Figure VII-3. Comparison of flow injection detection peaks for fructose using dc and pulsed amperometric detection

Injection: 50 µL of 1.0 mM fructose (50 nmol) in 0.20 M NaOH.

Carrier Stream: 0.20 NaOH at 0.50 mL min^{-1}.

Peaks: (A) Gold electrode.

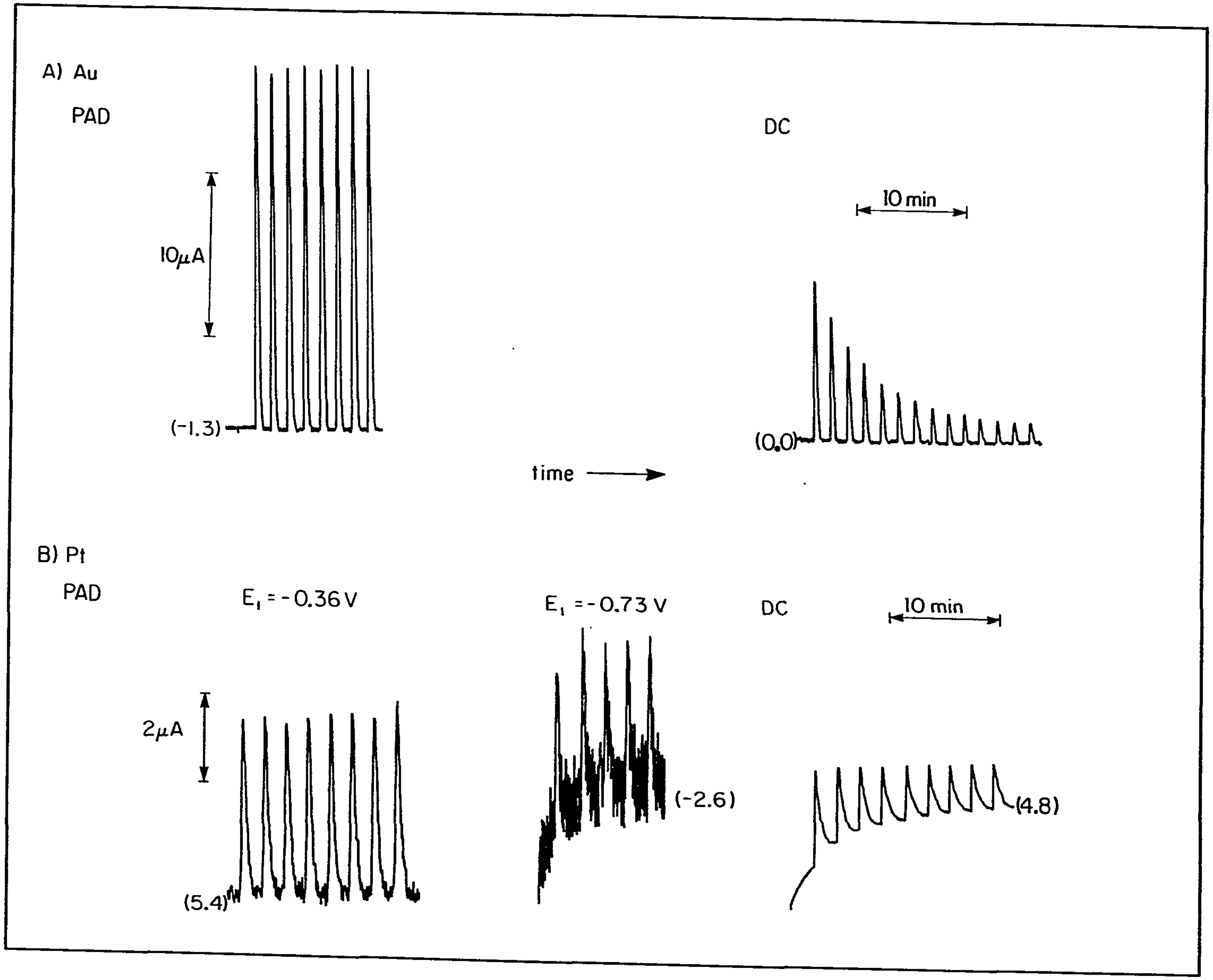
PAD: E_1 = 0.15V (250 ms);
E_2 = 0.75V (100 ms);
E_3 = -1.00V (100 ms).

DC: E = 0.15V

(B) Platinum electrode.

PAD: E_1 = given in figure (500 ms);
E_2 = 0.48V (500 ms);
E_3 = -0.92V (250 ms).

DC: E = -0.73V.


A) Au
PAD
10μA
(-1.3)
DC
10 min
(0.0)
time
B) Pt
PAD
E₁ = -0.36 V
2μA
(5.4)
E₁ = -0.73 V
(-2.6)
DC
10 min
(4.8)

tion of potentials other the ca. -0.36V for detection with Pt electrodes results in much greater noise levels, as demonstrated for E_1 = -0.73V. The dispersion constant for the FI system (D_p), defined by the ratio of the peak or maximum concentration at the detector and the bulk analytical concentration of the sample injected (C_p/C^b), was 0.56.

As a final note we observe that mechanical polishing of electrode surfaces used in PAD can result in an unstable baseline. Because the alternate anodic formation and cathodic dissolution of surface oxide in the pulsed method results in a gradual microscopic roughening of the electrode surface,[13,14] the baseline signal of newly polished electrodes may require a long time to reach a steady-state value, i.e., a constant surface area. For example, we observe drift of the baseline for Pt over a several hour period whereas the baseline for a newly polished Au electrode usually reaches a steady value in 5-10 min. We recommend that users of PAD resist the traditional urge to polish electrodes regularly for the purpose of maintaining surface activity. The waveforms in PAD are designed to remove efficiently surface adsorbed reaction products and solution impurities; hence, mechanical polishing is seldom needed.

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VIII. PULSED AMPEROMETRIC DETECTION OF CARBOHYDRATES AT GOLD ELECTRODES WITH A TWO-STEP POTENTIAL WAVEFORM

A. Abstract

A two-step potential waveform is demonstrated for the detection of carbohydrates at a Au electrode in alkaline solutions for application in flow injection and liquid chromatography systems. Pulsed amperometric detection (PAD) of carbohydrates previously based on a three-step waveform, is now extended to potentiostats capable of programming an asymmetric square waveform (e.g., normal pulse voltammetric waveforms). Detection limits for glucose, sorbitol and sucrose are approximately 1 nmole in a 50-μL sample (i.e., 200 ng glucose and 360 ng sucrose) in a flow-injection system.

B. Introduction

There remains a need in the disciplines of human, plant, and animal nutrition and health, for sensitive detection of carbohydrates in a variety of complex samples. Many physiological disorders can be deduced from high or low levels of carbohydrates in biological fluids. The presence of galactose in urine is indicative of galactosemia, severe hepatitis or biliary atresia in neonatal infants.[1] An excess amount of fructose or xylulose may be a sign of an inherited metabolic defect, such as essential fructosuria or essential pentosuria, respectively.[2] Probably the largest number of clinical analyses are performed for the screening for serum glucose which may be an indication of the hyperglycemic disease diabetes mellitus or less frequently, hypoglycemia.[2]

Recent methods of analysis couple a nonselective detection method with a separations scheme, commonly chromatography. Several chromatographic methods are in use for carbohydrates but many fail in one respect or another. Gas chromatography, although rapid for the separation of carbohydrates, has the disadvantage of requiring prederivatization. Thin-layer and paper chromatography are relatively inexpensive, but there exists an undesirable trade-off between analysis time and resolution, and quantitative evaluation can be severely limited. State-of-the-art methods for the separation of carbohydrates are based on high-performance liquid chromatography (HPLC). Separations have been reported on polar and nonpolar columns, as well as anion-exchange and cation-exchange columns.[3-12]

Equally important to the analytical procedure is the detection of the carbohydrates. Commonly, refractive index detection is preferred over photometric detection because of the lack of strong absorption bands at wavelengths where the solvent does not absorb appreciably.[9] Refractive index detection suffers in that sensitivities are often unsatisfactory. Photometric detection following post-column derivatizations has been used[13] but the added complication motivates the search for more reliable and universal methods. The use of optical activity detection has been recently presented[14], but the scarcity of such instrumentation prohibits its use in modestly equipped laboratories. Flame ionization detectors[15] have also been used but they lack in sensitivity.

Pulsed amperometric detection (PAD) at Pt electrodes has been presented previously as a sensitive method for the determination of carbohydrates in flow-injection analysis (FIA) and HPLC.[16-18] The method is based on a three-step potential waveform with alternate anodic and cathodic polarizations of the electrode followed by the amperometric detection at a potential centered between the polarization potentials. The method has also been well described[19] for the detection of alcohols[20], amino acids[21], aminoglycocides[22] and many inorganic and organic sulfur compounds.[23,24] The three-step potential waveform has also been applied for PAD at gold electrodes.[12,25,26] In contrast, presented here, is a scheme utilizing a two-step potential waveform at a gold electrode resulting in increased sensitivities and lower detection limits over prior detection methods such as refractive index and absorption[9], and approximately equivalent sensitivities and detection limits with previous three-step PAD methods applied to Au electrodes.

The three-step potential waveform for the detection of carbohydrates has been discussed elsewhere[16-19] and is briefly summarized only for comparison to the proposed two-step waveform (Fig. VIII-1). The waveforms are similar; the two-step waveform results by elimination of the cathodic polarization step from the three-step waveform. Reduction of the gold surface oxide occurs quickly at E_1 in the two-step waveform, and preadsorption of carbohydrate, as achieved at E_3 for the three-step waveform applied to Pt electrodes, is not necessary for Au electrodes. The two-step waveform can be applied at a sufficiently high frequency (ca. 1-3 Hz.) to be applicable for amperometric detection in LC and FI systems.

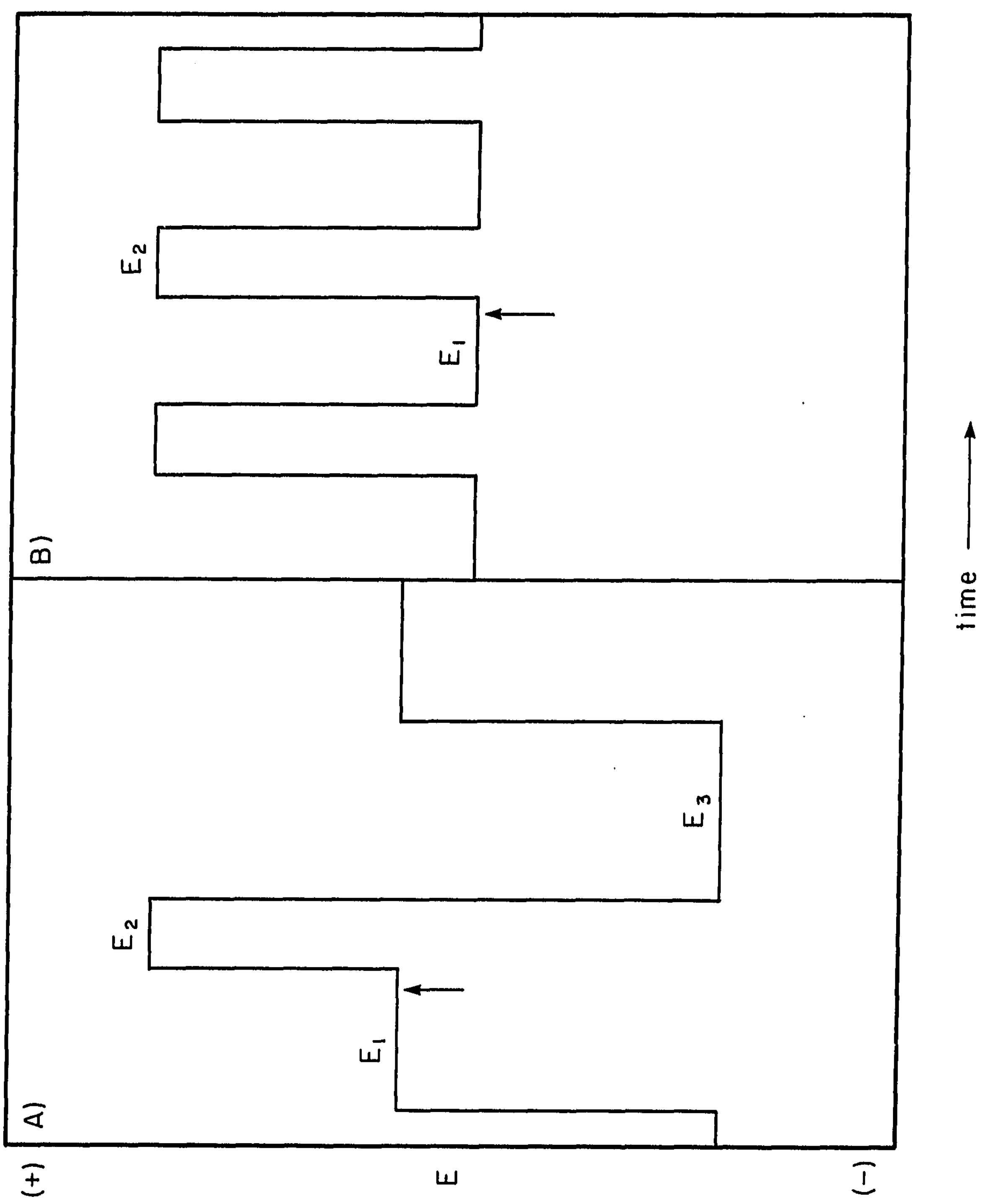
C. Experimental

1. Instrumentation

The majority of results were obtained with an electroanalytical system based on a PAR 174A potentiostat (EG&G Princeton Applied Research Corporation, Princeton, NJ) under computer control. An HP-86B personal computer (Hewlett Packard, Palo Alto, CA) was coupled to a mainframe HP-6942A multiprogrammer (Hewlett Packard). The multiprogrammer contained several plug-in cards for performing analog-to-digital conversion (HP-69751A), digital-to-analog conversion (HP-69720A), single or multiple pulse timer control (HP-69736A), and digital I/O control (HP-69731B). All cards can be programmed in several microseconds, and no time delay is observed when sending commands to the individual cards because of the mainframes buffering ability.

The two-step waveform was also demonstrated utilizing a

Figure VIII-1. Potential-time profiles for three-step (A) and two-step (B) waveforms


A)
B)
E₁
E₂
E₃
E₁
E₂
(+)
E
(−)
time

slightly modified PAR 174A potentiostat. This instrument is used commonly for normal pulse polarography; however, it was necessary to change the symmetry of the waveform for PAD as described here. Capacitor C214 was replaced by a 2μF mylar capacitor, and resistor R264 by a 220kohm resistor. This results in an asymmetric square wave with a time period of t_1 = 300 ms at E_1 and t_2 = 200 ms at E_2. Sampling of electrode current was achieved over a 16.7 ms period in the last 17 ms of period t_1.

The flow-through amperometric detector cell for FIA studies (Dionex Corporation, Sunnyvale, CA) consisted of two parallel blocks in which were mounted the Au indicating (0.02 cm^2), glassy carbon counter and Ag/AgCl reference electrodes. Current-potential curves were obtained using staircase voltammetry at a gold rotated disk electrode (RDE, 0.005 cm^2) in a model MSR rotator (Pine Instrument Co., Grove City, PA). The staircase waveform was applied with 10 mV increments at 18 ms intervals (i.e., ca. 2.4 V min^{-1}); current integration occurred for the last 16.67 ms. All potentials are reported vs. the SCE reference.

The FIA system consisted of a Minipuls-2 peristaltic pump (Gilson Medical Electronics, Inc., Middletown, WI) followed by a pulse dampener constructed from an inverted glass T-tube, a needle valve flow restrictor to produce back pressure, and a 10-foot coil of 0.5-mm Teflon tubing leading to the injection valve. The sample injection system was home-built with commercially available hardware to allow for control with TTL level digital I/O lines. It was comprised of a model 7010 high-pressure six-port sample injection valve (Rheodyne Inc., Cotati, CA) mounted on a model 5701 pneumatic actuator (Rheodyne Inc.) which was coupled to a model MBD005 solenoid valve (Skinner Inc., New Britain, CT) allowing for electronically controlled pneumatic actuation of the injection valve. A circuit was designed utilizing an optically isolated switch to allow for control of the solenoids via a digital output line.

2. Chemicals

All solutions were prepared from reagent grade chemicals (Fisher Scientific, Fair Lawn, NJ) and deionized, triply distilled water. The supporting electrolyte was 0.20 $\underline{M}$ NaOH. Due to the slow decomposition of carbohydrates in alkaline media, solutions were prepared just prior to use. Where applicable, dissolved oxygen was removed by purging with reagent grade argon (99.99%; Cooks Inc., Algona, IA).

D. Results and Discussion

In general, the appropriate values of potential for each step in the PAD waveform can be approximated from voltammograms obtained by cyclic, linear, or staircase sweep voltammetry. The voltammetric response at a Au electrode is shown in Figs. VIII-2 through VIII-5 for equivalent concentrations of glucose (a reducing monosaccharide; Fig. VIII-3), sorbitol (a sugar alcohol; Fig. VIII-5), and sucrose (a nonreducing disaccharide; Fig. VIII-4). For comparison, the residual i-E curve obtained in the absence of analyte also is shown (Fig. VIII-2). Casual inspection reveals similarities in the voltammetric behavior of the carbohydrates at the Au electrode. During the positive scan, oxidation of the carbohydrates occurs for E > ca. -0.2 V, but ceases with the concurrent formation of surface oxide for E > 0.6 V. At E > 0.9 V, anodic decomposition of the solvent is observed with rapid evolution of O_2. On the reverse scan (negative) cathodic stripping of the surface oxide is observed at ca. 0.3 V; however, the peak area appears to be greatly diminished when a carbohydrate is present. Although the amount of surface oxide formed can be somewhat less in the presence of a surface active compound, the decrease in the cathodic peak is quite dramatic in these cases. The asymmetry of the cathodic stripping peak for surface oxide (see especially Fig. VIII-4) indicates that an anodic process is occurring simultaneously with oxide reduction in the region 0.3 to 0.1 V. In the case of glucose and sorbitol, the negative sweep yields an oxidative current peak which is slightly greater than the current observed at the same potential for the positive sweep. This results because, upon stripping of the oxide, surface sites made free of oxide are immediately active for anodic os allowed for the two computers to work relatively independent of each other resulting in improved precision and rate of data

Figure VIII-2. Current-potential curves obtained with a staircase waveform applied to a Au RDE in 0.20 M NaOH

Pulse amplitude (ΔE): 10 mV

Scan Rate (ϕ): 2.4 V min^{-1}

Rotation rate: 1600 rev min^{-1}

Curves: [a] Ar sat'd residual
[b] air sat'd residual.

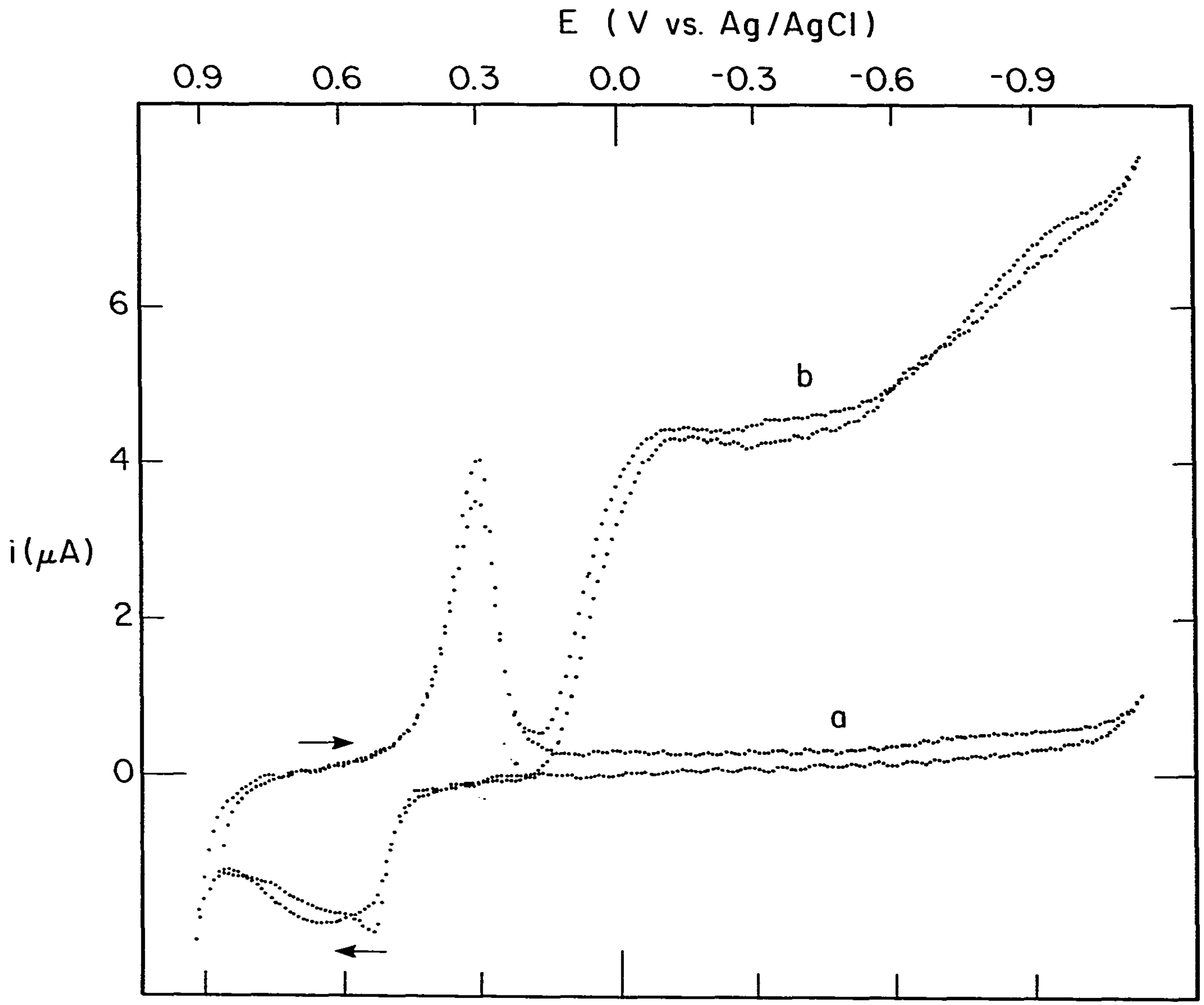

E (V vs. Ag/AgCl)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
i(μA)
6
4
2
0
b
a

Figure VIII-3. Current-potential curves obtained with a staircase waveform applied to a Au RDE in 1.0 m_M_ glucose/0.20 _M_ NaOH

Pulse amplitude (ΔE): 10 mV

Scan Rate (ϕ): 2.4 V min^{-1}

Solution: 1.0 m_M_ glucose, Ar sat'd

Rotation speed (rev min^{-1}):

[a]	400
[b]	900
[c]	1600
[d]	2500
[e]	3600

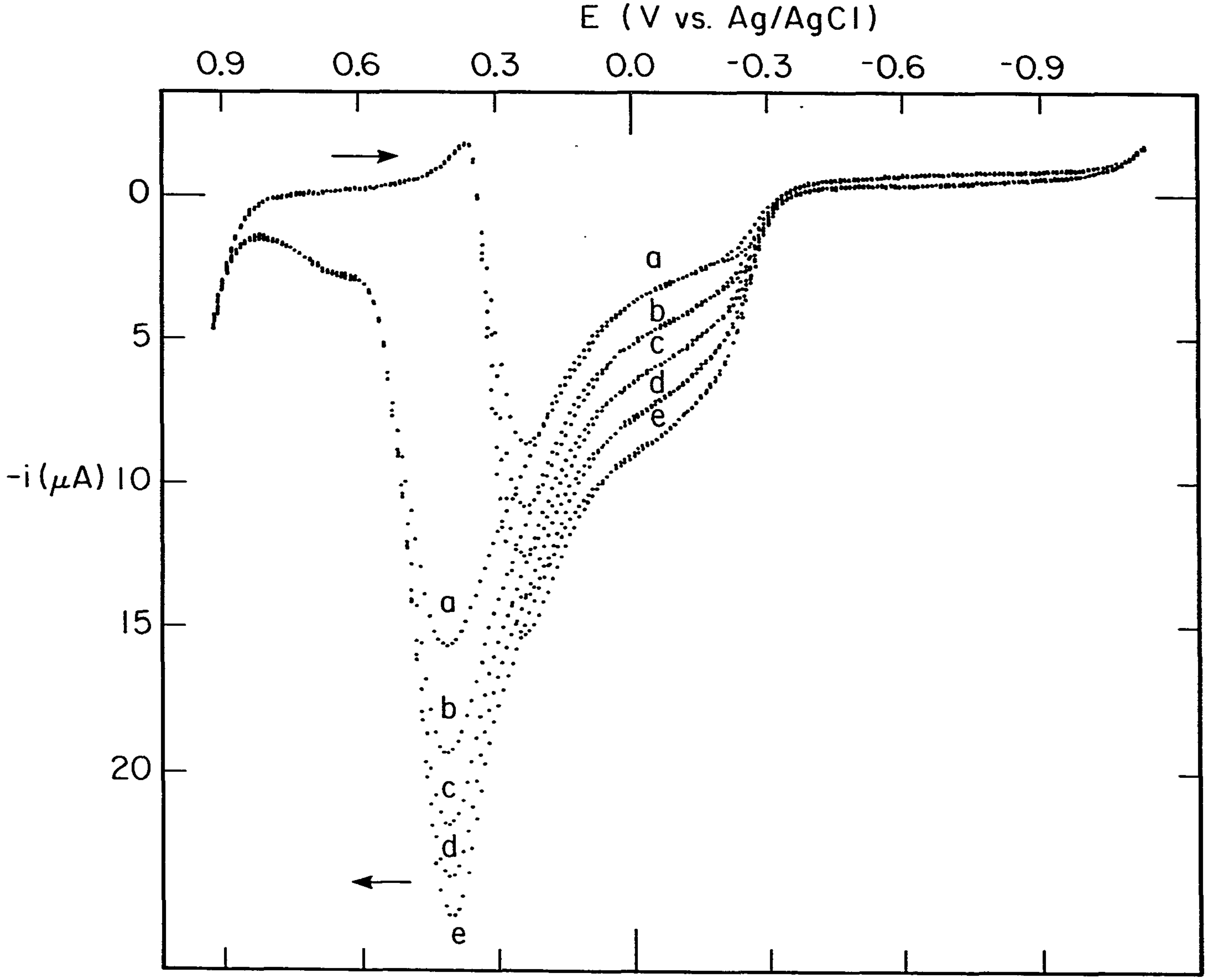

E (V vs. Ag/AgCl)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
-i (μA)
0
5
10
15
20
a
b
c
d
e
a
b
c
d
e

Figure VIII-4. Current-potential curves obtained with a staircase waveform applied to a Au RDE in 1.0 mM sucrose/0.20 M NaOH

Pulse amplitude (ΔE): 10 mV

Scan Rate (ϕ): 2.4 V min^{-1}

Solution: 1.0 mM sucrose, Ar sat'd

Rotation speed (rev min^{-1}):
[a] 400
[b] 900
[c] 1600
[d] 2500
[e] 3600

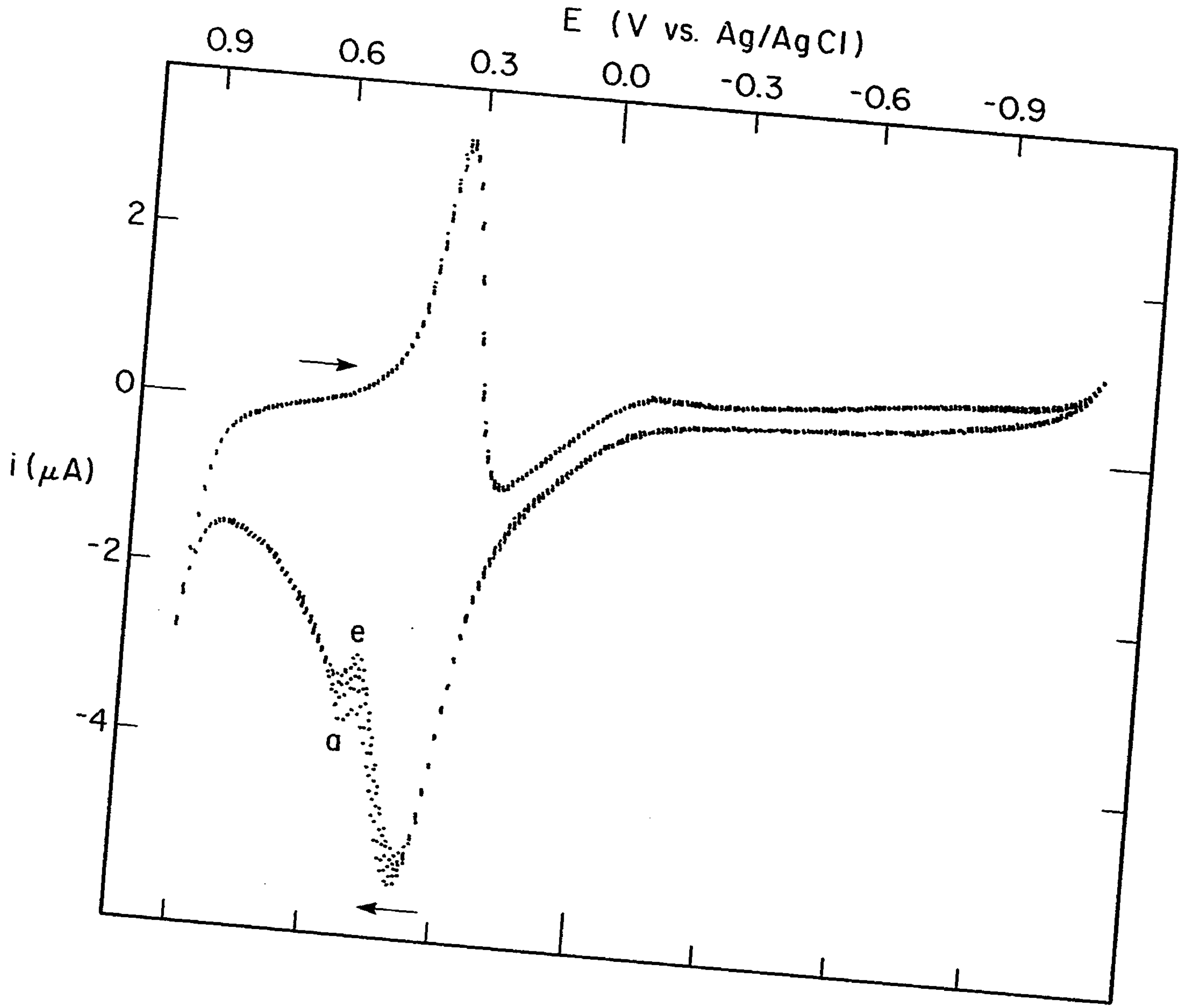

E (V vs. Ag/AgCl)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
2
0
-2
-4
i (μA)
e
a

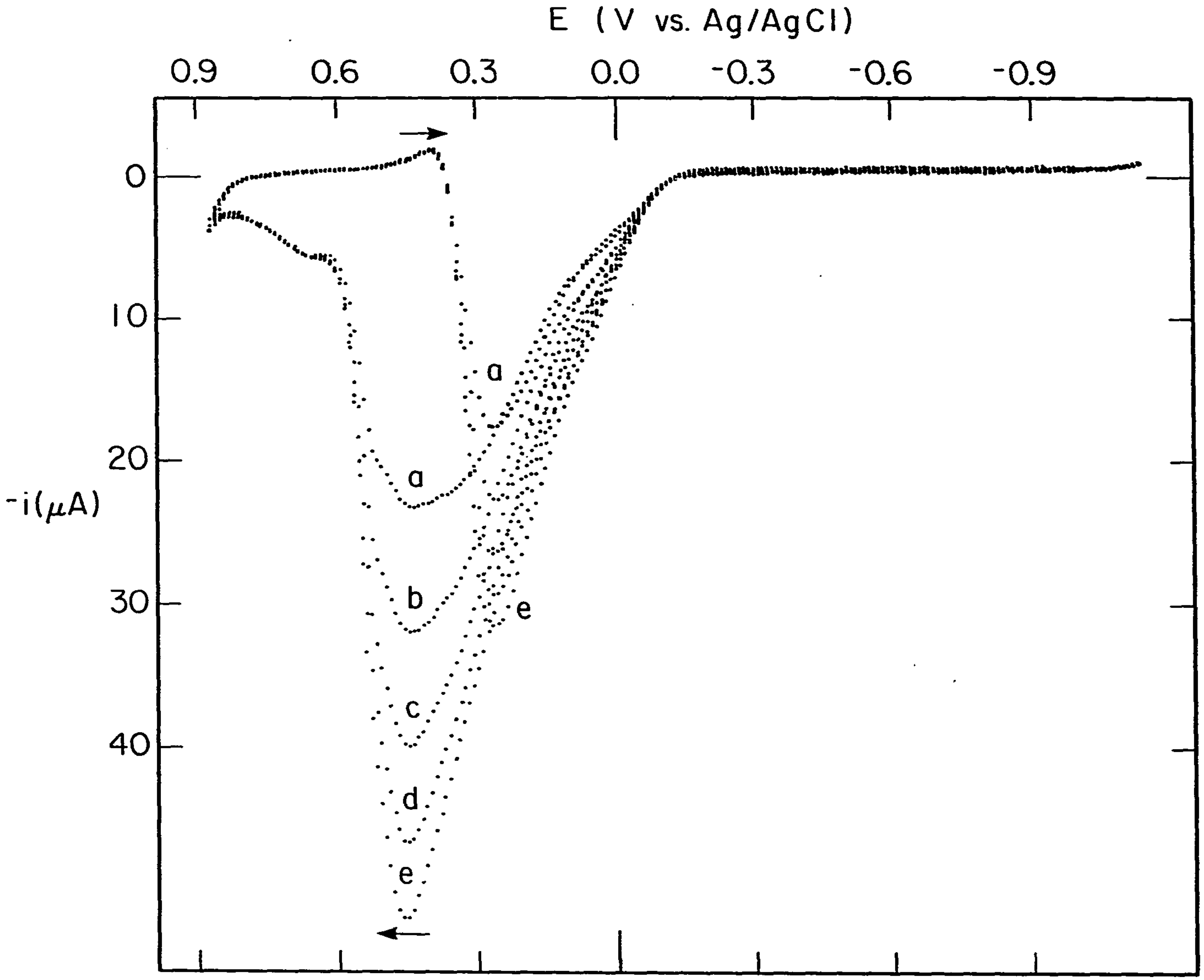
Figure VIII-5. Current-potential curves obtained with a staircase waveform applied to a Au RDE in 1.0 mM sorbitol/0.20 M NaOH

Pulse amplitude (ΔE): 10 mV

Scan Rate (ϕ): 2.4 V min^{-1}

Solution: 1.0 mM sorbitol, Ar sat'd

Rotation speed (rev min^{-1}):
[a] 400
[b] 900
[c] 1600
[d] 2500
[e] 3600


E (V vs. Ag/AgCl)
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
0
10
20
30
40
-i(μA)
a
a
b
c
d
e
e

acquisition.

The interface between the potentiostat and 6942A mainframe contained circuits for amplification, integration, control of electrode rotation speed, and sample-and-hold operations. Analog signal integration was accomplished after the current at the working electrode was converted to a proportional voltage and onal velocity. The anodic current for glucose (Fig. VIII-3) at 0.0 V on the positive and negative scans is approximately a linear function of the half-root of rotational velocity, which is indicative of a mass-transport limited reaction mechanism. Virtually no dependence on rotational velocity is observed for sucrose (Fig. VIII-4) which is indicative of a slow heterogeneous reaction for the nonreducing carbohydrate. Sorbitol (Fig. VIII-5) exhibits a response intermediate that of glucose and sucrose. Regardless of the large differences in the apparent heterogeneous rate constants for the three model carbohydrates, they each can be detected very well by PAD using three-step and, now, two-step potential waveforms.

Optimization of the two-step waveform for PAD should not be made merely on the basis of the i-E curves in Figs. VIII-2 through VIII-5 but should be based on an examination of the effects of variation of time periods in the wave form, in addition to the detection and cleaning potentials. Plots displaying the amperometric response for variation of these parameters are shown for glucose in Figs. VIII-6 through VIII-

9. Estimation of the optimum detection potential (E_1 in the two-step waveform) is made from inspection of Fig. VIII-6. The response for glucose goes through a maximum at ca. 0.15 V vs. Ag/AgCl. Note in Fig. VIII-2 that this potential is bounded anodically by the stripping of the gold oxide, and cathodically by the reduction of dissolved oxygen. The variation of background current with potential must also be considered when making a choice of optimum detection potential. The background current in Fig. VIII-6 is essentially constant and very near zero for the region 0.3 to 0.05 V, and increases dramatically at more negative potentials where oxygen is reduced. The selected value E_1 = 0.15 V corresponds to the largest signal-to-background ratio. A similar analysis can be performed for the selection of the anodic cleaning potential (E_2 in the two-step waveform). The observed peak current for glucose (E_1 = 0.15 V) increases linearly with increasing E_2, as shown in Fig. VIII-7. The background current increases when shifting E_2 to more positive values because a greater amount of surface oxide is produced which must be reduced subsequently at E_1. The optimum value of E_2 = 0.75 V corresponds to the largest signal-to-background ratio.

Because of the chronoamperometric basis of PAD, variation of the time periods t_1 and t_2 for application of E_1 and E_2, respectively, can produce an increase in sensitivity, a decrease in the background current and an overall increase in detectability. The results of variation of t_1 for E_1 = 0.15 V

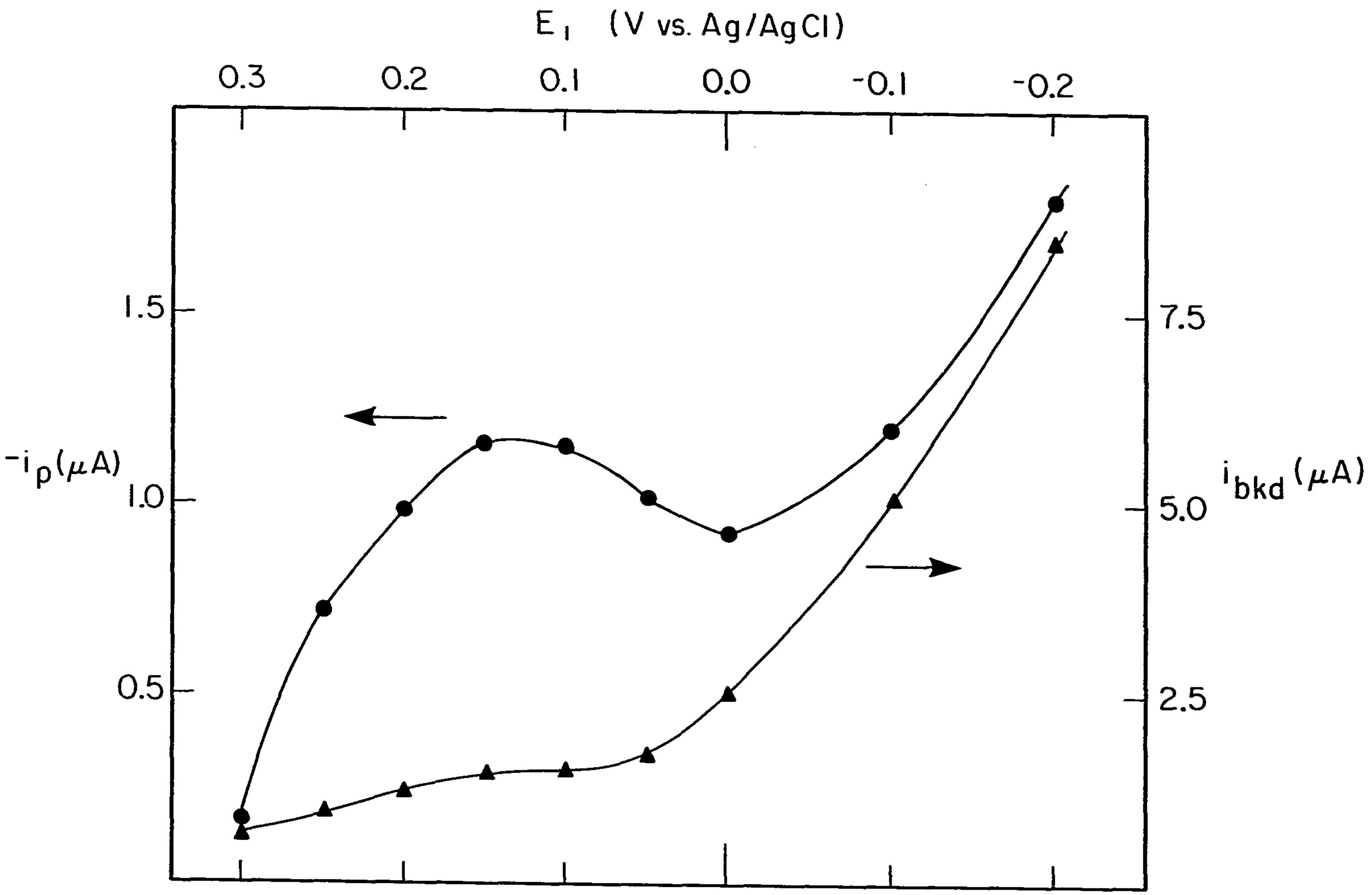
Figure VIII-6. Optimization of two-step potential waveform by FI-PAD: variation of detection potential

Samples injected: 50 μL of 1.0 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH.

Carrier stream: 0.20 $\underline{M}$ NaOH at 0.5 mL min^{-1}

Curves: Variation of detection potential (E_1):

E_2 = 0.70 V,
t_1 = 250 ms,
t_2 = 200 ms.



E₁ (V vs. Ag/AgCl)
0.3
0.2
0.1
0.0
-0.1
-0.2
-iₚ(μA)
1.5
1.0
0.5
i_bkd (μA)
7.5
5.0
2.5

Figure VIII-7. Optimization of two-step potential waveform by FI-PAD: variation of anodic cleaning potential

Samples injected: 50 μL of 1.0 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH.

Carrier stream: 0.20 $\underline{M}$ NaOH at 0.5 mL min^{-1}

Curves: Variation of anodic cleaning potential (E_2):

E_1 = 0.15 V,
t_1 = 250 ms,
t_2 = 200 ms.

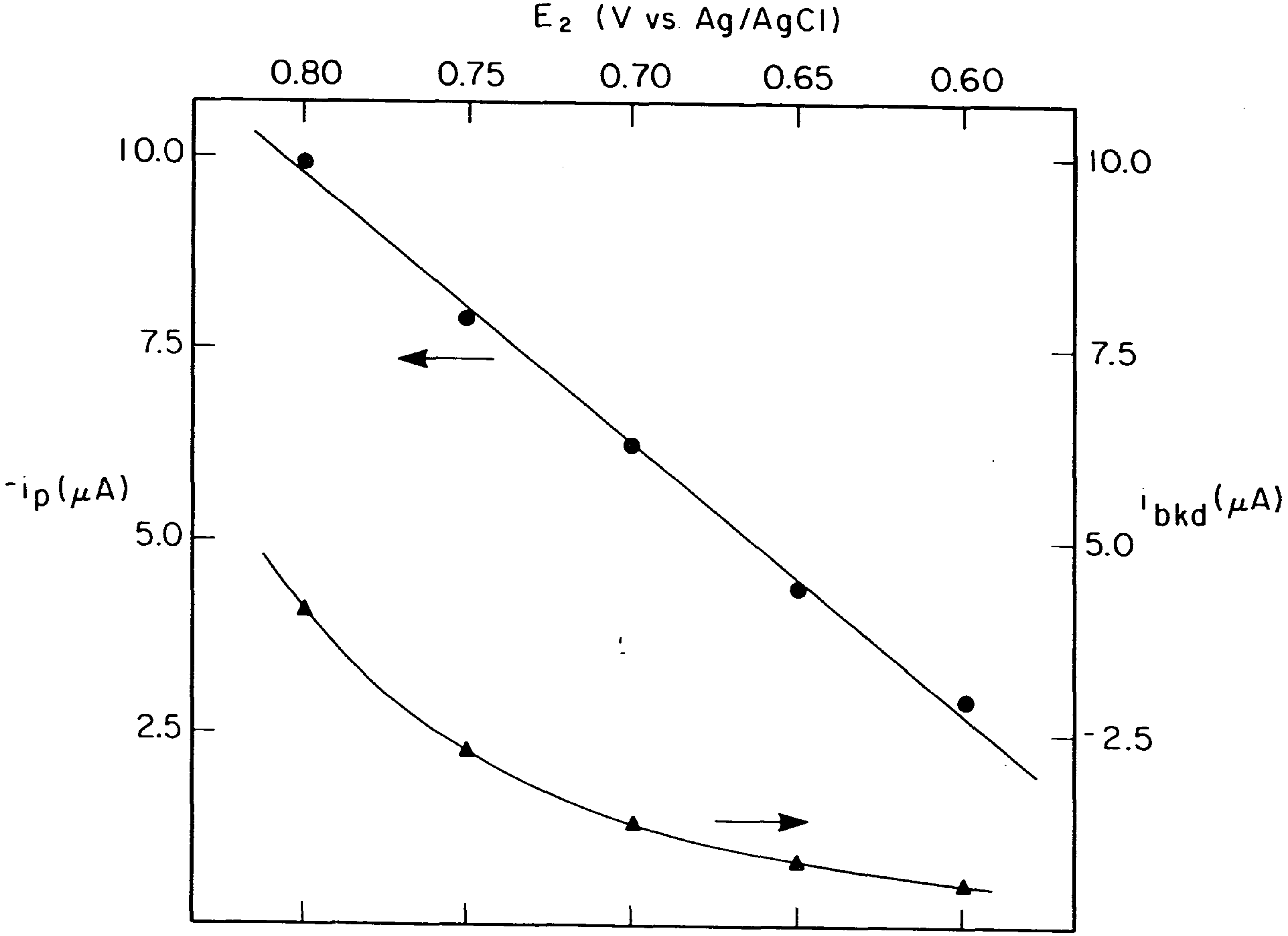

E₂ (V vs. Ag/AgCl)
0.80
0.75
0.70
0.65
0.60
10.0
7.5
5.0
2.5
-ip(μA)
10.0
7.5
5.0
2.5
ibkd(μA)

Figure VIII-8. Optimization of two-step potential waveform by FI-PAD: variation of detection time

Samples injected: 50 μL of 1.0 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH.

Carrier stream: 0.20 $\underline{M}$ NaOH at 0.5 mL min^{-1}

Curves: Variation of detection time (t_1):

E_1 = 0.15 V,
E_2 = 0.75 V,
t_2 = 200 ms.

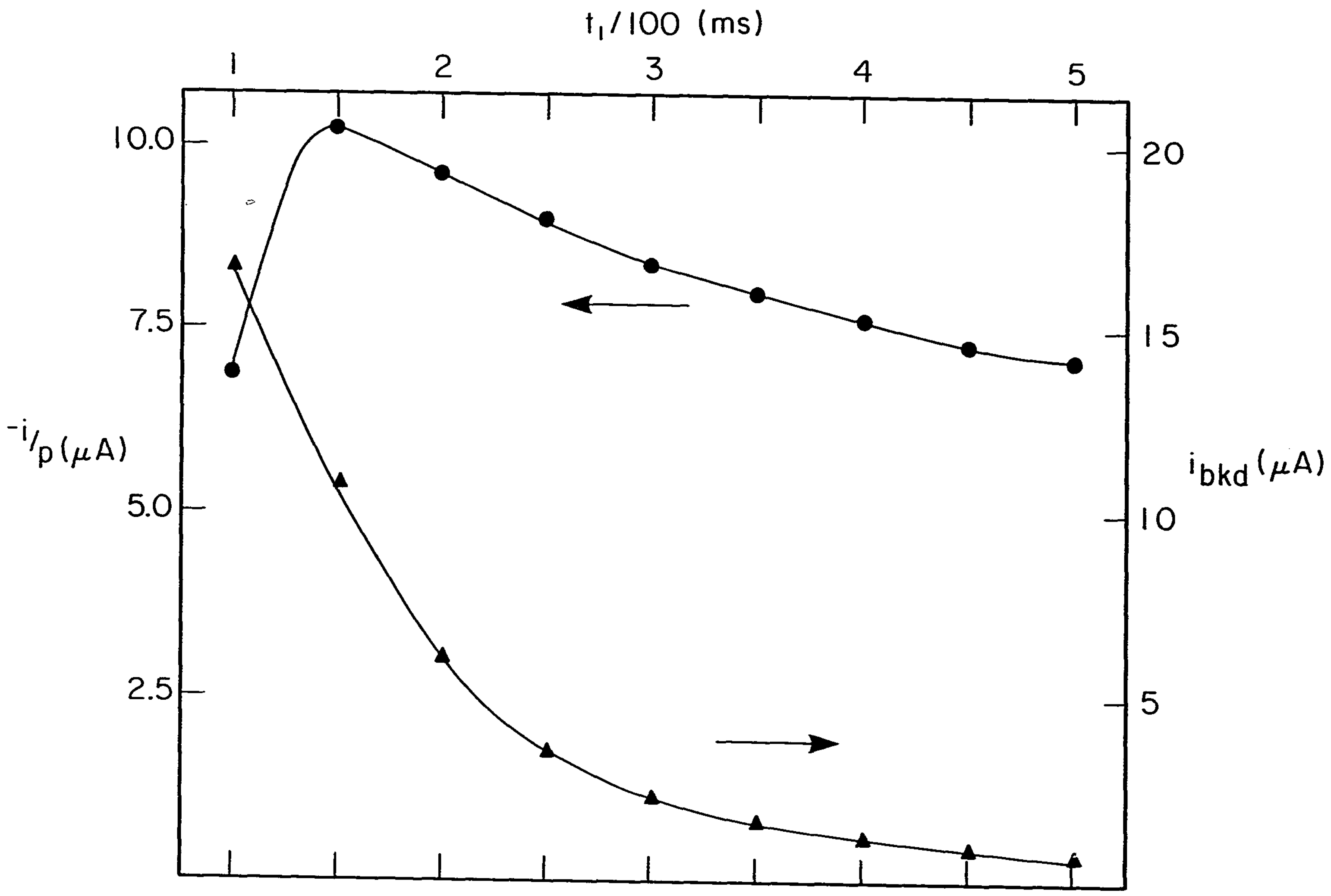

t1/100 (ms)
1
2
3
4
5
10.0
7.5
5.0
2.5
-i/p (μA)
20
15
10
5
ibkd (μA)

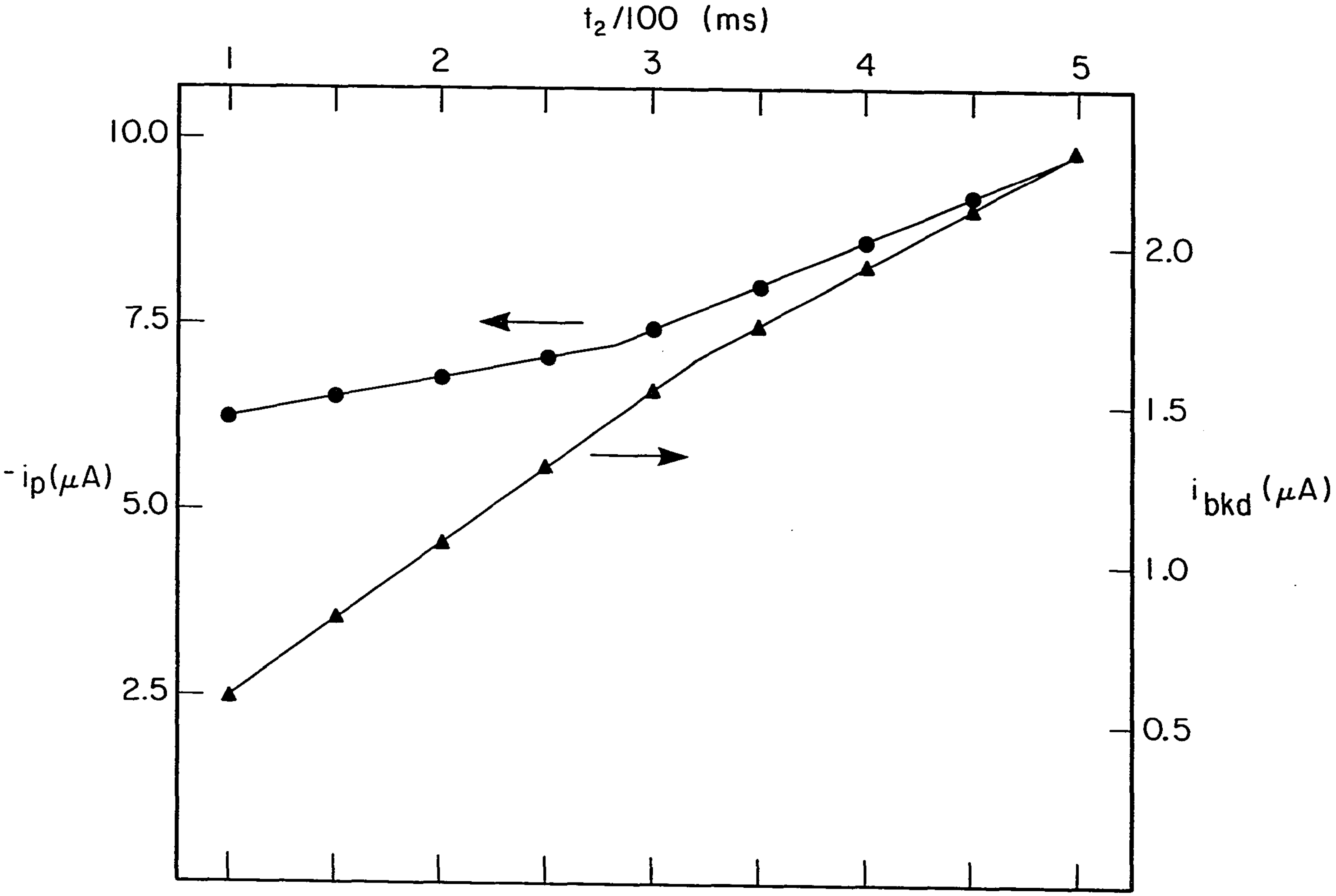
Figure VIII-9. Optimization of two-step potential waveform by FI-PAD: variation of anodic cleaning time

Samples injected: 50 μL of 1.0 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH.

Carrier stream: 0.20 $\underline{M}$ NaOH at 0.5 mL min^{-1}

Curves: Variation of anodic cleaning time (t_2):

E_1 = 0.15 V,
E_2 = 0.75 V,
t_1 = 350 ms.


t$_2$/100 (ms)
1
2
3
4
5
10.0
7.5
5.0
2.5
$-i_p$ (μA)
2.0
1.5
1.0
0.5
i_{bkd} (μA)

is shown in Fig. VIII-8. The cathodic background current observed for small t_1 results from the reduction of the surface oxide generated at E_2. The peak height for glucose decreases for $t_1 > 500$ ms, probably as a result of poisoning of the electrode surface by adsorbed detection products.[27] Any value for t_1 in the range 300-500 ms is satisfactory; the choice of $t_1 = 350$ ms as the optimum was based simply on the desire for maximization of the frequency of the waveform. The effect of variation of the time for anodic cleaning (t_2) is shown in Fig. VIII-9. The increase in peak current for glucose for increasing t_2 is concluded to result from the more thorough oxidative removal of adsorbed detection products from the electrode surface. An increase in background current observed with increasing t_2 probably is due to the formation of more oxide on the Au substrate which must be reduced at E_1. The choice of $t_2 = 200$ ms as the optimum was based upon the desire for a minimal background current.

The strategy for optimization of the design for the two-step waveform demonstrated here was useful for graphical illustration of the dependence of the peak current and background current on the values of E_1, E_2, t_1, and t_2. We hasten to point out that use of simplex optimization gave virtually the same values of waveform parameters for maximization of the signal-to-background ratio.

Calibration plots for FI-PAD for the three model carbohydrates of interest are shown in Fig. VIII-10 obtained using the optimum waveform. Plots of peak height vs. concentration (i_p - C^b) are nonlinear whereas $1/i_p$ - $1/C^b$ plots are linear. Previous arguments have interpreted these observations for PAD at Pt using the three-step waveform as resulting from adsorption-controlled detection, defined sufficiently well by the Langmuir isotherm.[18,19] Recently,[27] it was concluded for PAD at Au electrodes, that fouling of the electrode surface by adsorbed reaction products, particularly for long detection periods (t_1), caused severe deviation from linearity in the i_p-C^b calibration plots for carbohydrates. Because of the relatively long value of t_1 selected, nonlinearity of i_p-C^b plots is attributed to surface fouling at high C^b. The theoretical basis of linear $1/i_p$-$1/C^b$ plots is under development.

To demonstrate the applicability of this method utilizing common instrumentation, multiple FI-PAD peaks obtained with the modified PAR 174A potentiostat are shown in Fig. VIII-11 for 50-μL of 1.0 m<u>M</u> glucose and sucrose. The baseline currents are shown in parentheses. The relative standard deviation of peak height over an 8-hour period was less than 2%.

E. Conclusions

The method of PAD is now applicable for the detection of carbohydrates at Au electrodes utilizing commercially available potentiostats with asymmetric square-wave potential

Figure VIII-10. Calibration plots (i_p-C^b and $1/i_p$-$1/C^b$) for glucose, sucrose and sorbitol by FI-PAD

Samples injected: 50 μL of carbohydrate in 0.20 M NaOH.

Carrier stream: 0.20 M NaOH at 0.5 mL min^{-1}

Waveform: E_1 = 0.15 V (t_1 = 350 ms)
E_2 = 0.75 V (t_2 = 200 ms)

Curves:
[A] glucose (▲)
[B] sucrose (●)
[C] sorbitol (■)

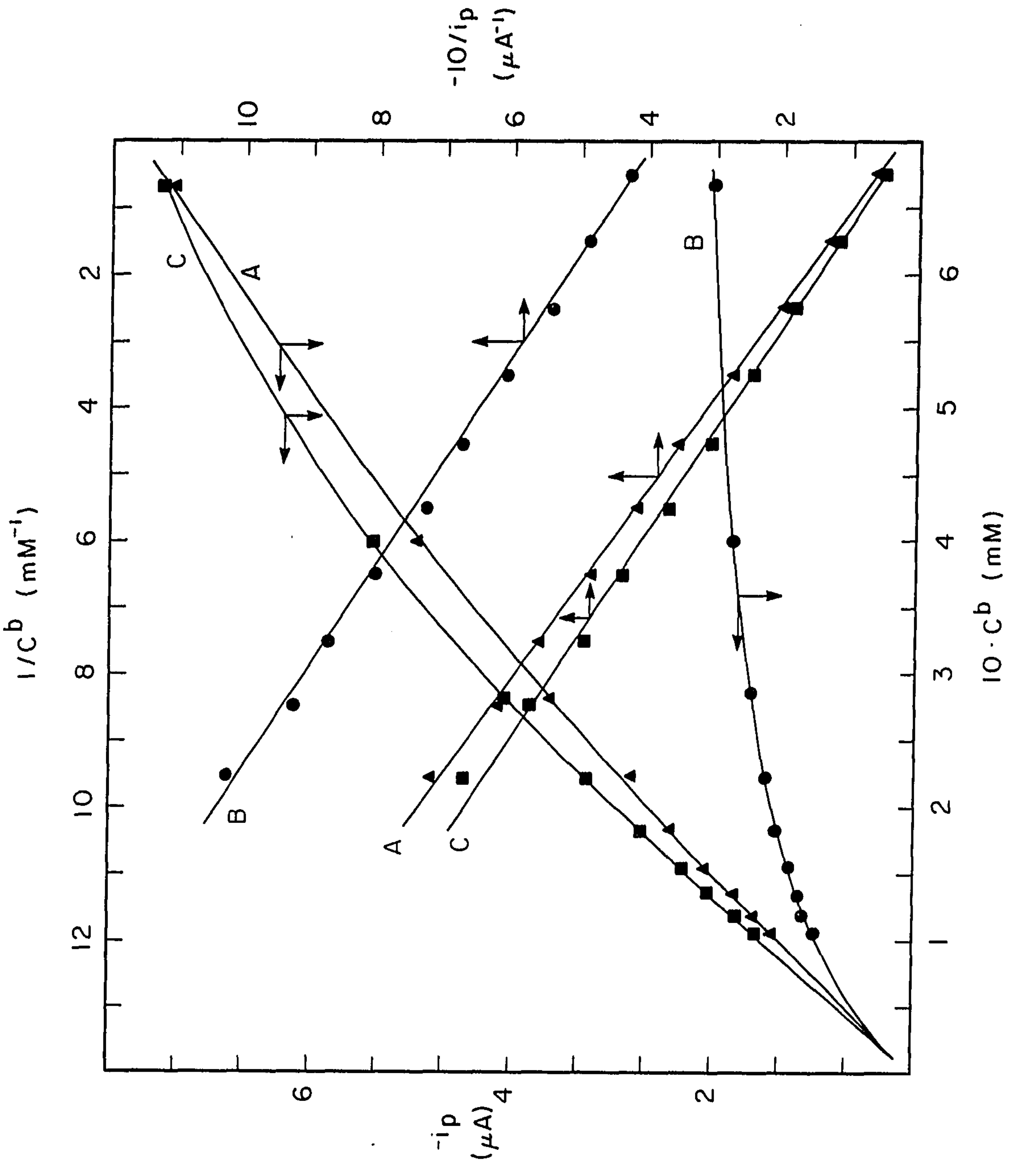
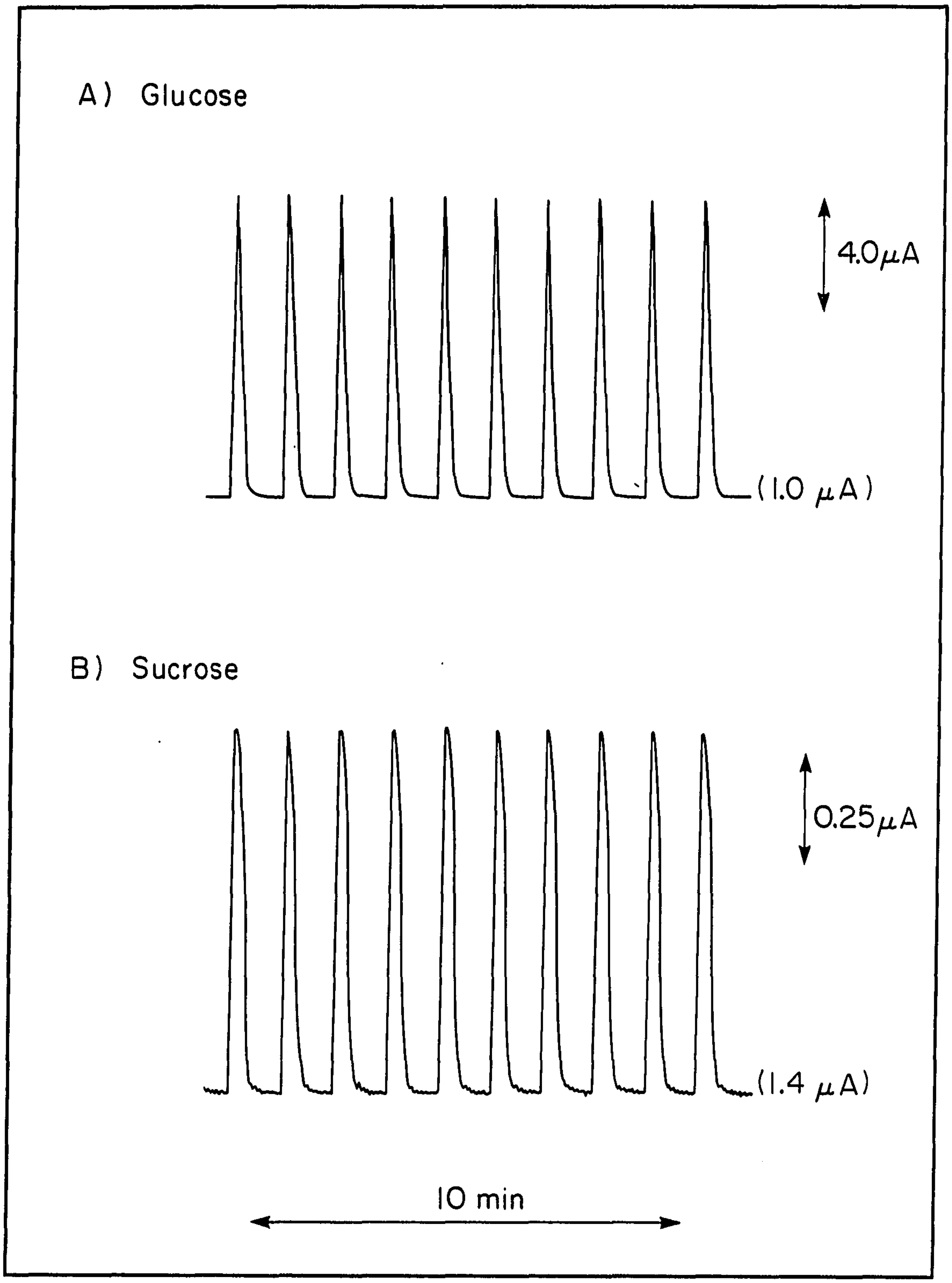

1/C^b (mM^-1)
2
4
6
8
10
12
-10/i_p (μA^-1)
10
8
6
4
2
-i_p (μA)
6
4
2
10·C^b (mM)
1
2
3
4
5
6
A
B
C
A
B
C

Figure VIII-11. Multiple flow injection peaks with pulsed amperometric detection utilizing a Princeton Applied Research Model 174A potentiostat for glucose and sucrose

Waveform:	E_1 = 0.15 V (t_1 = 300 ms) E_2 = 0.75 V (t_2 = 200 ms)
Samples injected:	50 µL of 1.0 m<u>M</u> carbohydrate in 0.20 <u>M</u> NaOH.
Carrier stream:	0.20 <u>M</u> NaOH at 0.5 mL min^{-1}
Peaks:	[A] glucose [B] sucrose


A) Glucose
4.0μA
(1.0 μA)
B) Sucrose
0.25μA
(1.4 μA)
10 min

waveforms. Detection limits with the two-step waveform at Au electrodes are virtually equivalent to previous three-step methods at Au electrodes. However, because of the elimination of the adsorption period, deviation from linearity of the i-C response is less severe with the two-step method. With the greatly improved detection limits at Au as compared to Pt electrode and ease of application of the two-step waveform utilizing existing instrumentation, it is anticipated that his method will find increasing application for carbohydrate detection in liquid chromatographic and flow injection systems.

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IX. PULSED COULOMETRIC DETECTION OF CARBOHYDRATES AT A CONSTANT DETECTION POTENTIAL AT GOLD ELECTRODES IN ALKALINE MEDIA

A. Abstract

A significant increase in the signal-to-noise ratio for the pulsed amperometric detection (PAD) of carbohydrates at Au electrodes is obtained by increasing the length of the current integration period from the traditional value of 16.7 ms (i.e., 1/60 Hz). For $t_i >> 16.7$ ms, the integrated response (q, coulombs) is plotted as the analytical signal and we name the technique ***pulsed coulometric detection*** (PCD) when applied to flow injection (FI) and liquid chromatographic (LC) systems. For $t_i = 500$ ms, FI-PCD had a detection limit of 1 $\mu\underline{M}$ (S/N = 2) for glucose which is a significant improvement from the value 35 $\mu\underline{M}$ for FI-PAD. The absolute detection limits for glucose and sucrose are ca. 50 pmoles and 125 pmoles, respectively, in 50 μL samples. Calibration plots ($q_p - C^b$) for PCD are linear over a significantly larger dynamic range than observed for PAD because of the decrease in detection limits.

B. Introduction

Pulsed amperometric detection (PAD) at Pt and Au electrodes has been applied successfully to flow injection (FI) and liquid chromatographic (LC) systems for numerous aliphatic compounds including alcohols and carbohydrates[1-8], amines and amino acids[9-10] and, recently, sulfur compounds.[11-13] The majority of these compounds are not detected under dc conditions and photometric detection does not offer suitable sensitivity without prior chemical derivatization. LC-PAD has been commercialized successfully for analysis of carbohydrate mixtures.[5-7] A disadvantage of PAD at noble metal electrodes in FI and LC systems is that the linear dynamic range (i_p-C^b) is observed to be rather limited.[4] Because of the surface-controlled nature of the detection mechanism, calibration plots of $1/i_p$ vs. $1/C^b$ have been suggested to linearize data over a larger dynamic range.[4,10,11] However, the use of such "reciprocal plots" is not now being recommended.[12] Our present effort to improve on the analytical convenience of PAD is to increase the linear dynamic range by lowering substantially the limit of detection. We have made significant improvement in the detectability of carbohydrates by PAD at Au electrodes by integration of the amperometric response over a period substantially longer than is applied conventionally for PAD.

The success of PAD at noble metal electrodes for aliphatic organic compounds results because the multistep potential waveform manages sequentially the process of detection followed by oxidative and reductive reactivation of the electrode surfaces.[1,2,8,9,11] The effectiveness of surface cleaning and reactivation resulting from formation and dissolution of surface oxides at noble metal electrodes has been well recognized.[14-17] Cleaning of carbon electrode surfaces resulting from potential pulsed also is known,[18-23] although the mechanism probably does not involve formation followed by dissolution of an analog to surface oxide.

It is the customary practice in pulsed amperometric techniques, e.g., *pulse polarography*, to integrate the transient amperometric response for 16.7 ms (1/60 Hz). The integral divided by the integration period (coulombs/sec) is presented to a digital or analog recording device as an amperometric signal. The choice of the 16.7 ms period is intended to reject the high-frequency noise originating from the ac power supply. Brumleve et al.[24] explained the benefit of this practice as the result of minimizing "high- and low-frequency noise received and amplified by the high impedance circuitry associated with the reference and working electrodes." This same procedure for discrimination against 60-Hz noise has been applied in the development of the first generation of instruments for PAD.[5-7] However, with the use of microprocessor controlled instrumentation, the integration period can easily be varied, adding another dimension to the optimization of the pulsed detection techniques.

C. Theory

The total amperometric response observed at a noble metal electrode for anodic detection following a positive potential step in PAD is described by

$$i_{tot}(t) = i_{ox}(t) + i_{dl}(t) + i_{ads}(t) + i_{mt}(t) \qquad [1]$$

where $i_{ox}(t)$, $i_{dl}(t)$, $i_{ads}(t)$ and $i_{mt}(t)$ represent, respectively, the partial currents due to oxide formation on the electrode surface, charging of the double layer, oxidation of adsorbed analyte and oxidation of analyte reaching the electrode by convective-diffusional mass transport during the detection period. Including superposition of sinusoidal ac noise of amplitude A_j and time constant τ_j, the total amperometric response is given by

$$\begin{aligned} i_{tot}(t) = i_{ox}(t) + i_{dl}(t) + i_{ads}(t) + i_{mt}(t) \\ + \sum_j A_j \sin(2\pi t/\tau_j) \qquad [2] \end{aligned}$$

Integration of Eqn. 2 over a time period $t_i = t'' - t'$ yields,

$$q_{tot}(t_i) = \int_{t'}^{t''} i_{tot}(t)\,dt \qquad [3]$$

$$\begin{aligned} = q_{ox}(t_i) + q_{dl}(t_i) + q_{ads}(t_i) + q_{mt}(t_i) \\ + \sum_j \int_{t'}^{t''} A_j \sin(2\pi t/\tau_j) \qquad [4] \end{aligned}$$

The enhancement in signal-to-noise ratio resulting from increasing values of t_i can be illustrated by the simple example of a constant amperometric response with a superimposed sinusoidal noise component of single frequency and low amplitude. Integration of $i_{tot}(t)$ produces a time-dependent response, $q_{tot}(t)$, with a noise component of amplitude and frequency equal to that of the noise in $i_{tot}(t)$ but which is 180° out of phase with the noise in $i_{tot}(t)$. The contribution of the ac noise in itot(t) to noise in qtot(t) is at a minimum for t_i equal to integral multiples (k) of τ_j ($k=t_i/\tau_j$). Since the predominant source of ac noise in electroanalytical measurements is correlated with the 60-Hz line frequency, τ_j is equal to 16.7 ms. Hence, the coulometric response is characterized by a S/N which increases with increasing values of t_i = k 16.7 ms (k = integer) and this increase in S/N is a result of increased signal strength and is not due to a decrease in the noise component.

The use of the integration of the transient amperometric response for the minimal value of t_i = 16.7 ms in pulsed amperometric techniques is out of necessity for minimizing noise; however, the goal remains that of approximating the amperometric signal at some time value following application of a potential pulse. The fact that the integrated amperometric response for t_i >> 16.7 ms, when divided by t_i, does not give a meaningful approximation of the transient amperometric response caused us to plot the integrated signal (coulombs) as a function of real time (t). Hence, we name the technique ***pulsed coulometric detection*** (PCD) when applied to FI and LC systems. As with PAD, several variations of the applied potential waveform are possible. Here, we discuss PCD with $t_i >> 16.7$ ms for a constant detection potential. The increase in S/N for PCD (i.e., $k >> 1$) as compared to PAD (i.e., $k = 1$) can be estimated directly from a comparison of the integration times for the two experiments:

$$\frac{(S/N)_{PCD}}{(S/N)_{PAD}} = \frac{t_{i_{PCD}}}{t_{i_{PAD}}} = \frac{t_{i_{PCD}}}{16.7} = k \qquad [5]$$

where t_i values are expressed in ms. In effect, a ten-fold increase in integration time for a constant current signal should yield a ten-fold increase in S/N. This approximation (Eqn. 5) becomes exact only for systems which yield a steady-state amperometric response. Smaller improvements are expected for more complicated detection mechanisms in which diffusional transport has not yet achieved a steady-state value following a potential step, i.e., short time, and where surface fowling and catalytic deactivation cause a significant attenuation of the signal below the steady-state value during the detection period. Hence, improvements in PCD over PAD are not expected to be as large as predicted by Eqn. 5 for these complex systems.

The waveform for pulsed coulometric detection is summarized in Fig. IX-1. At the detection potential E_1 (period

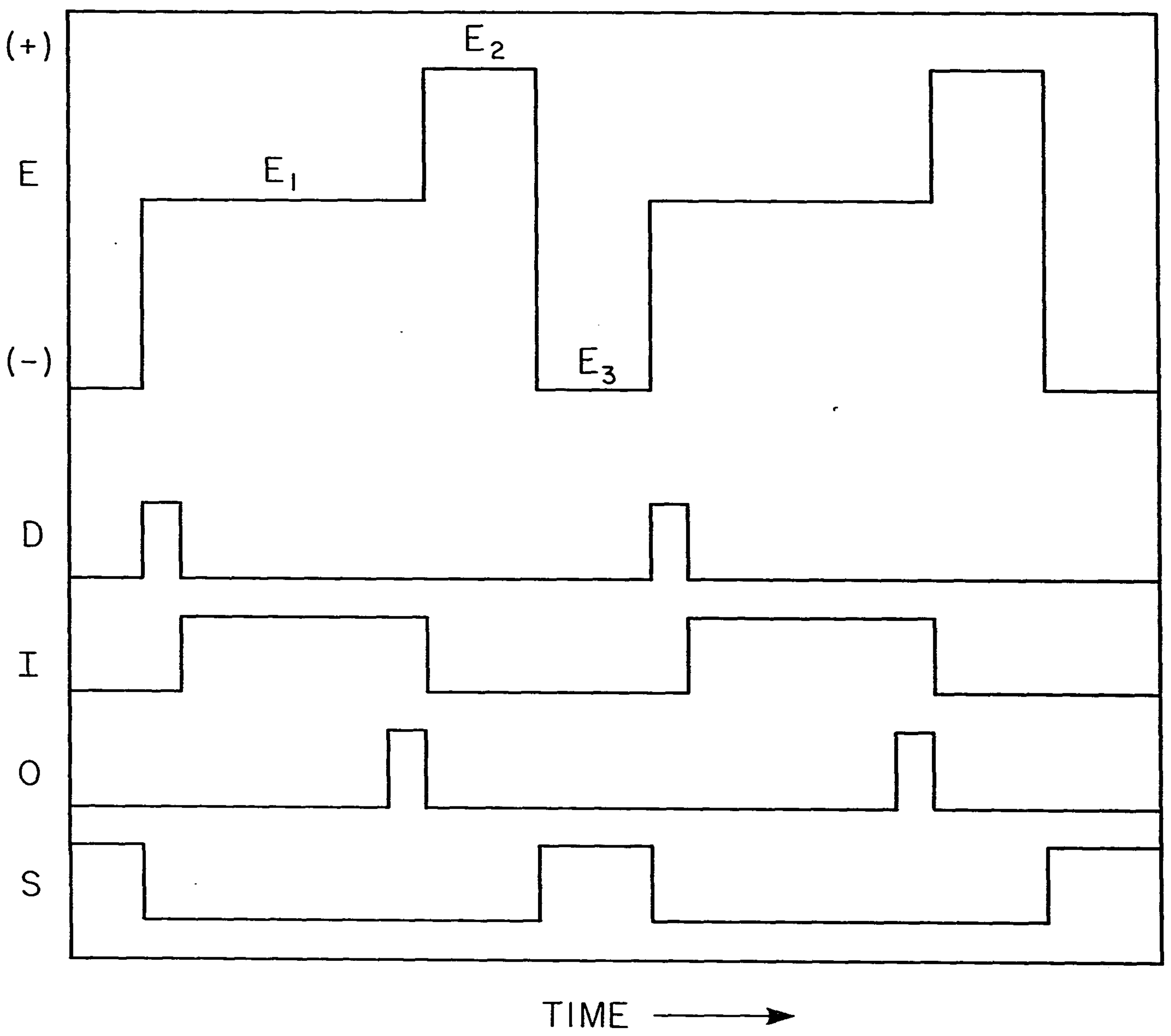
Figure IX-1. Potential-time profile for the three-step waveform used in PCD at a constant detection potential

Timing parameters: (D) delay time before integration;

(I) integration time;

(O) sampling time for signal output;

(S) shorting time of integrator.


(+)
E
(−)
E_2
E_1
E_3
D
I
O
S
TIME

t_1), integration is performed for a period t_i (digital control I in Fig. IX-1) by an analog integrator. The integral is sampled for 16.7 ms (digital control O) during the last 18 ms of period t_i in t_1. A delay period t_d in t_1 (digital control D) is added prior to the start of the integration period for discrimination against the background currents i_{ox} and i_{dl}; hence, $t_1 = t_d + t_i$ After the detection period, the potential is stepped to a more positive value E_2 (period t_2) to ensure anodic removal of all adsorbed detection products, reactants or solution impurities. The surface is renewed further by the negative step of potential to E_3 which results in the cathodic dissolution of surface oxide with concomitant adsorption of analyte. At E_3 (period t_3) the integrator is reset (digital control S) prior to the start of the new cycle. This waveform differs from PAD only in the width of the integration period t_i at the end of t_1 for E_1.

D. Experimental

1. *Instrumentation*

The computer-controlled pulsed amperometric and pulsed coulometric instrumentation was based on two Hewlett Packard computers (models 86B and 6942A) coupled to a Model 174A potentiostat (EG&G Princeton Applied Research Corporation, Princeton, NJ) via a home-built interface. The basic computer system has been described[7] and differs only in the addition of the circuitry needed to accomplish digital control of analog integration. The power of the system lay in the coupling of two computers with the microcomputer in control of all waveform variables, based on user-defined criteria, whereas the mainframe had the sole task to output the predefined waveform and acquire and store data at specified times. This allowed for the two computers to work relatively independent of each other resulting in improved precision and rate of data acquisition.

The interface between the potentiostat and 6942A mainframe contained circuits for amplification, integration, control of electrode rotation speed, and sample-and-hold operations. Analog signal integration was accomplished after the current at the working electrode was converted to a proportional voltage and amplified. The integration cycle was initiated by the closing of a signal switch concurrently with the opening of a shorting switch. At the close of the integration cycle, the opposite switching operation was performed after the output had been sampled by the S&H circuit for 16.67 ms. This latter signal was monitored by a recording device or sampled by an A/D converter. Alternately, the amperometric response could be sampled by measuring the output voltage of the I/E converter. All operations were controlled via simple BASIC statements from the microcomputer which posed no speed limitations because of the independent nature of the coupled computer systems.

The flow injection (FI) system was based on a low-pressure peristaltic pump with computer controlled injection of samples and has been described.[7] The flow-through detector for FIA studies (Dionex Corporation, Sunnyvale, CA) was of the thin-layer design containing a Au indicating (0.02 cm^2), glassy carbon counter and reference electrodes. The normal Ag/AgCl reference electrode was substituted by a miniature SCE electrode (Fisher Scientific, Fair Lawn, NJ) connected to the reference port of the flow-through detector by a home-built interface constructed from Kel-F.

Charge-potential (q-E) plots were obtained by the application of a three-step PCD waveform (Fig. IX-1) with variation of the detection potential E_1 at a gold rotated disk electrode (RDE, 0.005 cm^2, Pine Instrument Co., Grove City, PA) mounted in a model MSR rotator (Pine Instrument Co.) under computer control.

2. *Chemicals*

All solutions were prepared from reagent grade chemicals (Fisher Scientific, Fair Lawn, NJ) and deionized/triply distilled water. The supporting electrolyte was 0.20 M NaOH. Due to the slow decomposition of carbohydrates in alkaline media, solutions were prepared just prior to use. Where applicable, dissolved oxygen was removed by purging with reagent grade nitrogen (99.99%, Cooks Inc., Algona, IA).

E. Results and Discussion

An understanding of the expected increase in S/N for PCD in comparison to PAD can be obtained with the application of these techniques to the detection of $Fe(CN)_6^{4-}$ in H_2SO_4. The anodic response for $Fe(CN)_6^{4-}$ is characterized by mass-transport limited currents in a region of applied potential where no appreciable Au oxide is formed. Furthermore, the reaction does not suffer from surface fouling caused by adsorption of reaction products. The plot of the peak value of charge (q_p) vs. t_i obtained with the FI system (Fig. IX-2) is linear for t_i = 100-1000 ms. The linearity of q_p vs. t_i is characteristic of a steady-state, mass-transport limited response at the RDE for t_i > 100 ms. The background noise level does not change with a change in t_i. Both of these observations are consistent with the conclusion that S/N increases as a result of an increased signal strength and is not due to a decrease in the noise.

The primary motivation for the development of PCD was an increased linear dynamic response resulting from the lowering of detection limits. The nonlinear response of FI-PAD for detection of glucose and fructose at concentrations above 0.1 m$\underline{M}$ is shown by the normalized plots in Fig. IX-3, where N is a normalization constant which was chosen so $N''i_p/C^b = 1$ for the linear response obtained at a bulk concentration C^b < 0.1 m$\underline{M}$. Nonlinear response at high C^b is the result of electrode

Figure IX-2. Charge response as a function of the integration time by PCD for 3 m$\underline{M}$ ferrocyanide in 0.18 $\underline{M}$ H_2SO_4

Waveform:

E_1 = 0.90 V (t_i varied; t_d = 1 μs)
E_2 = 1.70 V (t_2 = 200 ms)
E_3 = 0.40 V (t_3 = 200 ms)

Conditions:

0.50 mL min^{-1} flow rate
50 μL sample injected

Curves:

(●) Peak charge response

(▲) Peak-to-peak background noise

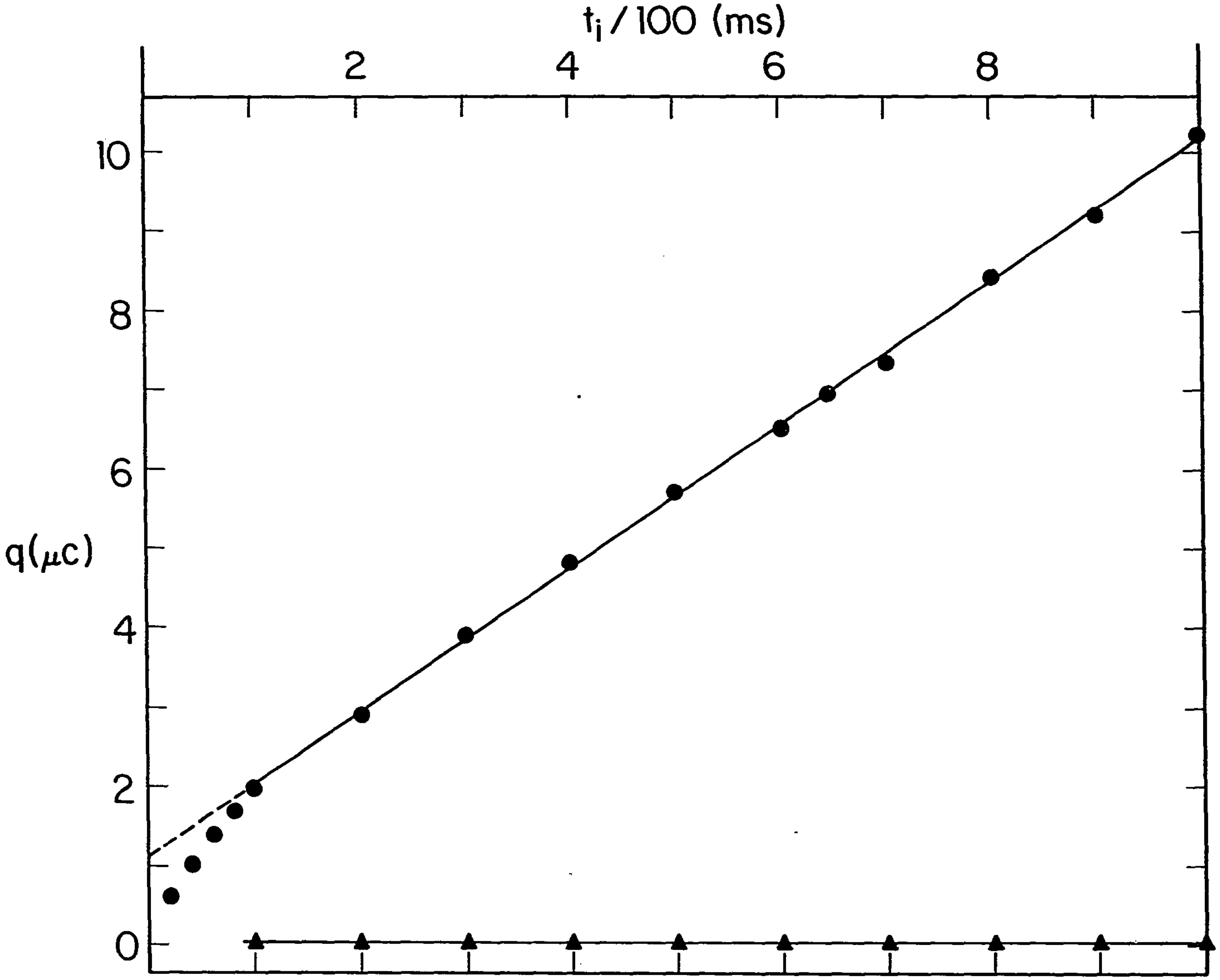

t_i / 100 (ms)
2
4
6
8
q(μc)
10
8
6
4
2
0

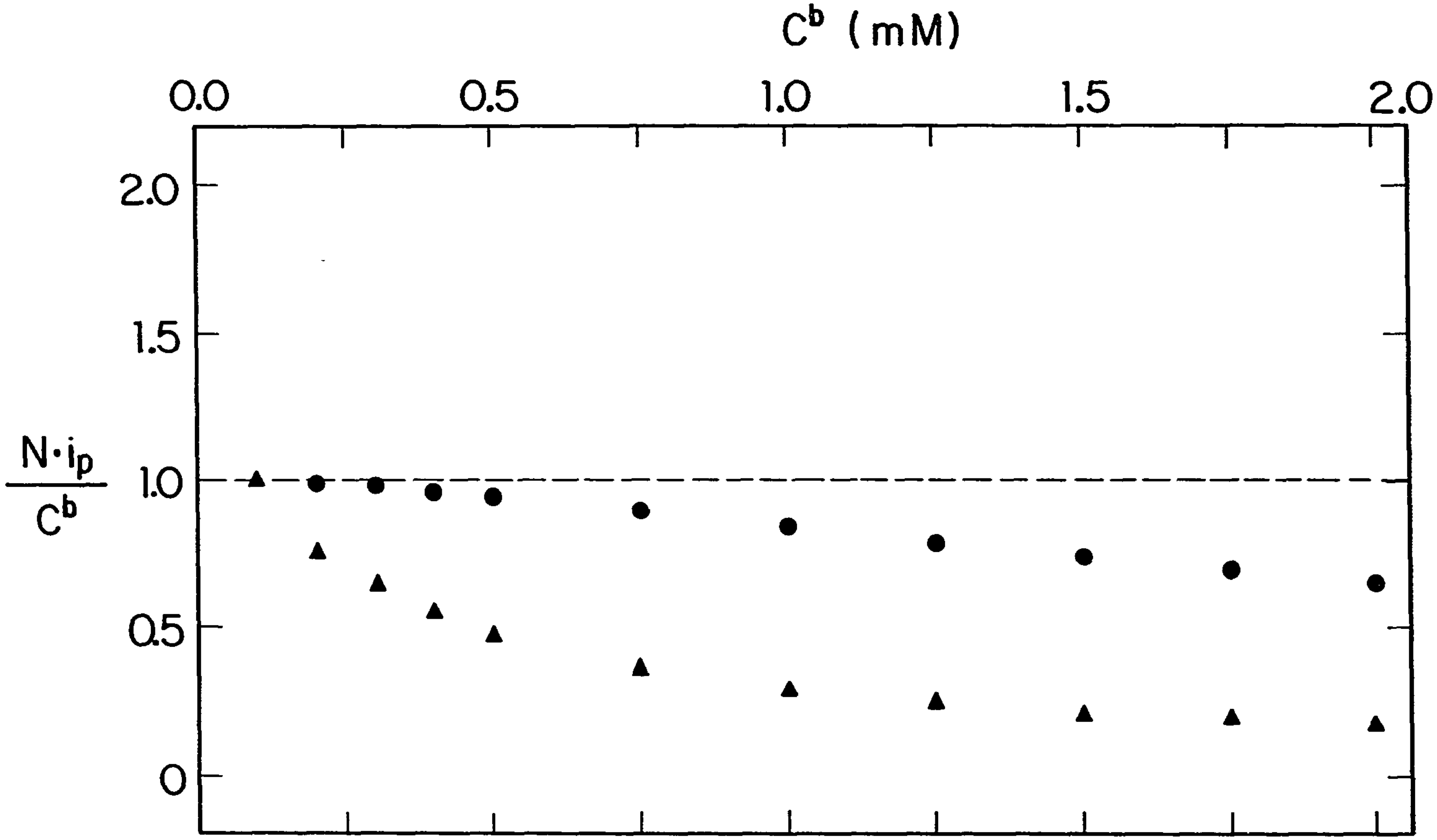
Figure IX-3. Normalized calibration plots by FI-PAD for glucose and sucrose obtained with a three-step PAD waveform in 0.20 M NaOH

Waveform:
E_1 = 0.175 V (t1 = 250 ms)
E_2 = 0.75 V (t_2 = 100 ms)
E_3 = -1.00 V (t_3 = 100 ms)

Conditions:
0.50 mL min^{-1} flow rate
50 μL sample injected

Curves:
(●) Normalized peak current response of glucose (N = 5.32 x 10^{-2} mM μA^{-1})

(▲) Normalized peak current response of sucrose (N = 5.00 x 10^{-2} mM μA^{-1})



C^b (mM)
0.0
0.5
1.0
1.5
2.0
2.0
1.5
$\frac{N \cdot i_p}{C^b}$
1.0
0.5
0

fouling during the detection process by adsorbed detection product. The detection limits in this case (50-μL samples) were ca. 0.035 m$\underline{M}$ for glucose and 0.050 m$\underline{M}$ for sucrose. The linear dynamic response is very limited for these compounds by PAD, i.e., less than one decade.

The implementation of PCD, with particular emphasis upon background rejection, is simplified after examination of q - E plots for glucose at a RDE in 0.20 $\underline{M}$ NaOH (Fig. IX-4). At the potential of maximum response, ca. 0.175V vs. SCE, there is very little background charge; that observed is due only to charging of the double layer. Normalized calibration plots for glucose and sucrose are shown in Fig. IX-5 for PCD in the FI system using a waveform of E_1 = 0.175V (t_1 = 500 ms, t_d = 1 μs, t_i = 500 ms), E_2 = 0.75V (t_2 = 200 ms), and E_3 = -1.0V (t_3 = 200 ms). The plots are linear over the concentration range of 5-50 $\mu\underline{M}$ with intercepts of 1.0 which correspond to intercepts of 0.0 in the more common q_p - C plots. Based on studies of the effects of scan rate and rotation speed at a Au rotated disk electrode, it is concluded that adsorption of the carbohydrate at E_3 contributes an insignificant amount to the signal measured at E_1. Furthermore, at these low concentrations, fouling of the surface by adsorption of reaction products is minimal.

It is apparent from the normalized calibration plots that the detection limits for PCD have been greatly lowered as compared to PAD. For direct comparison of detection limits

Figure IX-4. Charge-potential plots by PCD for 1.0 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH

Waveform:
E_1 = varied (t_1 = 500 ms; t_d = 1 μs)
E_2 = 0.75 V (t_2 = 200 ms)
E_3 = -1.00 V (t_3 = 200 ms)

Conditions:
0.50 mL min^{-1} flow rate
50 μL sample injected

Curves:
[A] Air sat'd 0.20 $\underline{M}$ NaOH;
[B] N_2 sat'd 0.20 $\underline{M}$ NaOH;
[C] Air sat'd 1.0 m$\underline{M}$ glucose/0.20 $\underline{M}$ NaOH;
[D] N_2 sat'd 1.0 m$\underline{M}$ glucose/0.20 $\underline{M}$ NaOH.

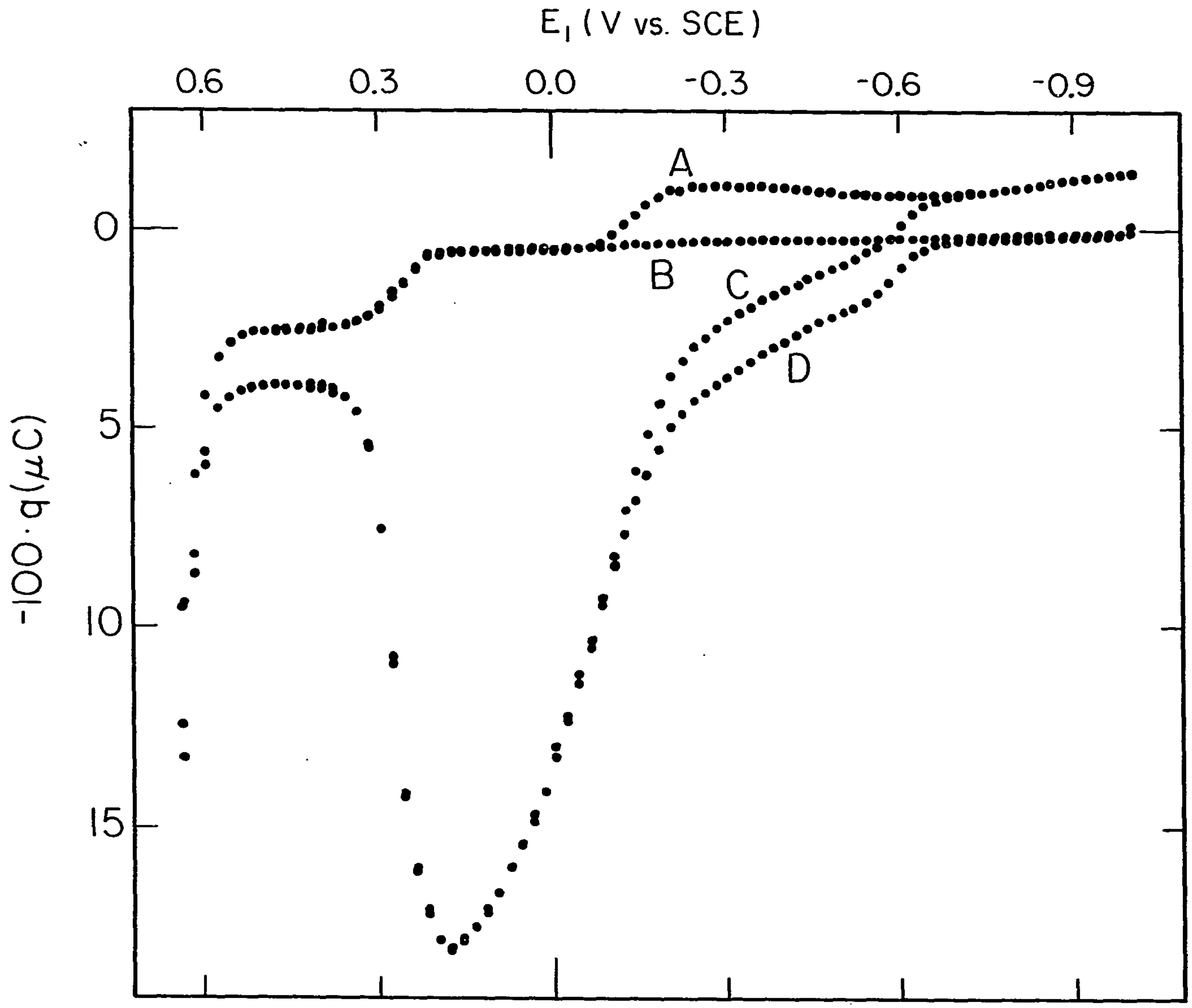
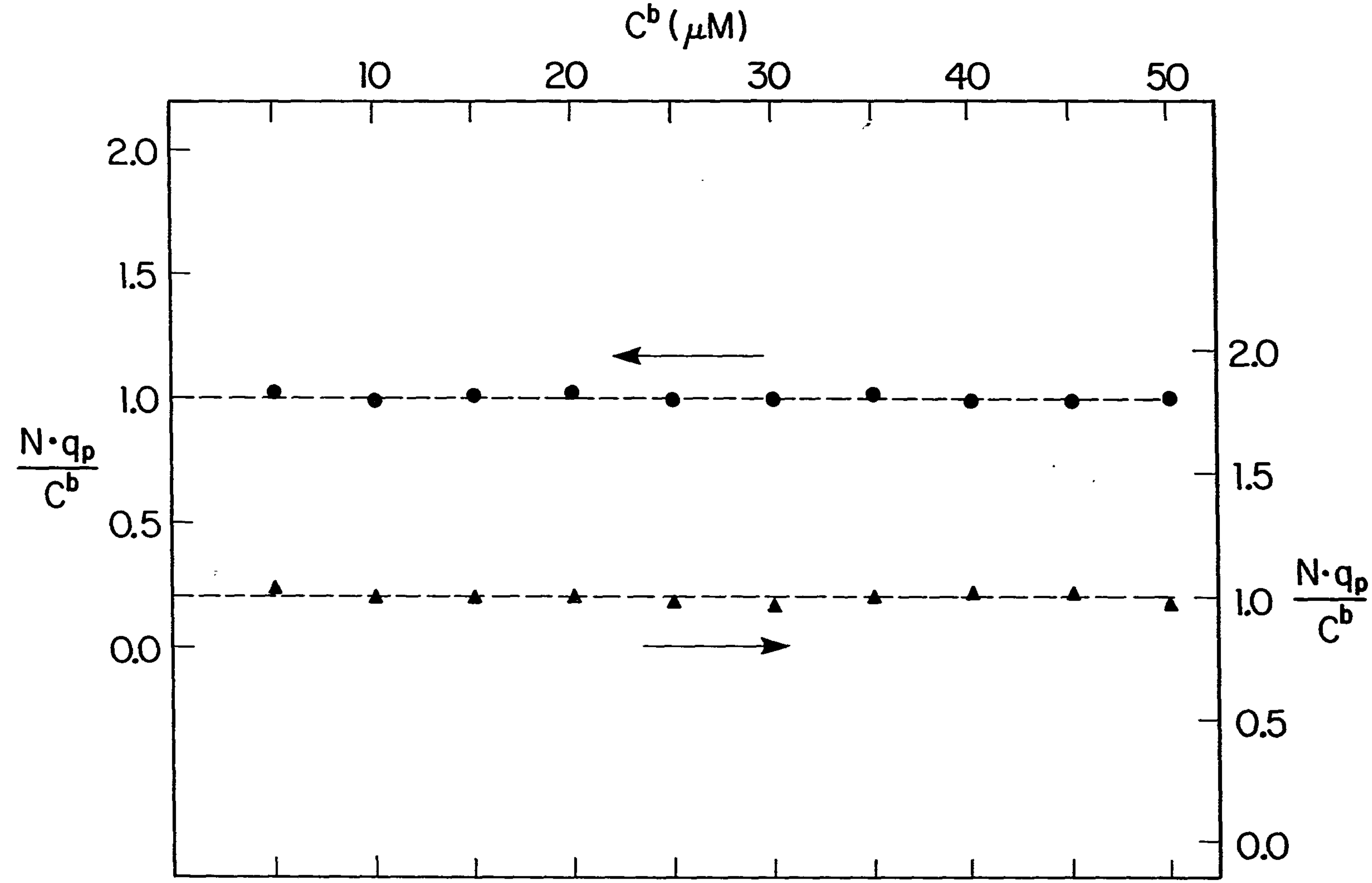

E$_1$ (V vs. SCE)
0.6
0.3
0.0
-0.3
-0.6
-0.9
-100·q(μC)
0
5
10
15
A
B
C
D

Figure IX-5. Normalized calibration plots by FI-PCD for glucose and sucrose in 0.20 M NaOH

Waveform:
E_1 = 0.175 V (t_i = 500 ms; t_d = 1 μs)
E_2 = 0.75 V (t_2 = 200 ms)
E_3 = -1.00 V (t_3 = 200 ms)

Conditions:
0.50 mL min^{-1} flow rate
50 μL sample injected

Curves:
(●) Normalized peak charge response for glucose (N = 6.19 x 10^1 μM $\mu coul^{-1}$)
(▲) Normalized peak charge response for sucrose (N = 9.42 x 10^1 μM $\mu coul^{-1}$)



C^b (μM)
10
20
30
40
50
2.0
1.5
1.0
0.5
0.0
$\frac{N \cdot q_p}{C^b}$
2.0
1.5
1.0
0.5
0.0
$\frac{N \cdot q_p}{C^b}$

between the methods of PCD and PAD, a well worked electrode was used, i.e., further surface reconstruction over the time period of the comparison was negligible. Detection limits (S/N = 2) obtained for glucose and sucrose by PAD were 0.035 m$\underline{M}$ and 0.05 m$\underline{M}$, respectively. Detection limits for glucose and sucrose by PCD were found to be 1.0 $\mu\underline{M}$ and 2.5 $\mu\underline{M}$, respectively. The decrease in detection limits of 20-35X reported here was typical of those obtained for other monosaccharides, e.g., sorbitol and fructose. The upper values of C^b at which negative deviation from linear response occurred were virtually the same for PCD and PAD. Hence, the linear dynamic range for glucose by PCD was ca. 2.2 decades and, for sucrose, ca. 1.7 decades. A comparison of the S/N obtained for 35 $\mu\underline{M}$ glucose utilizing both methods of detection is shown in Fig. IX-6.

F. Conclusions

The improvement in detectability and linear dynamic range observed here for PCD, in comparison to PAD, was demonstrated for only one class of compounds, carbohydrates. Similar improvements are to be expected for all classes of compounds for which PAD has been found applicable.

G. Acknowledgements

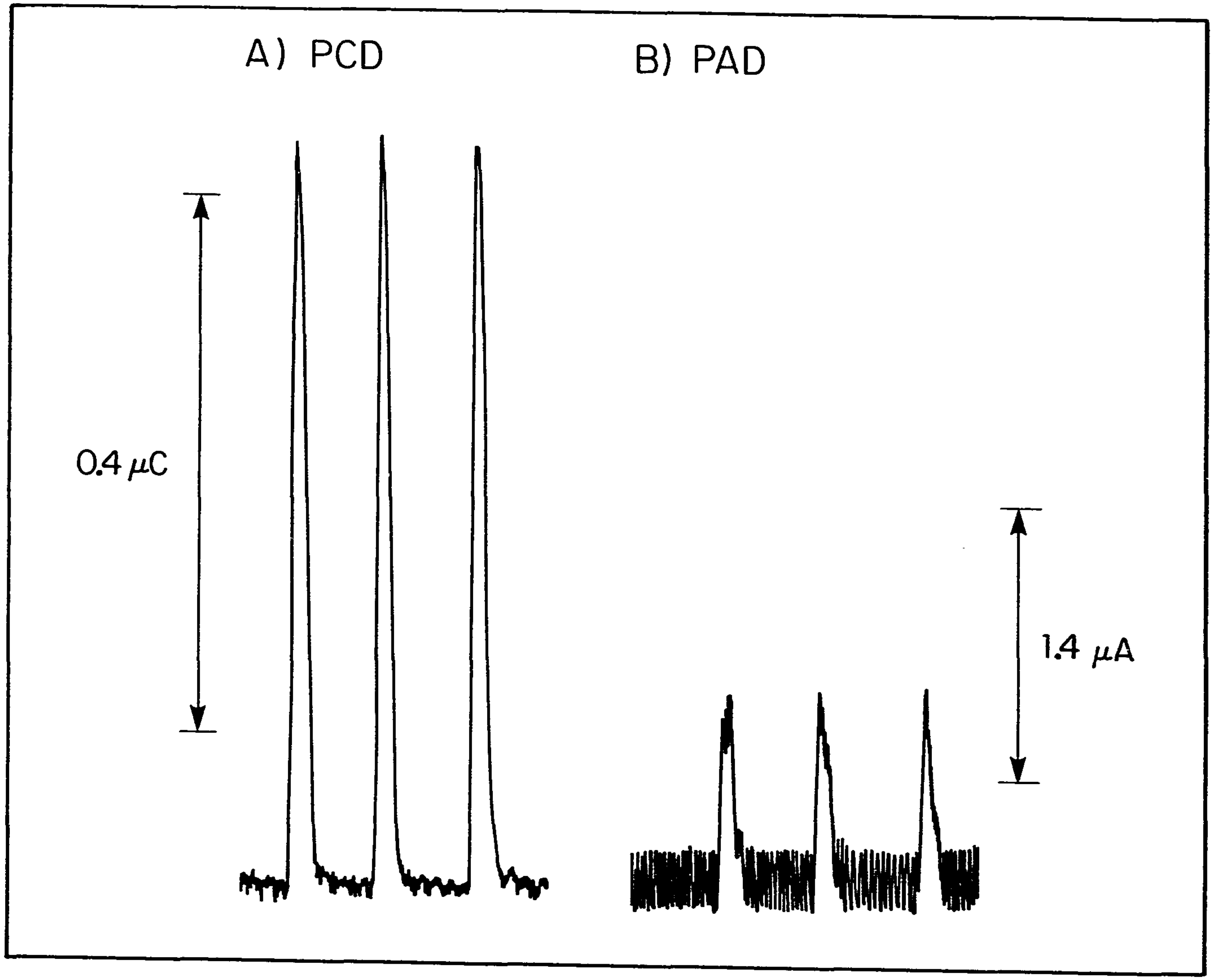
The authors gratefully acknowledge Rob Synovec for his enlightening discussions of concepts included here.

Figure IX-6. Comparison of the peak response obtained by FI-PAD and FI-PCD for 35 $\mu\underline{M}$ glucose

PCD waveform: $E_1 = 0.175$ V ($t_i = 500$ ms; $t_d = 1$ μs)
$E_2 = 0.75$ V ($t_2 = 200$ ms)
$E_3 = -1.00$ V ($t_3 = 200$ ms)

PAD waveform: $E_1 = 0.175$ V ($t_1 = 250$ ms)
$E_2 = 0.75$ V ($t_2 = 100$ ms)
$E_3 = -1.00$ V ($t_3 = 100$ ms)

Conditions: 0.50 mL min^{-1} flow rate
50 μL sample injected


A) PCD
B) PAD
0.4 μC
1.4 μA

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The development of pulsed waveforms for the electrochemical detection of inorganic and organic compounds in flow-injection analysis and liquid chromatography

by

Glen Gary Neuburger

Volume 2 of 2

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

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Major: Analytical Chemistry

Approved:

In Charge of Major Work

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For the Major Department

D. J. Zaffarano
For the Graduate College

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Ames, Iowa

1987

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X. POTENTIAL-SWEEP PULSED COULOMETRIC DETECTION OF SULFUR COMPOUNDS AND CARBOHYDRATES IN NEUTRAL AND ALKALINE MEDIA

A. Abstract

Prior applications of pulsed amperometric and pulsed coulometric methods of detection (PAD and PCD) for various organic compounds have been restricted to carrier streams of fixed pH in flow-injection systems and isocratic elution in liquid chromatography. In addition, these methods frequently required the utilization of offset circuitry to compensate for large background signals resulting from electrode oxide formation or oxygen reduction. A technique is presented here which is compatible with pH gradient chromatography with exact background rejection. The technique is demonstrated for flow-injection detection of carbohydrates in alkaline media and sulfur compounds in neutral and alkaline media.

B. Introduction

With the advent of more complex liquid chromatographic techniques which employ a variety of gradient elution methods, it is necessary to develop detectors which are capable of sustaining sensitivity and detectability with changes in the composition of the mobile phase. Many detectors are capable of this feat but few can reject automatically the accompanying variation in background signal.

Detectors commonly used for carbohydrates cannot be used in pH-gradient liquid chromatography (LC) because they are inherently affected by changes in ionic strength. Absorption detection fails in two respects. First, direct photometric detection of carbohydrates is difficult owing to the absence of π-bonding and generally requires pre-injection or post-column derivatization. Second, the measured absorbance is a function of the refractive index (η) of the solution, and large changes in η can cause a baseline shift. Refractive index detection is strongly affected by concentration gradients and the baseline shift observed for a large change in ionic strength, e.g., $\Delta\mu$ = 0.5$\underline{M}$, would overwhelm the detection of small analyte concentrations.

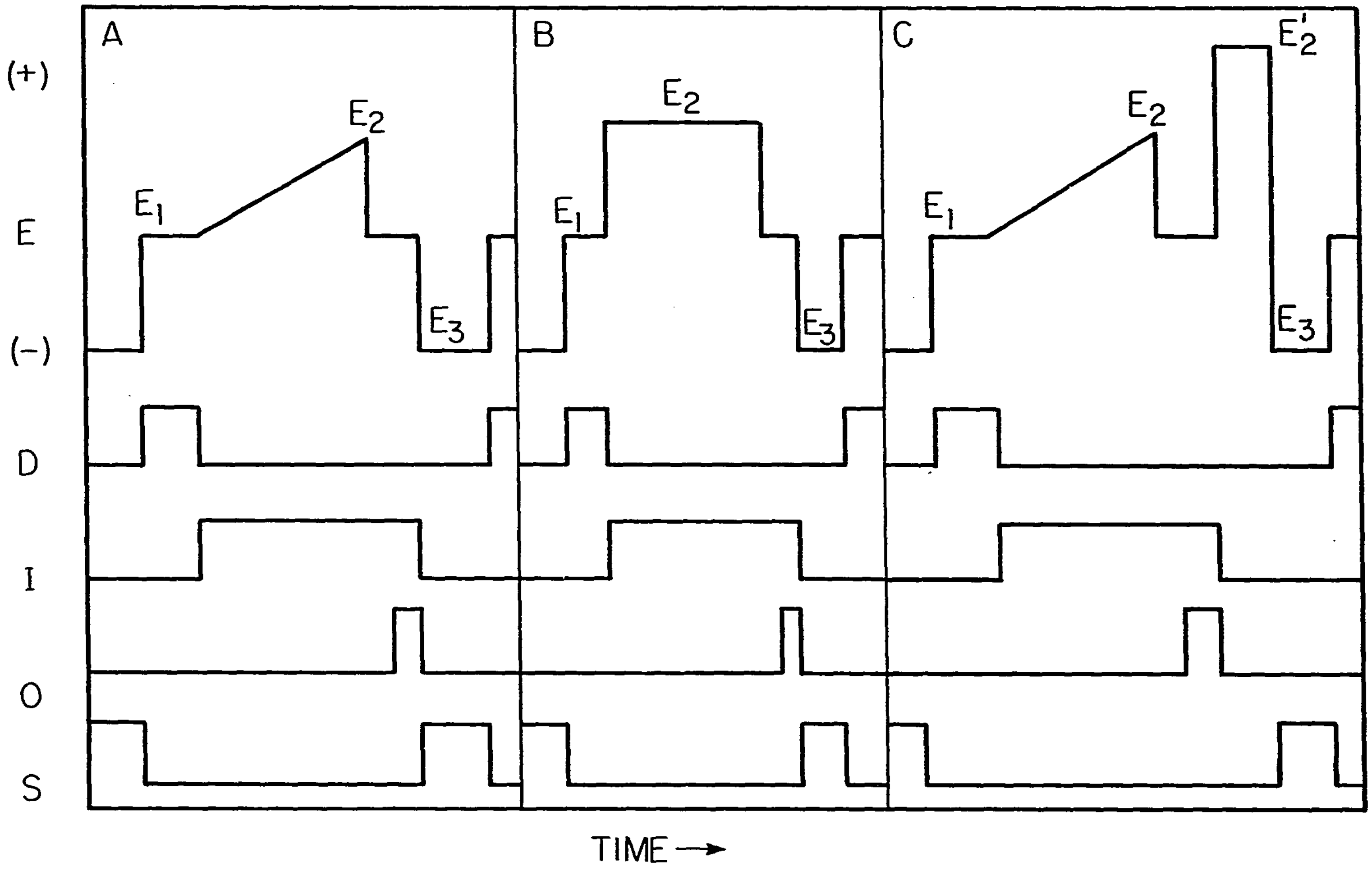
The methods of pulsed amperometric detection[1-13] (PAD) and, more recently, pulsed coulometric detection[14] (PCD) have been introduced for detection of numerous aliphatic organic compounds in conjunction with flow-injection (FI) analysis and liquid chromatography. Additionally, several papers have appeared recently dealing with the low-frequency electrochemical pretreatment of solid electrodes.[15-22] However, the ability of any of these techniques to resist even a slight pH change is strongly dependent on the selection of the detection potential and electrode material. In fact, PAD at a Pt electrode in a FI system has been demonstrated for the determination of pH changes in caustic media.[23] We now present ***potential-sweep pulsed coulometric detection*** (PS-PCD) for use in analytical schemes utilizing pH-gradient or pH-step elution.

Schematic diagrams of the waveforms used to accomplish PS-PCD are shown in Figs. X-1A and X-1B. The waveform is quite different than those previously presented for PAD and PCD[14] at constant detection potentials. Upon stepping from the adsorption-reset potential (E_3) to the initial detection potential (E_1), the analog integrator is activated (digital control I) after a time delay t_d (digital control D). The electrode potential is then scanned to the value E_2 ($E_2 > E_1$) during the period t_2. Subsequently, the potential is stepped back to E_1 for a time period t_1 during which the oxide formed for the scan to E_2 is cathodically stripped. The integrator is active for the entire sequence of changing the applied potential from E_1 to E_2 and back to E_1. At the end of the detection cycle ($t_{det} = t_d + t_2 + t_1$), the output signal from the integrator is measured for 16.7 ms (to discriminate against 60 Hz line noise) and fed to a recording device (digital control O). Finally, the potential is stepped to a more negative value (E_3) where the integrator is reset prior to the next cycle of the waveform (digital control S). Adsorption of the analyte can occur at E_3 and, for a sufficiently long period t_3, the concentration of analyte in the diffusion layer can become reestablished to the bulk analytical concentration, i.e., $C^s = C^b$ for $t_3 >> 0$.

The rate of potential sweep from E_1 to E_2 (period t_2) is

Figure X-1. Potential-time profiles for the PS-PCD waveforms

Timing parameters:	(D) delay time before integration;
	(I) integration time;
	(O) sampling time for signal output;
	(S) shorting time of integrator.


A
B
C
(+)
E
(−)
D
I
O
S
E_1
E_2
E_3
E'_2
TIME →

variable and in the extreme case of a very fast sweep is effectively a potential step, as illustrated in Fig. X-1B. The waveform in Fig. X-1B has been found to be particularly useful for surface-controlled reactions such as the anodic detection of sulfur compounds at a Au electrode. However, E_2 is chosen always to be sufficiently positive to achieve oxidative removal (cleaning) of adsorbed analyte(s) and/or detection products with simultaneous formation of surface oxide. The value of E_2 should not be so large as to cause significant evolution of O_2. In the event that the time period t_2 at potential E_2 does not provide sufficient cleaning of the electrode, an additional "step" can be added to the waveform ($E_2' > E_2$) immediately following the detection period and prior to the step to E_3 (see Fig. X-1C). It is the incorporation of such an oxidative cleaning step following the detection cycle which has been characteristic of PAD and PCD at Pt and Au electrodes.[1-14]

The beneficial feature of baseline rejection results because the anodic charge for surface oxide formation ($q_{a,ox}$) during the change $E_1 \rightarrow E_2$ is automatically countered by the cathodic charge for oxide reduction ($q_{c,ox}$) with the change $E_2 \rightarrow E_1$. Baseline rejection is exact if $q_{c,ox} = -q_{a,ox}$. Sensitivity for detection of analyte is greatest if the anodic process is totally irreversible such that no cathodic signal is obtained for reduction at E_1 of the products of oxidation for the change $E_1 \rightarrow E_2$.

C. Experimental

1. Instrumentation

All data were obtained with a computer controlled PAR 174A potentiostat (Hewlett Packard, Palo Alto, CA; EG&G Princeton Applied Research Corporation, Princeton, NJ). This system has been described in detail for PAD[7] and PCD[14] at constant detection potentials. The definition of the PS-PCD waveform, as well as the timing and switching circuitry, was under software control.

For the waveform in Fig. X-1A, it was necessary to simulate the voltage ramp by a low amplitude staircase waveform. However, this resulted in the necessity of choosing between optimal frequency of the waveform (i.e., < ca. 1 Hz.), and the desire for simulating the anodic voltage ramp with small voltage increments, ΔE; the paradox being a result of the finite time necessary for passing instructions from one computer to the other. The optimal values of waveform frequency and sweep rate for this work were determined to be ca. 0.5 Hz and 600-1500 mV s^{-1}, respectively. Typically, then, $E_2 - E_1 \cong 1$ V, and $\Delta E = 50$ mV.

The FI system used in carbohydrate studies was of all-steel construction to allow for elimination of dissolved O_2 by purging the mobile phase in the storage container with dispersed N_2, if desired. The FI system consisted of a reciprocating pump (LDC Milton Roy mini Pump, Riviera Beach, FL), in line with a pulse dampener, a six-port sample injection valve (Rheodyne Inc., Cotati, CA), and the electrochemical cell. The FI system used in conjunction with detection of sulfur compounds has been described[14] and is based on the use of a peristaltic pump and Teflon tubing; the presence of dissolved oxygen did not interfere in these studies.

The electrochemical cells were of either the "wall-jet" design (Oxford Electrodes, Rochester, England) or the "thin-layer" design (Dionex Corporation, Sunnyvale, CA) with ca. 0.005-cm^2 Au working electrodes. For both cells, a SCE was substituted for the manufacturer supplied Ag/AgCl reference electrode to reduce problems associated with "bleeding" of electrolyte across the reference junction.

Staircase voltammograms were obtained at a Au rotated disk electrode (RDE; 0.005 cm^2; Pine Instrument Co., Grove City, PA) mounted in a model MSR rotator (Pine Instrument Co.). The staircase waveform was applied with 20-mV increments at 18-ms intervals (i.e., ca. 4.8 V min^{-1}); current integration occurred for the last 16.67 ms of each step. Charge-potential (q-E) plots were obtained by analog integration of the amperometric response produced by the application of a staircase waveform. PAD voltammograms were obtained by the application of a three-step waveform with variation of the detection potential in 20-mV increments. All potentials are reported versus the SCE reference electrode.

2. *Chemicals*

Solutions were prepared from reagent grade chemicals (Fisher Scientific, Fair Lawn, NJ) and water from a NANOpure II water purification system (Barnsted Company, Boston, MA). Alkaline carbohydrate solutions were prepared on the day of use to minimize their slow decomposition in this caustic media. Where noted, dissolved oxygen was removed by purging with reagent grade nitrogen (99.99%; Cooks Inc., Algona, IA).

D. Results and Discussion

1. *Equilibration of baseline signal*

The waveforms depicted in Fig. X-1 incorporate a sampling methodology which results in the rejection of background signal commonly observed for PAD and PCD at a constant detection potential which is caused by oxide formation at the electrode surface and as the result of charging of the double-layer. For example, the anodic charge from oxide formation for the positive potential step $E_1 \rightarrow E_2$ is subtracted automatically by the equivalent but opposite charge from the cathodic stripping of the oxide for the negative potential step $E_2 \rightarrow E_1$. The validity of this subtractive technique is supported by the observation of near-zero baselines and the speed at which the baseline returns to this equilibrium value following the mechanical polishing of the electrode surface. Commonly, the baseline is seen to reach its equilibrium value (zero) within ca. 20 cycles of the waveform applied to a freshly polished electrode (i.e., < 1 min, see Fig. X-2) and deviations from this value for a several-hour period is less than or equivalent to the magnitude of the high frequency noise on the background. A small uncompensated baseline may persist for three reasons: 1) A slight offset of the integrated-circuit devices; however, these are of no concern here due to the ease of their correction. 2) A very short period for the second application of E_1 (i.e., period t_1) may not permit complete cathodic removal of all surface oxide formed during the preceding change $E_1 \rightarrow E_2$. 3) In the case of an electrode material for which $q_{c,ox} \neq q_{a,ox}$, a baseline offset is expected; however, these offsets are anticipated to be far less severe than observed in PAD or PCD at a constant detection potential.

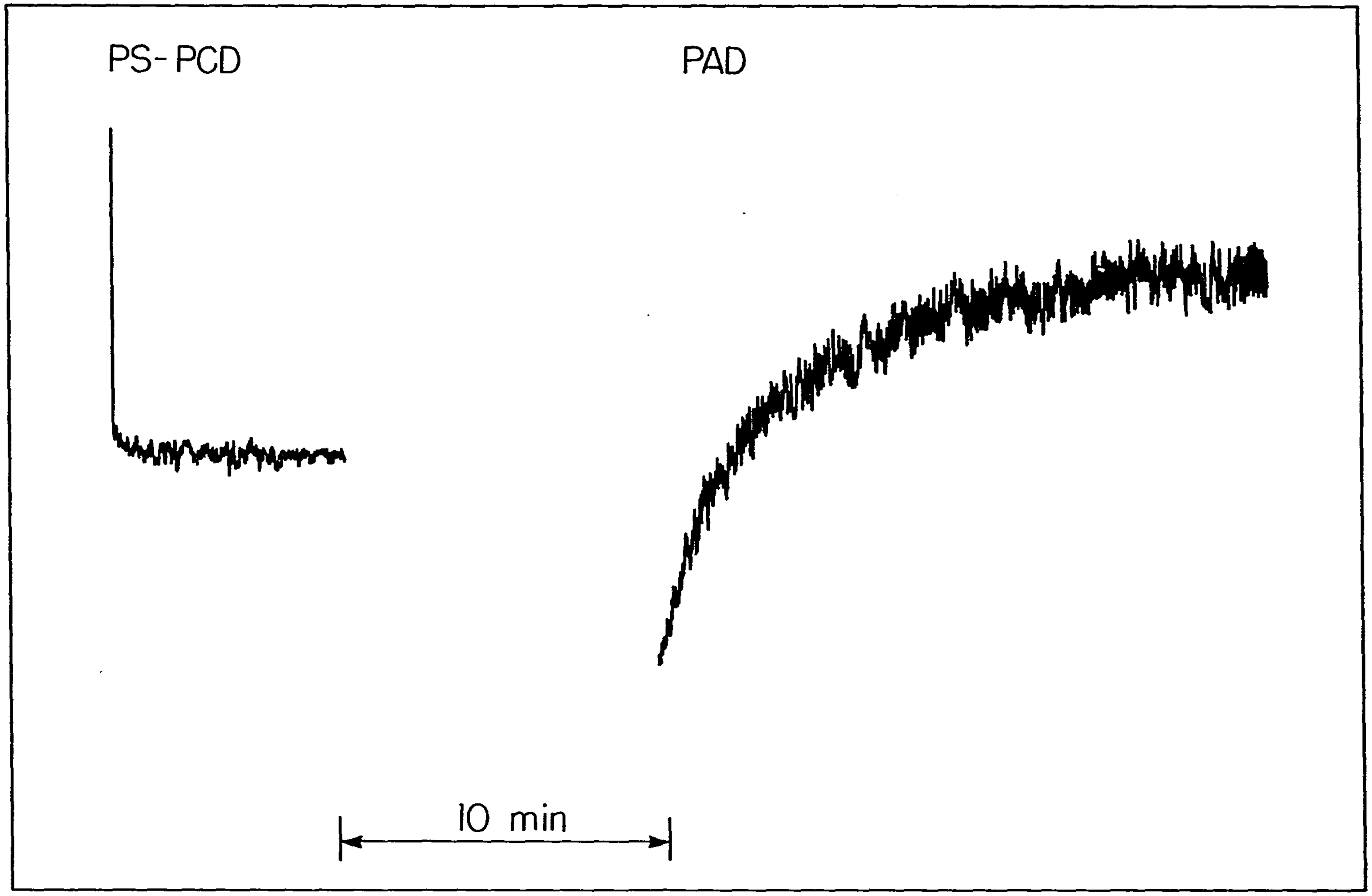
The rates of equilibration of the baseline for PS-PCD and PAD are contrasted in Fig. X-2 for a newly polished Au working electrode. It is seen that for PAD a minimum of ca. 10 min is required to attain a nearly constant baseline; however, a small baseline drift may persists for long periods of time, even hours. The equilibration rate and the degree of baseline drift for PS-PCD is virtually independent of the state of the electrode, i.e., whether the electrode has been "well-worked" or newly polished. The rate of equilibration was demonstrated for a newly polished electrode because of the inability to reproduce the state of a "well-worked" electrode; however, we hasten to point out that the rate of equilibration for a

Figure X-2. A comparison of the settling times for a newly polished Au RDE (0.005 cm^2) by PS-PCD and PAD in 0.25 M NH_4NO_3

PS-PCD waveform (1B): E_1 = 0.15 V (t_d = 100 ms; t_1 = 300 ms)
E_2 = 1.2 V (t_2 = 400 ms)
E_3 = -0.6 V (t_3 = 500 ms)

PAD waveform: E_1 = 1.0 V (t_1 = 400 ms)
E_2 = 1.2 V (t_2 = 300 ms)
E_3 = -0.6 V (t_3 = 500 ms)

Conditions: 0.5 mL min^{-1} flow rate


PS-PCD
PAD
10 min

"well-worked" electrode with PAD was observed to be substantially longer and the baseline drift was much more severe than depicted in Fig. X-2 (see Figs. X-5 and X-15 and associated discussions).

2. Detection of sulfur compounds

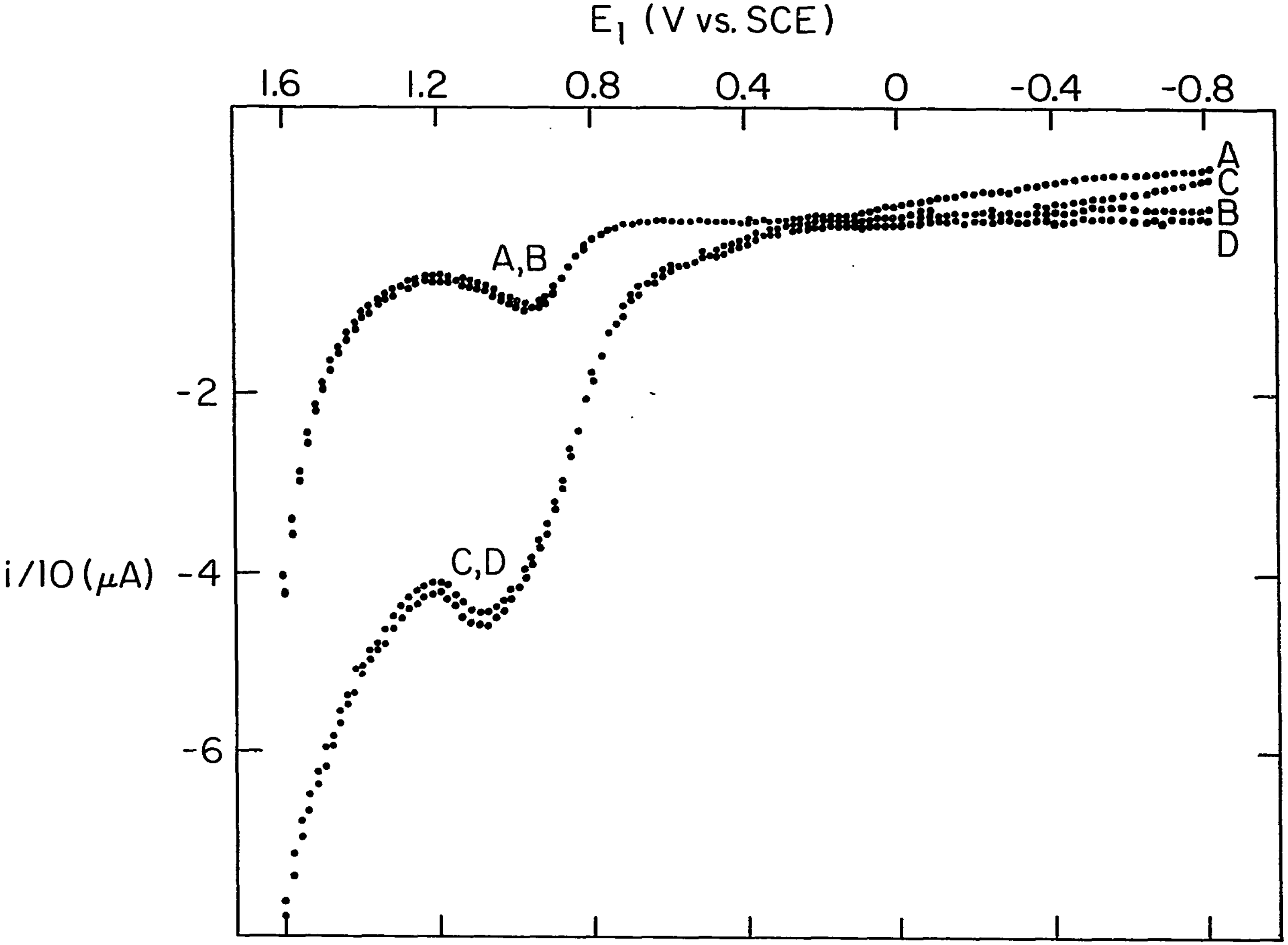
Sulfur compounds, in strong contrast to carbohydrates, exhibit a behavior which is controlled primarily by adsorption at potentials cathodic of the region for oxidation. This is illustrated by the PAD voltammograms of Fig. X-3 obtained with the variation of the detection potential E_1 by finite increments ΔE while holding all other parameters of this three-step waveform constant for each trace. Note, that thiourea is oxidized significantly (0.4 to 1.6 V) in the presence and absence of surface oxides; the molecules being pre-adsorbed at -0.8 V in this three-step waveform. The signal response (the difference between curves C and A), equivalent to that obtained with the application of this waveform to a FI or LC system, is essentially constant and independent of applied potential for E_1 in the range 1.0 to 1.5 V. This demonstrates the ability to use the potential-step waveform of Fig. X-1B in addition to the waveform of Fig. X-1A, with E_2 defined to be near the anodic limit of this region to maximize signal response for the PS-PCD waveform.

The signal measurement in PS-PCD for the detection of thiourea in 0.25 $\underline{M}$ NH_4NO_3 is demonstrated by the q - E plots of Fig. X-4 (curves C and D); these are contrasted with the

Figure X-3. PAD voltammograms for 1.0 mM thiourea in 0.25 M NH_4NO_3 obtained at a Au RDE (0.005 cm^2; 900 rev min^{-1})

Waveform:
E_1 = varied (t_1 = 250 ms)
E_2 = 1.6 V (t_2 = 100 ms)
E_3 = -0.80 V (t_3 = 500 ms)

Curves:
[A] Air sat'd 0.20 M NaOH;
[B] N_2 sat'd, 0.20 M NaOH;
[C] Air sat'd, 1.0 mM thiourea/0.20 M NaOH;
[D] N_2 sat'd, 1.0 mM thiourea/0.20 M NaOH.


E$_1$ (V vs. SCE)
1.6
1.2
0.8
0.4
0
-0.4
-0.8
A,B
C,D
A
C
B
D
i/10 (μA)
-2
-4
-6

staircase voltammograms (curves A and B). In the residual q-E trace (curve C), oxide is initiated on the anodic sweep at ca. 0.9 V and is subsequently stripped at ca. 0.4 V on the cathodic sweep. Thiourea begins to be oxidized at ca. 0.6 V (curve D) with the charge increasing rapidly up to the anodic limit. The net charge gained on the cathodic sweep for oxidation of thiourea contributes only slightly to the total charge; a result of the initial potential of oxidation of thiourea being positive of the stripping potential for surface oxide. Note, that the amount of oxide formed in the presence of thiourea is less than in its absence, i.e., the difference in the areas of the stripping peaks of curves A and B is non-zero. It is our general observation that the area of the cathodic peak for surface oxide formed is a function of bulk analyte concentration for many of the sulfur compounds. In the end, this can cause two errors in the experimentally determined calibration plots obtained by FI- or LC-PAD: 1) an overall error in the extrapolated y-intercepts, and 2) premature negative deviation; these effects being a result of incorrect baseline extrapolation for peak height or peak area measurement of the respective chromatograms. A representative example of this phenomenon is shown in Fig. X-5. The post-peak dips are a result of less surface oxide being formed in the presence of adsorbed thiourea, and, that a finite amount of time is required to "reactivate" the surface. For PS-PCD, the variation in surface oxide coverage is automatically

Figure X-4. Charge-potential and current-potential curves for 0.10 m$\underline{M}$ thiourea in 0.25 $\underline{M}$ NH_4NO_3 at a Au RDE (0.005 cm^2; 900 rev min^{-1})

Curves:
- [A] Staircase; N_2 sat'd 0.25 $\underline{M}$ NH_4NO_3;
- [B] Staircase; N_2 sat'd 0.1 m$\underline{M}$ thiourea/0.25 $\underline{M}$ NH_4NO_3;
- [C] Integrated staircase; N_2 sat'd 0.25 $\underline{M}$ NH_4NO_3;
- [D] Integrated staircase; N_2 sat'd 0.1 m$\underline{M}$ thiourea/0.25 $\underline{M}$ NH_4NO_3;

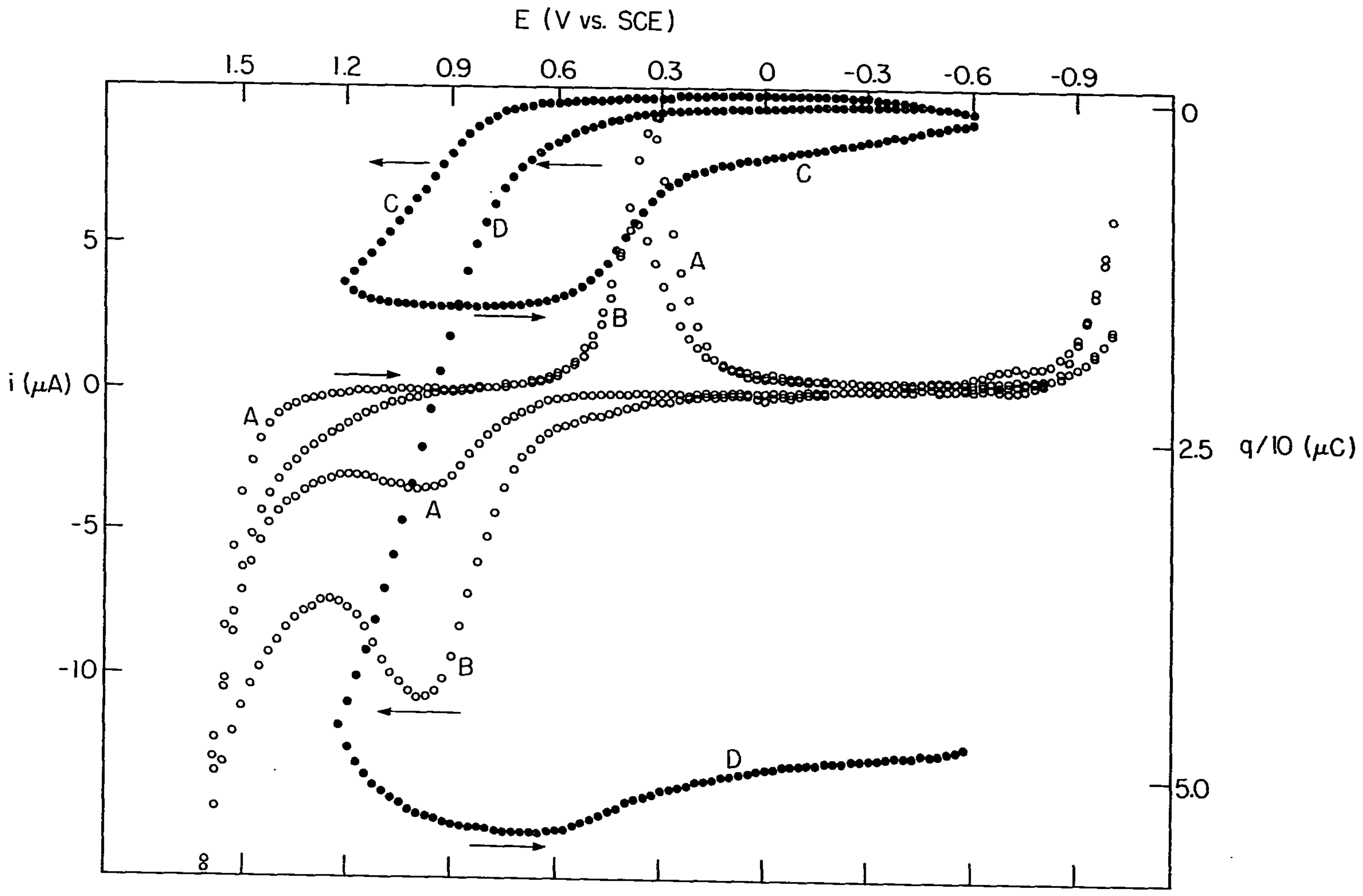

E (V vs. SCE)
1.5
1.2
0.9
0.6
0.3
0
-0.3
-0.6
-0.9
i (μA)
5
0
-5
-10
q/10 (μC)
0
2.5
5.0
A
B
C
D

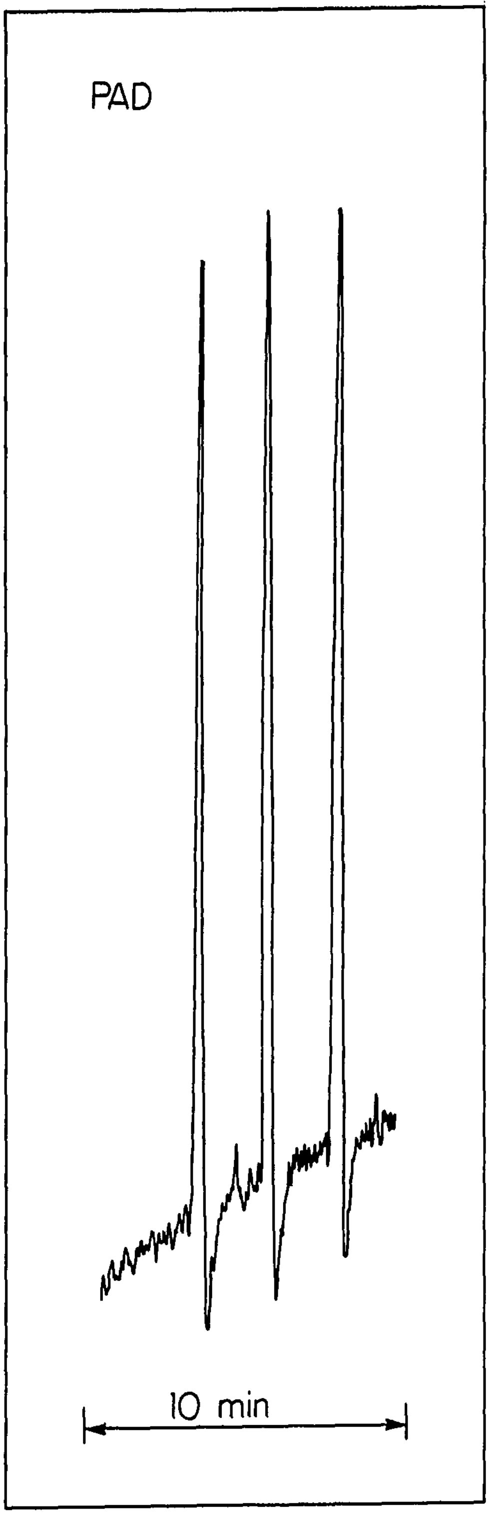
Figure X-5. Peak current response for 100 μM thiourea in 0.25 M NH_4NO_3 by PAD showing post-peak dips.

PAD Waveform:

E_1 = 1.0 V (t_1 = 400 ms)
E_2 = 1.2 V (t_2 = 300 ms)
E_3 = -0.6 V (t_3 = 500 ms)

Conditions:

0.50 mL min^{-1} flow rate
100 μL sample injected


PAD
10 min

compensated for, since all oxide formed at E_2 is subsequently reduced at E_1, the net charge for this process being zero.

To aid in the use of these waveforms in FIA and LC, it is necessary that the potential region for current integration be defined so as not to include currents resulting from solvent decomposition or reduction of dissolved oxygen. In 0.2 M NaOH (Fig. X-6A), the difference of the peak potential for oxide stripping at Au is ca. 200 mV positive of the half-wave potential for reduction of dissolved oxygen. With such a small potential region for definition of E_1, errors are expected for application in air saturated solutions. Unlike carbohydrates, which show a large decrease in reaction rate with decreasing pH, many sulfur compounds show little variation in reaction kinetics with variation of solution pH. This, in combination with the observation that the peak potential for oxide stripping shifts at twice the rate with solution pH as the half-wave potential for oxygen reduction, allows for the definition of PS-PCD waveforms for the anodic detection of sulfur compounds in neutral solutions with minimal interferences from dissolved oxygen. The separation of the two reductive processes is shown in Figs. X-6A and B with a change in electrolyte from 0.2 M NaOH to 0.25 M NH_4NO_3 (pH = 5.1), respectively.

To demonstrate the use of PS-PCD in comparison to PAD for the determination of sulfur compounds in pH-gradient or pH-step chromatographic systems, injections of 100 μM thiourea

Figure X-6A. Staircase voltammograms for 0.20 mM thiourea in 0.20 M NaOH obtained at a Au RDE (0.005 cm^2; 1600 rev min^{-1})

Conditions: scan rate = 4.8 V/min

Supporting Electrolyte: 0.20 M NaOH

Curves:
- [a] air sat'd residual
- [b] N_2 sat'd residual
- [c] air sat'd 0.20 mM thiourea
- [d] N_2 sat'd 0.20 mM thiourea

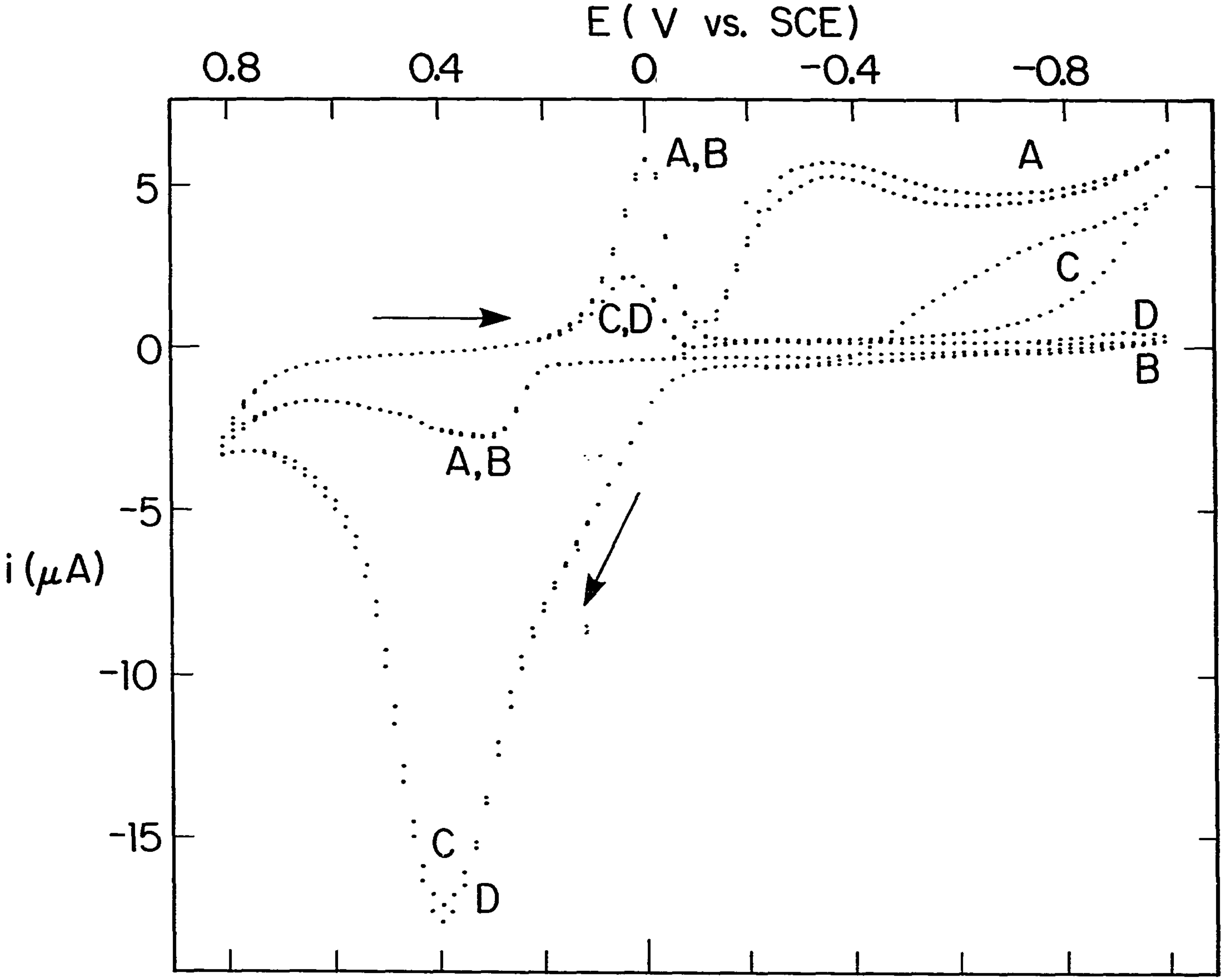

E (V vs. SCE)
0.8
0.4
0
−0.4
−0.8
5
0
−5
−10
−15
i (μA)
A,B
A
C
C,D
D
B
A,B
C
D

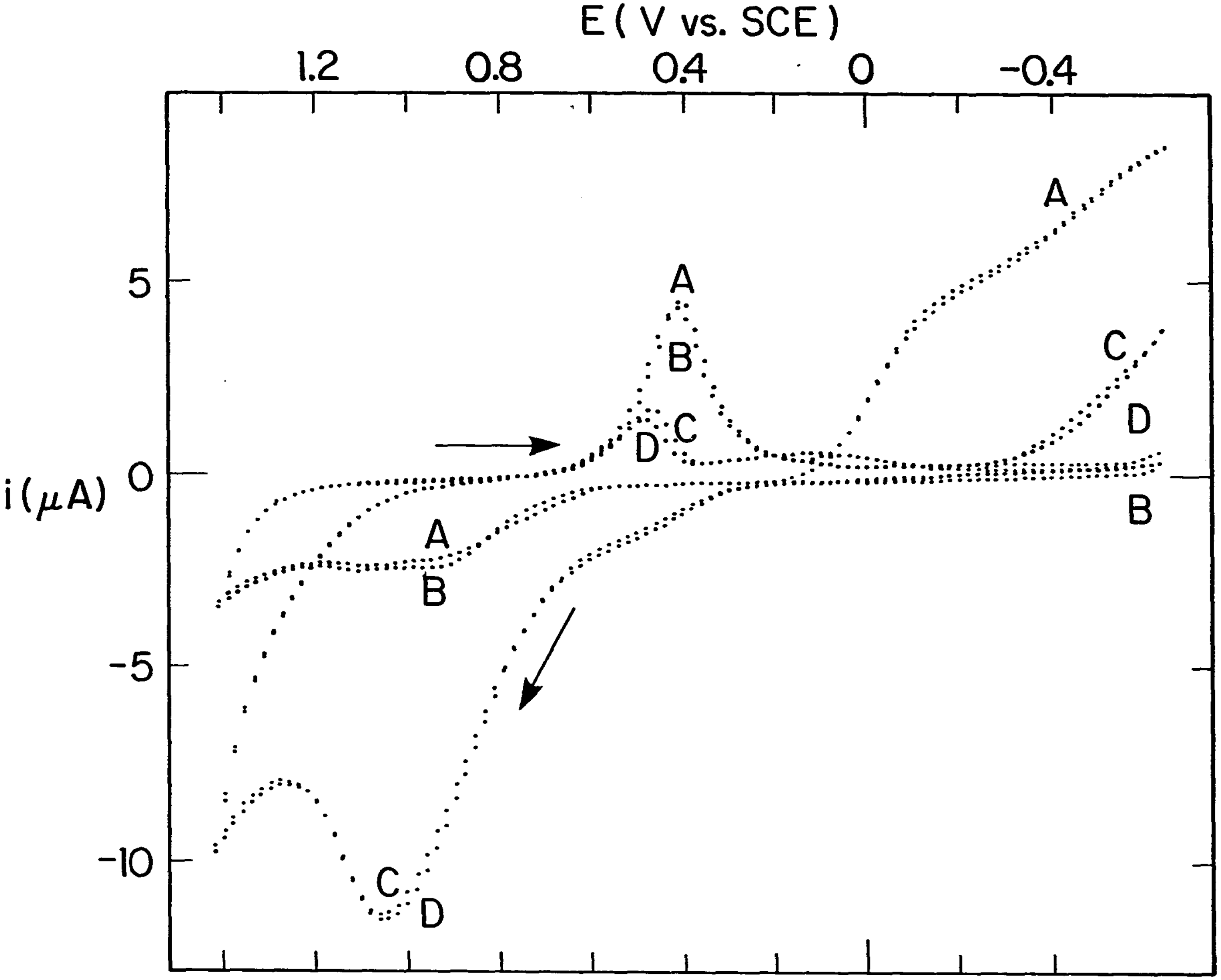
Figure X-6B. Staircase voltammograms for 0.20 m$\underline{M}$ thiourea in 0.25 $\underline{M}$ NH_4NO_3 obtained at a Au RDE (0.005 cm^2; 1600 rev min^{-1})

Conditions: scan rate = 4.8 V/min

Supporting Electrolyte: 0.25 $\underline{M}$ NH_4NO_3

Curves:

[a] air sat'd residual
[b] N_2 sat'd residual
[c] air sat'd 0.20 m$\underline{M}$ thiourea
[d] N_2 sat'd 0.20 m$\underline{M}$ thiourea


E (V vs. SCE)
1.2
0.8
0.4
0
-0.4
5
0
-5
-10
i (μA)
A
B
C
D
A
B
C
D
A
B
C
D
B

were made in 0.25 M NH_4NO_3 carriers of pH 3.8 and 5.1 (Fig. X-7). The arrows depict the sudden pH-steps between these carriers. For PS-PCD the shift in baseline response was small, whereas the baseline shift for PAD was far more severe. In addition, the sensitivity remained constant for PS-PCD, but decreased for PAD at the lower pH. This results because of the shift of E_{peak} with a change in pH. These experiments were performed such that the peak height response was ca. constant for PS-PCD and PAD; however, it is apparent that the S/N is far superior for PS-PCD.

3. Detection of carbohydrates

Monosaccharides and disaccharides exhibit a nearly mass-transport limited behavior at a Au electrode in a potential region where no surface oxides are formed (ca. 0.0 V vs. SCE, Fig. X-8). This is best illustrated by the PAD voltammograms of Fig. X-8. A mass-transport limited response is observed in the region -0.6 to 0.3 V, but oxidation of the carbohydrate ceases with concurrent formation of surface oxide, i.e., $E_1 >$ ca. 0.3 V. This potential dependent behavior implies that waveform 1B would give a much lower signal response for $E_2 >$ ca. 0.3 V with $E_1 \cong 0$ V (note the differences in response for plots A and C of Fig. X-8 for the two potentials 0.15 V and ca. 0.4 V) since the reaction rate has decreased several times at potentials greater than ca. 0.3 V in comparison to the optimum potential of 0.15 V. However, the use of a potential ramp from ca. -0.6 to 0.3 V allows for integration of the

Figure X-7. Comparison of baseline shift from a pH-step in FIA for PS-PCD and PAD for the detection of 100 $\mu\underline{M}$ thiourea in 0.25 $\underline{M}$ NH_4NO_3

PS-PCD waveform (1B):
$E_1 = -0.4$ V ($t_1 = 400$ ms)
$E_2 = 1.2$ V ($t_2 = 400$ ms)
$E_3 = -0.6$ V ($t_3 = 500$ ms)

PAD waveform:
$E_1 = 1.0$ V ($t_1 = 400$ ms)
$E_2 = 1.2$ V ($t_2 = 300$ ms)
$E_3 = -0.6$ V ($t_3 = 500$ ms)

Conditions:
0.50 mL min^{-1} flow rate
100 μL sample injected

pH-step:
5.1 to 3.8, point of step marked by arrow

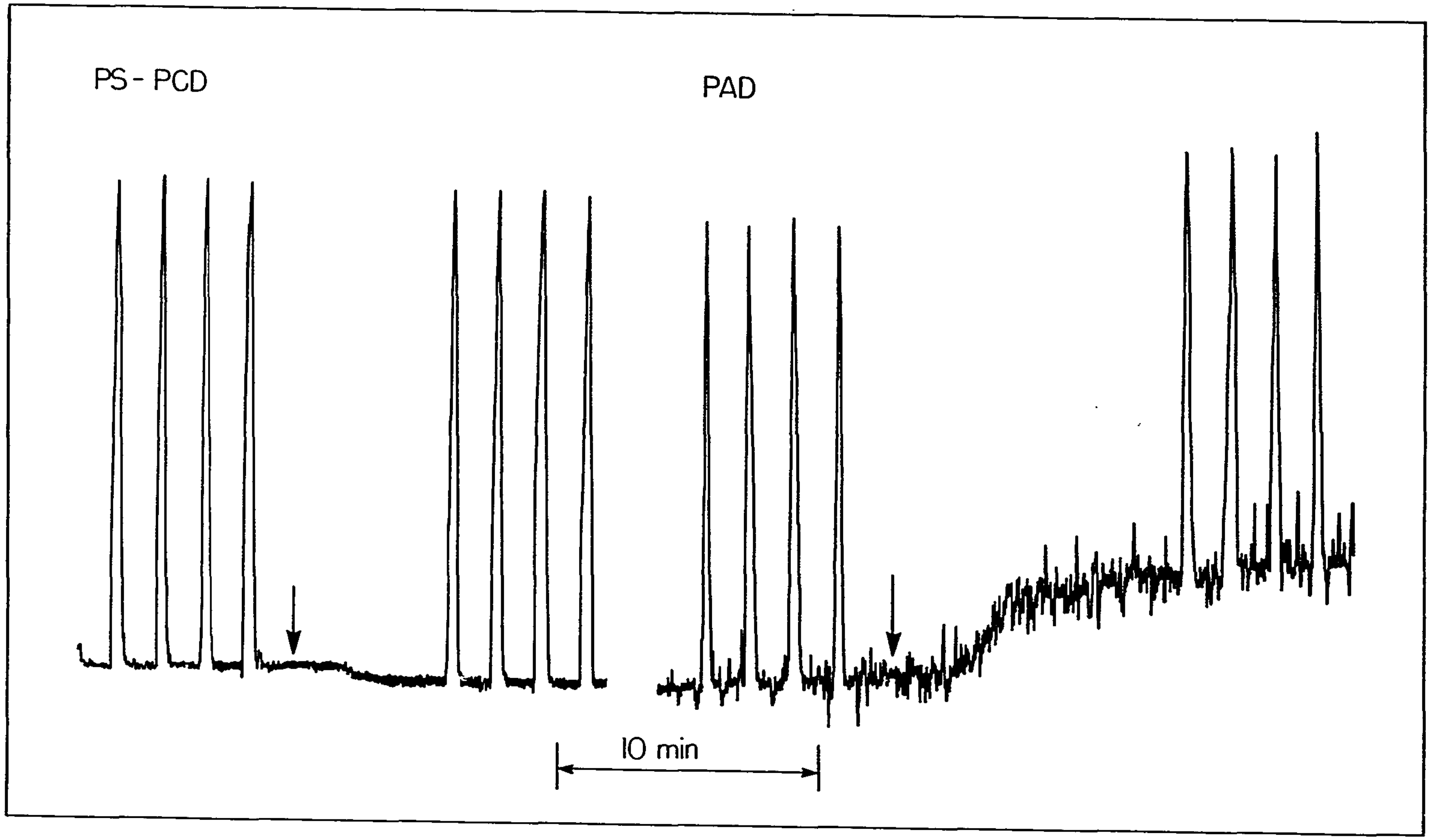

PS - PCD
PAD
10 min

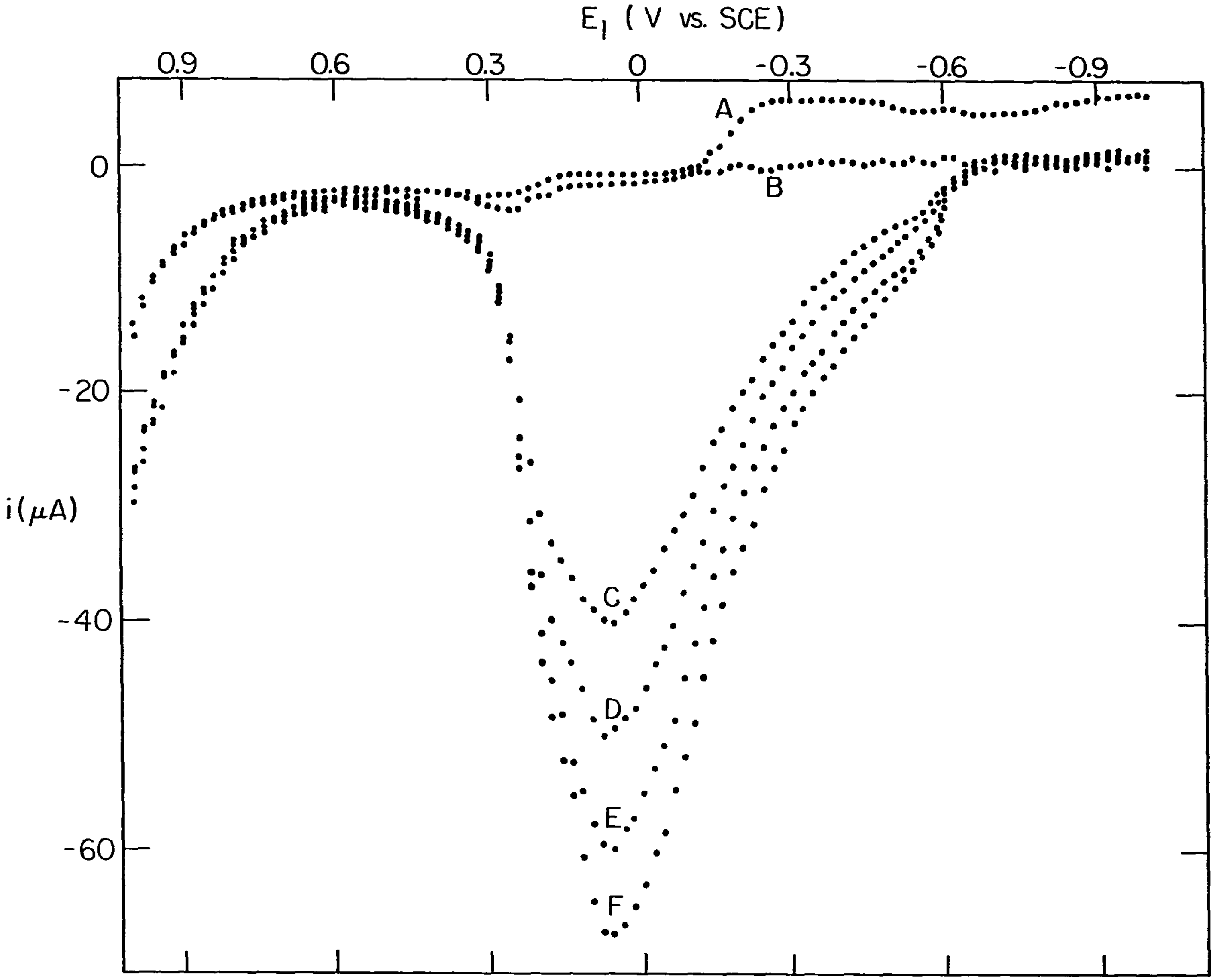
Figure X-8. PAD voltammograms for 2.0 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH obtained at a Au RDE (0.005 cm^2; 900 rev min^{-1})

Waveform:

E_1 = varied (t_1 = 200 ms)
E_2 = 1.0 V (t_2 = 200 ms)
E_3 = -1.00 V (t_3 = 600 ms)

Curves:

[A] Air sat'd 0.20 $\underline{M}$ NaOH;
[B] N_2 sat'd, 0.20 $\underline{M}$ NaOH;
[C]-[F] N_2 sat'd, 2.0 m$\underline{M}$ glucose/0.20 $\underline{M}$ NaOH; rotation speeds 400, 900 1600, 2500 rpm min^{-1}, respectively.

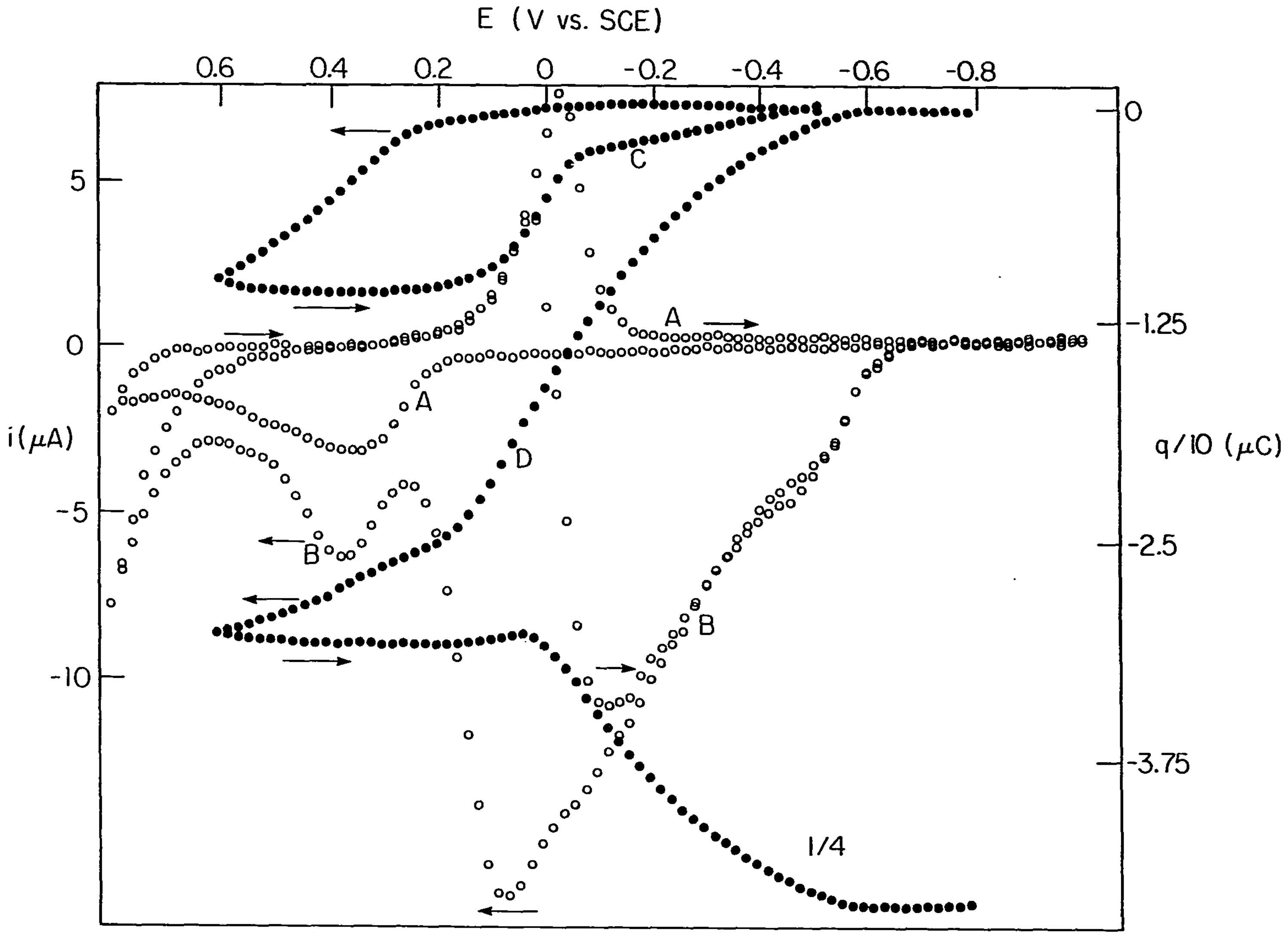

E$_1$ (V vs. SCE)
0.9
0.6
0.3
0
-0.3
-0.6
-0.9
i(μA)
0
-20
-40
-60
A
B
C
D
E
F

total amperometric peak signal. At voltages greater than ca. 0.6 V, solvent decomposition occurs with the evolution of oxygen; and, thus, sets the anodic limit for assignment of E_2. The cathodic wave with $E_{1/2} \cong -0.15$ V is a result of reduction of dissolved oxygen; this wave limits the region for assignment of E_1, and necessitates that E_1 be > ca. -0.1 V unless dissolved oxygen is removed from the flow system.

The sampling methodology of PS-PCD applicable for all carbohydrates is demonstrated by the q - E plots of Fig. X-9 for glucose. Staircase voltammograms are also shown to aid in their interpretation. During the anodic sweep of the residual trace (curve C), no charge flows until ca. 0.2 V where surface oxide is formed; the charge steadily increases indicating an overall increase in the amount of surface oxide formed with increasing electrode potential. Upon reversal of the scan direction the charge remains constant indicating that no appreciable oxide is formed or reduced, in agreement with the residual trace of the staircase voltammogram (curve A). At ca. 0.0 V, the total accumulated charge decreases rapidly resulting from cathodic stripping of the surface oxide with the inflection point potential of this q - E plot corresponding to the potential of current maxima in curve A. Eventually all charge is passed with a null net charge for one complete cycle, indicative of the near-zero background obtained with these waveforms. With the addition of glucose, oxidation is observed both on the anodic and cathodic sweeps, resulting in

Figure X-9. Charge-potential and current-potential curves for 1 m*M* glucose in 0.20 *M* NaOH at a Au RDE (0.005 cm^2; 900 rev min^{-1})

Curves:
- [A] Staircase; N_2 sat'd 0.20 *M* NaOH;
- [B] Staircase; N_2 sat'd 1.0 m*M* glucose/0.20 *M* NaOH;
- [C] Integrated staircase; N_2 sat'd 0.20 *M* NaOH;
- [D] Integrated staircase; N_2 sat'd 1.0 m*M* glucose/0.20 *M* NaOH (shown as 1/4 full scale).


E (V vs. SCE)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
i(μA)
5
0
-5
-10
q/10 (μC)
0
-1.25
-2.5
-3.75
A
B
C
D
1/4

a greater S/N. The net charge at the end of one cycle is now some finite value which is dependent upon the analyte concentration. The difference between the last and the first points of the q - E plot (curve D) is representative of the signal which is measured in the PS-PCD waveform.

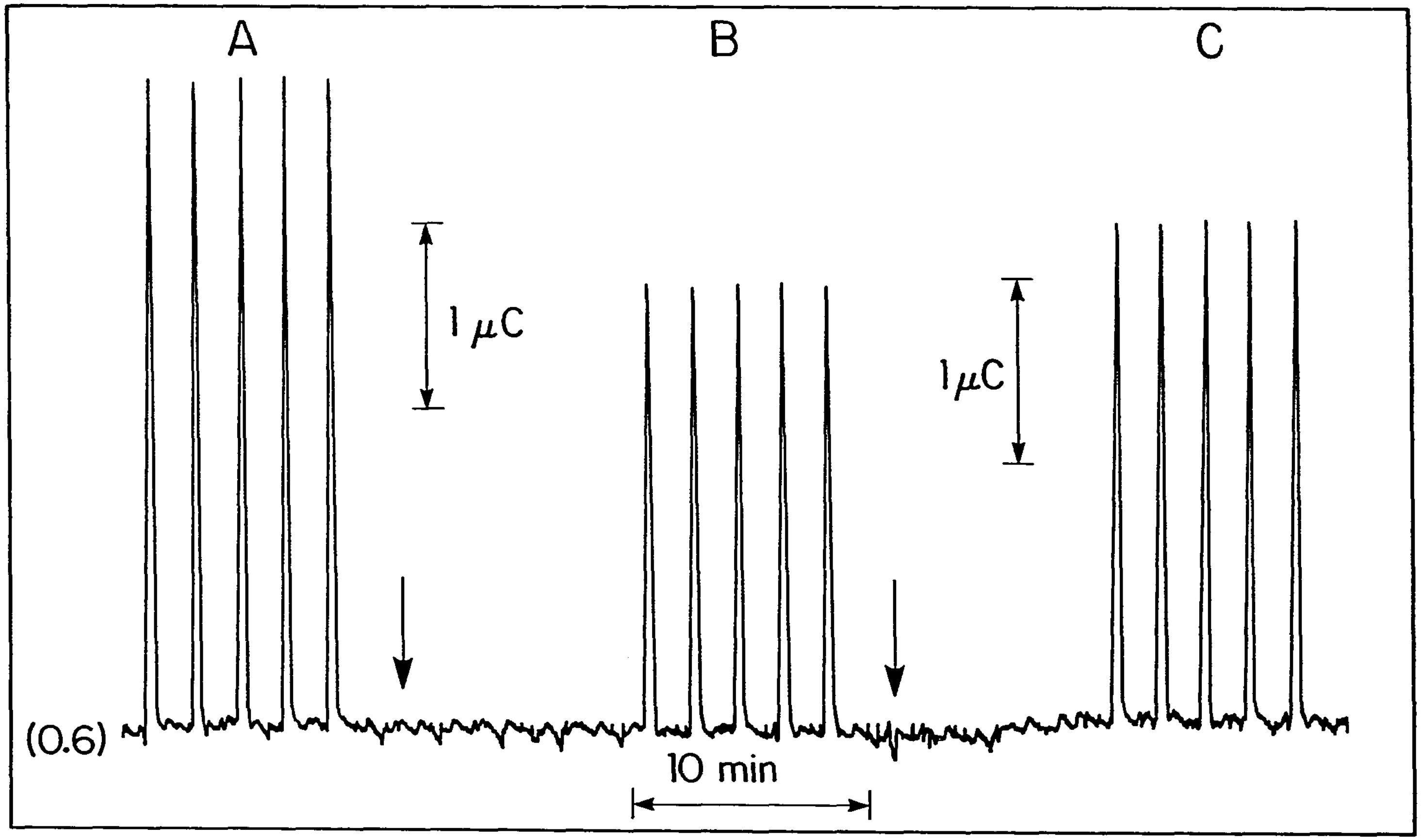
Some of the proposed advantages of PS-PCD are maximized when oxidation of the analyte occurs in a region where surface oxide is also formed, as is the case for sulfur compounds. For carbohydrates, which have a maximum amperometric response in a region where no surface oxide is formed, few advantages exist over PCD at a constant detection potential.[14] However, the ability for either PAD and PCD at constant detection potentials to resist even the slightest change in pH is strongly dependent on the definition of the waveform in conjunction with the change in pH, often requiring a unique waveform for each pH-step or gradient, since the peak shift is ca. 60 mV per pH unit. The ability of PS-PCD to reject alterations in the baseline caused by a change in pH was tested using an all steel FI system. The results are summarized in Fig. X-10. Regions A, B and C denote, respectively, the detection of 1.0 m<u>M</u> glucose in 0.20, 0.50 and 1.0 <u>M</u> NaOH. The arrows in Fig. X-10 designate the abrupt changes of NaOH concentration in the carrier solution. It is significant to note that the recording in Fig. X-10 was continuous and no significant shift in the baseline was observed with the abrupt change in NaOH concentration. The nonreproducible peak height

Figure X-10. Background and sensitivity variation for PS-PCD of 100 $\mu\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH with sudden ionic and pH changes of the carrier in FIA

Waveform (1A):
E_1 = -0.20 V (t_d = 1 μs, t_1 = 200 ms)
E_2 = 0.40 V
E_3 = -1.00 V (t_3 = 200 ms)
t_i = 1 s
ΔE = 30 mV

Conditions:
0.59 mL min^{-1} flow rate
100 μL sample injected

Regions:
[A] 0.20 $\underline{M}$ NaOH
[B] 0.50 $\underline{M}$ NaOH
[C] 1.0 $\underline{M}$ NaOH


A
B
C
1 μC
1 μC
(0.6)
10 min

for equivalent injections at each concentration of NaOH is the consequence of the relatively narrow peak widths, and, the use of a low frequency of the waveform and fluctuations in the flow rate of the reciprocating pump.

Whereas the baseline changes resulting from the pH steps are rejected in PS-PCD, sensitivity for detection of carbohydrates is pH dependent. The variation of sensitivity with pH is a result of two factors: 1) the simulation of the voltage ramp with finite voltage steps, and 2) the shift in the voltammetric region in which the potential ramp is applied. The former effect causes an oscillation of sensitivity with pH, whereas the latter results in a decrease in sensitivity with increasing pH. Overall, a decrease in peak height should be expected following an increase in the NaOH concentration of the carrier; however, the decrease was observed to be only ca. 25%.

Observed interferences due to baseline change resulting from pH alterations in the carrier stream can result from improper selection of either values E_1 or E_2. It is essential that E_1 corresponds to a value where, 1) no oxide exists on the electrode surface, and, 2) dissolved oxygen is not reduced, for all pH values to be encountered. It is also necessary that E_2 correspond to a value where solvent decomposition does not occur. The results of variations of both potentials are shown in Fig. X-11A for injections of 1.0 $\underline{M}$ NaOH in a 0.20 $\underline{M}$ NaOH carrier stream. Little peak height variation is seen for the variation of E_2 until it exceeds the value for significant oxygen evolution, because the oxygen formed at E_2 is only partially reduced at E_1. The anodic increase in the background for increasing values of E_2, is due in part to the short time spent subsequently at E_1. That is, with increasing E_2 more oxide is formed on the electrode surface, and as a result of the short integration time at E_1 not all of the oxide formed at E_2 is compensated for while integrating at E_1. This situation is aggravated if the rate of oxide reduction is slowed by making E_1 more positive. Note, the background increases dramatically when E_1 is at a value where the oxide formed at E_2 is no longer stripped at E_1.

The same consideration was applied for injections of 0.2 m<u>M</u> glucose in 0.20 <u>M</u> NaOH. The results are shown in Fig. X-11B. The background charge is equivalent to that in Fig. X-11A. The peak height (q_p) for the detection of glucose is seen to go through a maximum at ca. -0.20 V for the variation of E_1 and at ca. 0.40 V for the variation of E_2. For this reason, and for the minimal effects observed with pH variation of the carrier, these potentials were selected for general use in PS-PCD of carbohydrates in 0.20 <u>M</u> NaOH.

4. *Calibration*

Normalized calibration plots of $N_i\ i_p/C^b$ and $N_q\ q_p/C^b$ for thiourea in 0.25 <u>M</u> NH_4NO_3 by PAD and PS-PCD, respectively, are shown in Fig. X-12. The normalization constants N_i and N_q are

Figure X-11A. Peak height and background response for injection of 1.0 M NaOH into 0.20 M NaOH with variation of E_1 and E_2

Waveform (1A):
E_1 = -0.20 V or varied (t_d = 1 μs, t_1 = 100 ms)
E_2 = 0.40 V or varied
E_3 = -1.00 V (t_3 = 200 ms)
t_i = 1 s
ΔE = 30 mV

Conditions:
0.50 mL min^{-1} flow rate
100 μL sample injected

Curves:
(●) Peak height as a function of E_1.

(▲) Background as a function of E_1.

(■) Peak height as a function of E_2.

(○) Background as a function of E_2.

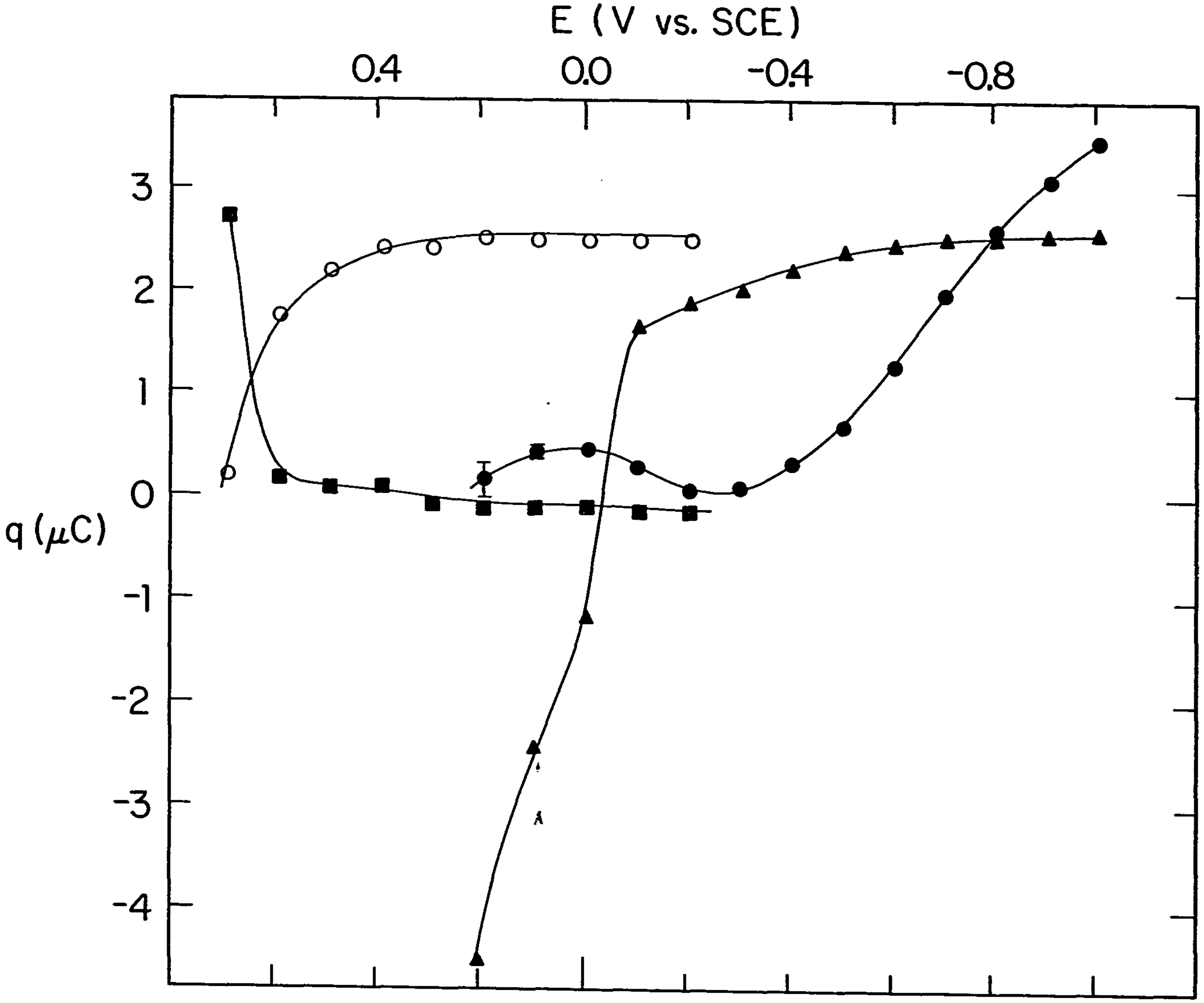

E (V vs. SCE)
0.4
0.0
-0.4
-0.8
3
2
1
0
-1
-2
-3
-4
q (μC)

Figure X-11B. Peak height and background optimization for the PS-PCD of 0.20 m<u>M</u> glucose in 0.20 <u>M</u> NaOH as a function of E_1 and E_2

Waveform (1A):
E_1 = -0.20 V or varied (t_1 = 100 ms, t_d = 1 μs)
E_2 = 0.40 V or varied
E_3 = -1.00 V (t_3 = 200 ms)
t_i = 1 s
ΔE = 30 mV

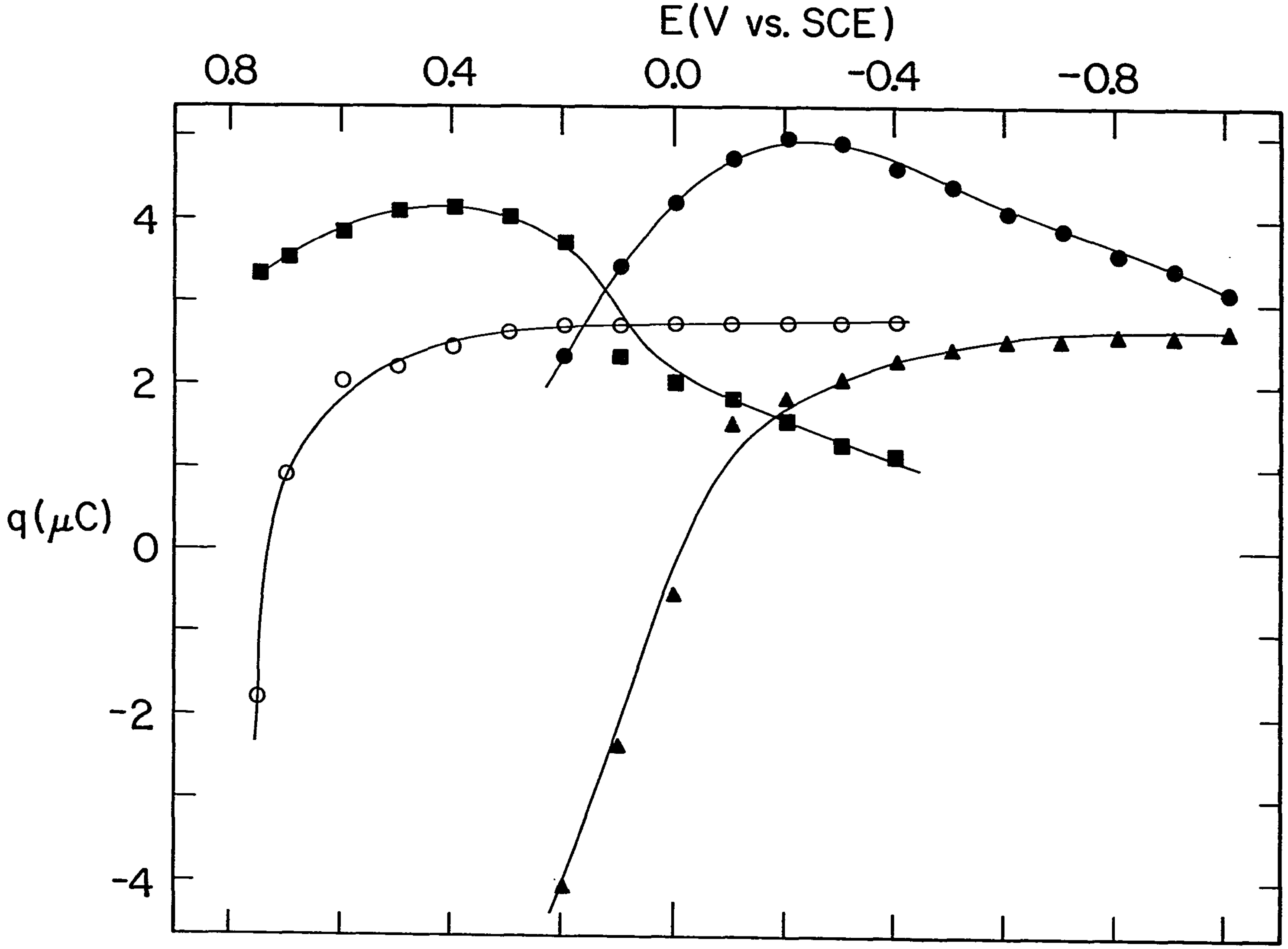
Conditions:
0.54 mL min^{-1} flow rate
100 μL sample injected

Curves:
(●) Peak height as a function of E_1.

(▲) Background as a function of E_1.

(■) Peak height as a function of E_2.

(○) Background as a function of E_2.


E(V vs. SCE)
0.8
0.4
0.0
-0.4
-0.8
q(μC)
4
2
0
-2
-4

the reciprocal values of the slopes obtained by regression analysis of the linear regions of the calibration plots of i_p vs. C^b and q_p vs. C^b, respectively, for small C^b. Hence, for a perfectly linear response all normalized experimental values are 1.0. The arrows at low C^b mark the detection limits (S/N = 3) for each method of detection; however, detection limits are anticipated to be much lower with utilization of commercially available potentiostats, and, thus values presented here should be used only for comparison of these detection schemes. For PS-PCD, the calibration plot is linear for ca. 1.7 decades, i.e., 2-100 μ<u>M</u>. The region of linearity for PAD is ca. 0.6 decade, i.e., 15-200 μ<u>M</u>. Significant errors may arise in PAD if there is insufficient cleaning of the electrode and post-peak dips are observed as shown in Fig. X-5. These errors are prominent at low C^b and lead to severe negative deviations from linear response (see Fig. X-12).

The increase in the upper limit of linearity for PAD is a result, in part, to the shift in peak potential for the oxidation of thiourea with C^b. This effect is shown in Fig. X-13. As the concentration of thiourea increases, the peak potential shifts more positive, with an ca. 60 mV shift from 0.1 to 0.5 m<u>M</u>. With the PAD detection potential E_1 = 1.0 V, the expected reduction in peak current from surface adsorption at cathodic potentials is offset by the increase from the shift in peak potential with the maximum at ca. 0.3 m<u>M</u>. Errors from the variation in potential of maximum current are

Figure X-12. Calibration data for thiourea in 0.25 M NH_4NO_3 by PS-PCD and PAD

PS-PCD waveform (1B):
E_1 = 0.15 V (t_1 = 300 ms)
E_2 = 1.2 V (t_2 = 400 ms)
E_3 = -0.6 V (t_3 = 500 ms)

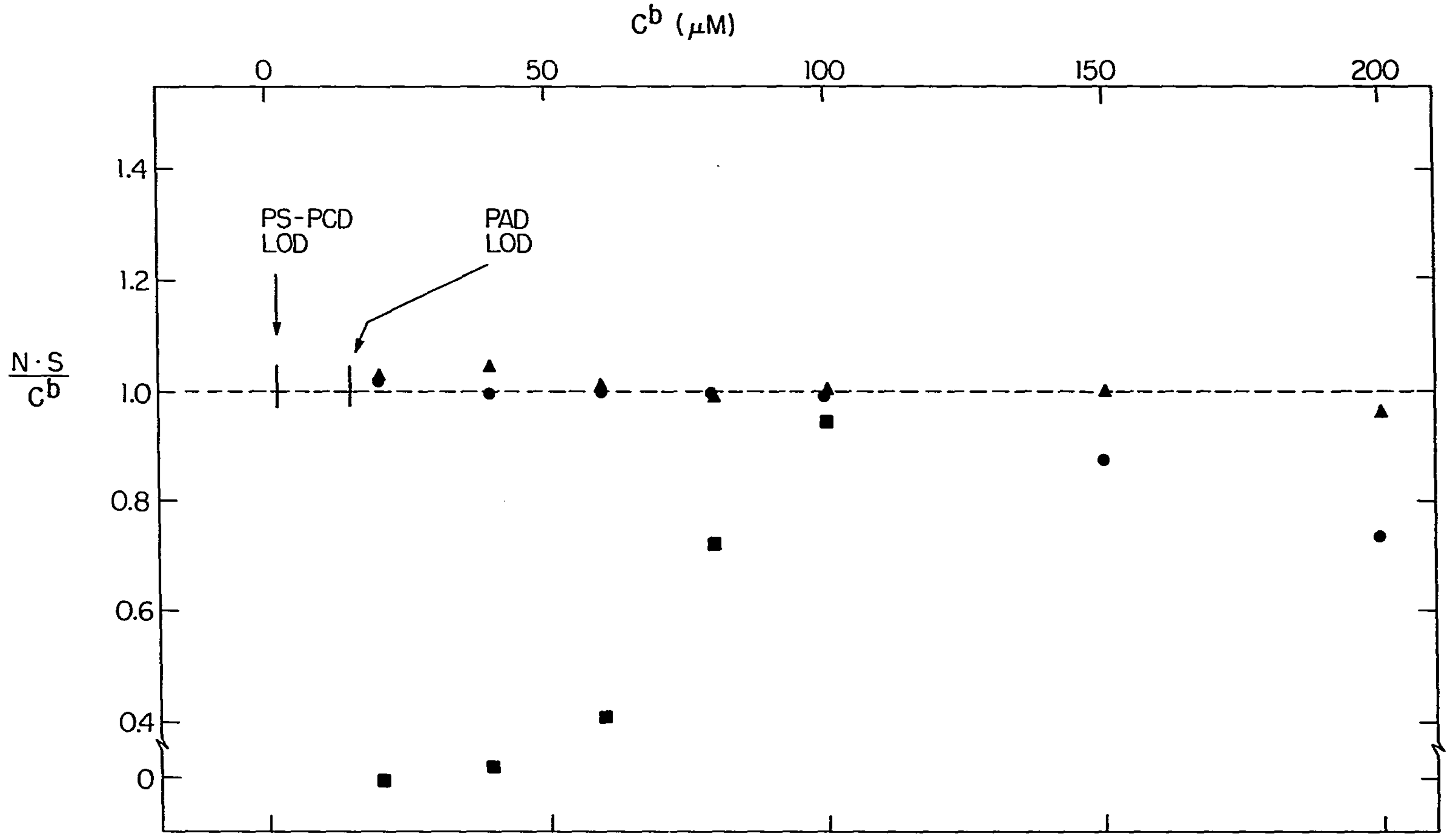
PAD waveform:
E_1 = 1.0 V (t_1 = 400 ms)
E_2 = 1.2 V (t_2 = 300 ms)
E_3 = -0.6 V (t_3 = 500 ms)

Conditions:
0.50 mL min^{-1} flow rate
100 μL sample injected

Curves:
[●] PS-PCD (N = 1.90 x 10^1 μM $\mu coul^{-1}$)

[▲] PAD (N = 1.71 x 10^4 μM μA^{-1})

[▪] PAD with post-peak dips


C^b (μM)
0
50
100
150
200
1.4
1.2
1.0
0.8
0.6
0.4
0
$\frac{N \cdot S}{C^b}$
PS-PCD LOD
PAD LOD

not expected for PS-PCD if $E_2 >> E_p$ and $E_1 << E_p$.

The use of constant potential detection schemes (PAD or PCD) for a class of compounds can also fail if the region for oxidation, i.e., the potential of maximum current, is compound specific. Thomas and Sturrock[13] have made the comment in reference to the detection of carbamates at a Pt electrode, "...all of the carbamates studied were detectable, although there was a considerable range of sensitivities and required [detection] potentials." Such effects are expected to be minimized with the use of PS-PCD.

The linear response for calibration of carbohydrates by PS-PCD is over 2 decades, in accord with the results for PCD at a constant detection potential. Both PCD schemes retain the advantage of increased linear dynamic range over PAD through a lowering in the limits of detection.

5. *Comparison of waveforms*

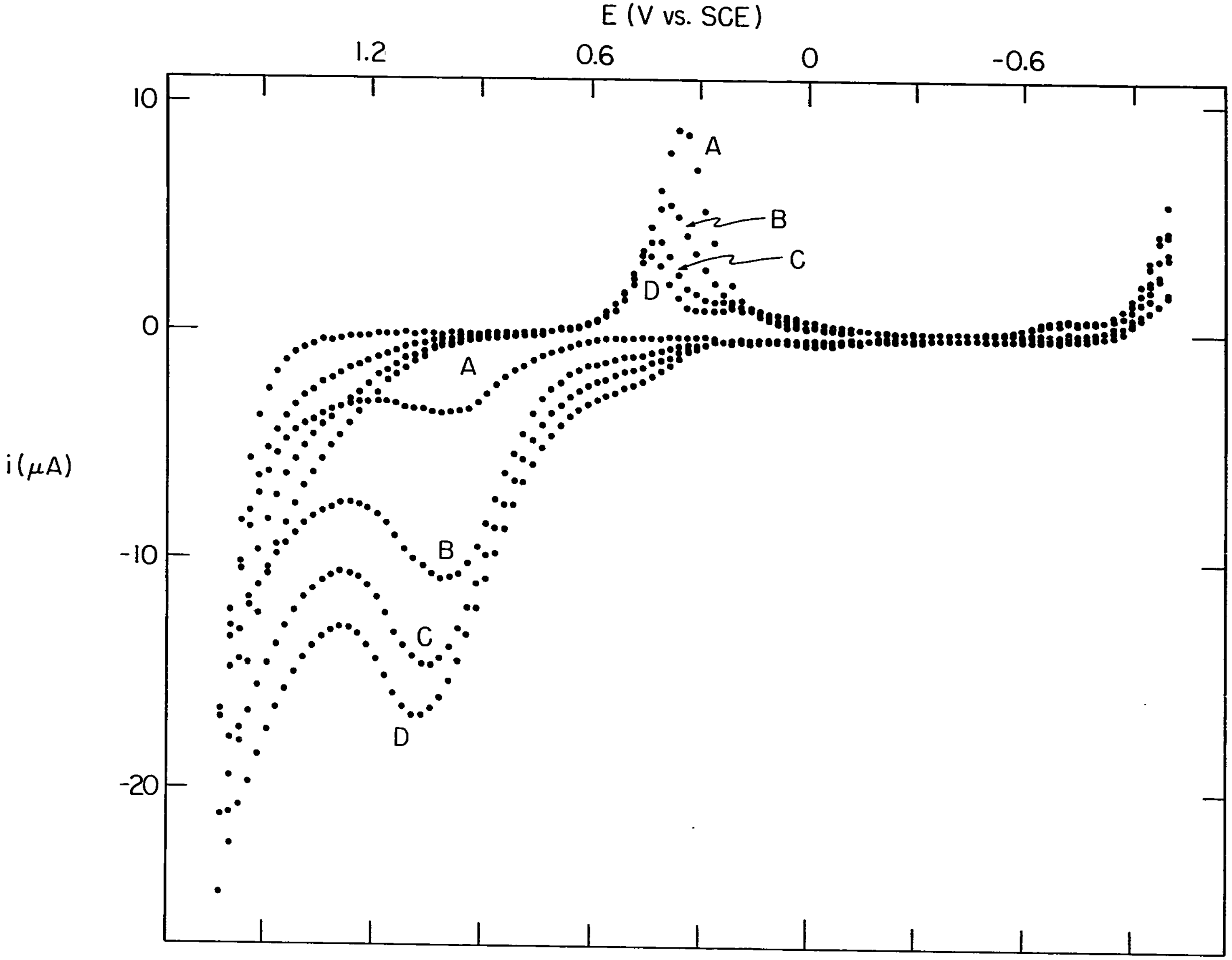
The selection of the optimum waveform can be dependent upon the analyte(s) of interest. For molecules which display potential-dependent mass-transport limited behavior, the waveform depicted in Fig. X-1A is more applicable, since a greater portion of the detection time (period t_2) is spent in the region of greatest voltammetric response. Analytes whose detection is governed by a strong surface-controlled reaction mechanism are detected equally by either waveform, but because of its greater simplicity waveform 1B is preferred. Results of comparison of the two waveforms for the FI-PS-PCD of

Figure X-13. Variation of voltammetric response with concentration for thiourea in N_2 saturated 0.25 $\underline{M}$ NH_4NO_3 at a Au RED (0.005 cm^2; 900 rev min^{-1})

Conditions: scan rate 4.8 V min^{-1}

Concentration of thiourea:

[A]	0.0 m$\underline{M}$
[B]	0.1 m$\underline{M}$
[C]	0.3 m$\underline{M}$
[D]	0.5 m$\underline{M}$


E (V vs. SCE)
1.2
0.6
0
-0.6
10
0
-10
-20
i (μA)
A
B
C
D
A
B
C
D

glucose and thiourea in 0.2 M NaOH are shown in Fig. X-14. Glucose shows a 10-fold increase in the detectability (S/N) with waveform 1A over 1B. Thiourea, on the other hand, limited by the adsorption at potentials more cathodic than the detection region, displayed only a 30% increase in S/N for waveform 1A over 1B. For comparison, the total period of detection was held constant at 1 s for both waveforms.

The present methods of PS-PCD retain all of the advantages of PCD at a constant detection potential as compared to PAD.[14] Sensitivity is higher and, consequently, the detection limits are decreased by at least 20X for carbohydrates[14] and ca. 5-10X for sulfur compounds at gold electrodes. A comparison of the detection of thiourea in 0.25 M at a Au electrode for the three detection schemes PAD, static-potential PCD, and PS-PCD, is shown in Fig. X-15. The magnitude of the baseline response is represented by the percentage offset from zero as compared to the peak response for the specific detection method. For example, the baseline response for PS-PCD is 20% of the peak response for 100 μM thiourea, whereas, the baseline response for PCD at a constant detection potential is twice (200%) the peak response. Such large background signals for PAD and static-potential PCD often require the use of sensitive offset circuits, especially for detection schemes which employ detection potentials in the region of oxide formation or oxygen reduction. The detection limits for PS-PCD of sulfur compounds are superior to PAD, and even PCD at a

Figure X-14. Comparison of the peaks obtained for glucose and thiourea with both waveforms of Fig X-1

Solutions: I) 0.20 m$\underline{M}$ glucose in 0.20 $\underline{M}$ NaOH
II) 0.10 m$\underline{M}$ thiourea in 0.20 $\underline{M}$ NaOH

Conditions: 0.40 mL min^{-1} flow rate
100 μL sample injected

I) Glucose

A) Waveform 1A:

E_1 = -0.20 V (t_d = 1 μs,
t_1 = 100 ms)
E_2 = 0.40 V
E_3 = -1.0 V (t_3 = 200 ms)
t_i = 1 s
ΔE = 30 mV

B) Waveform 1B:

E_1 = -0.20 V (t_d = 100 ms,
t_1 = 300 ms)
E_2 = 0.40 V (t_2 = 1000 ms)
E_3 = -1.0 V (t_3 = 200 ms)

II) Thiourea

A) Waveform 1A:

E_1 = -0.20 V (t_d = 1 μs,
t_1 = 200 ms)
E_2 = 0.50 V
E_3 = -1.0 V (t_3 = 500 ms0
t_i = 1 s
E_s = 35 mV

B) Waveform 1B:

E_1 = -0.20 V (t_d = 100 ms,
t_1 = 200 ms)
E_2 = 0.50 V (t_2 = 1000 ms)
E_3 = -1.0 V (t_3 = 500 ms)

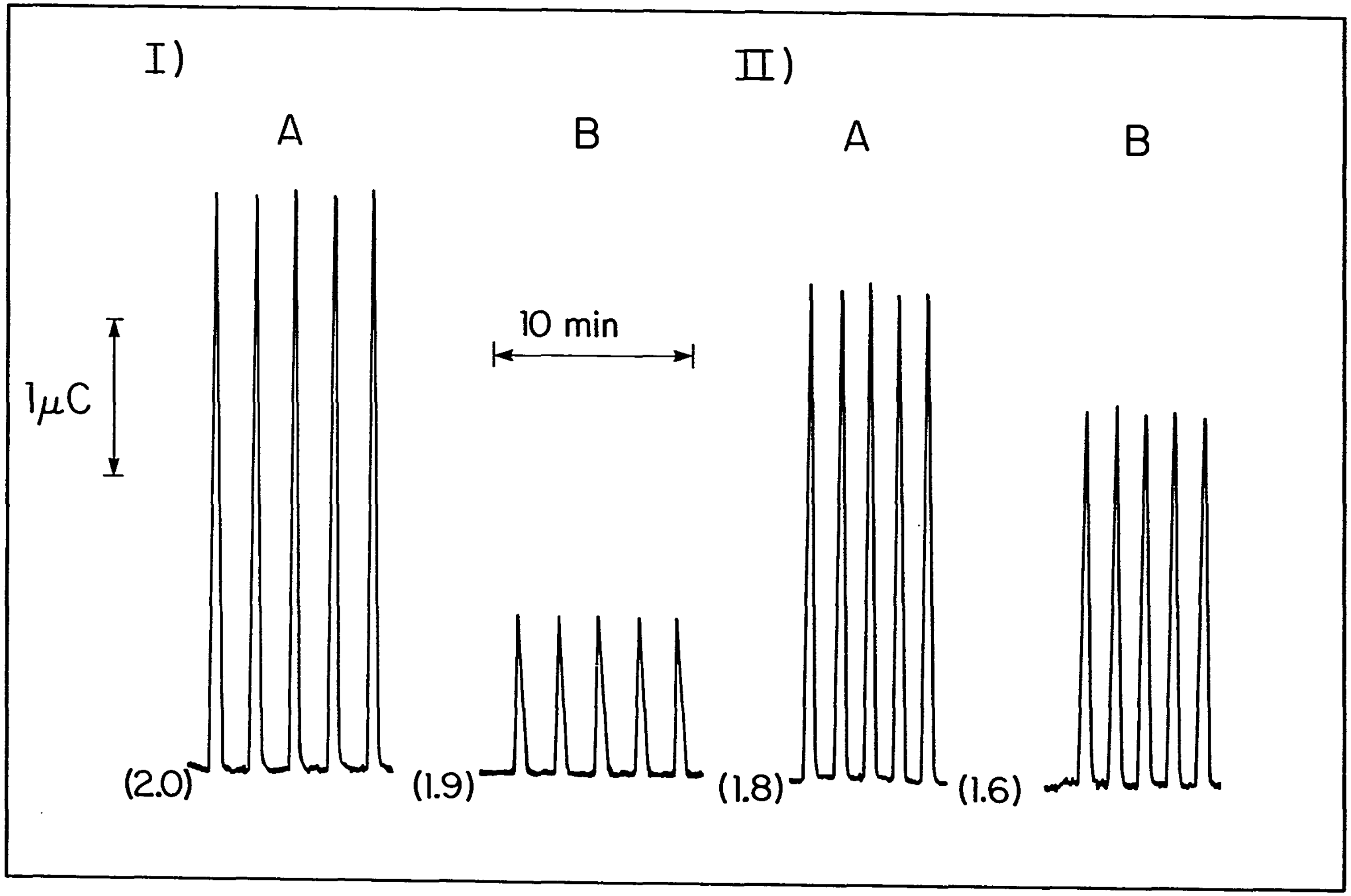
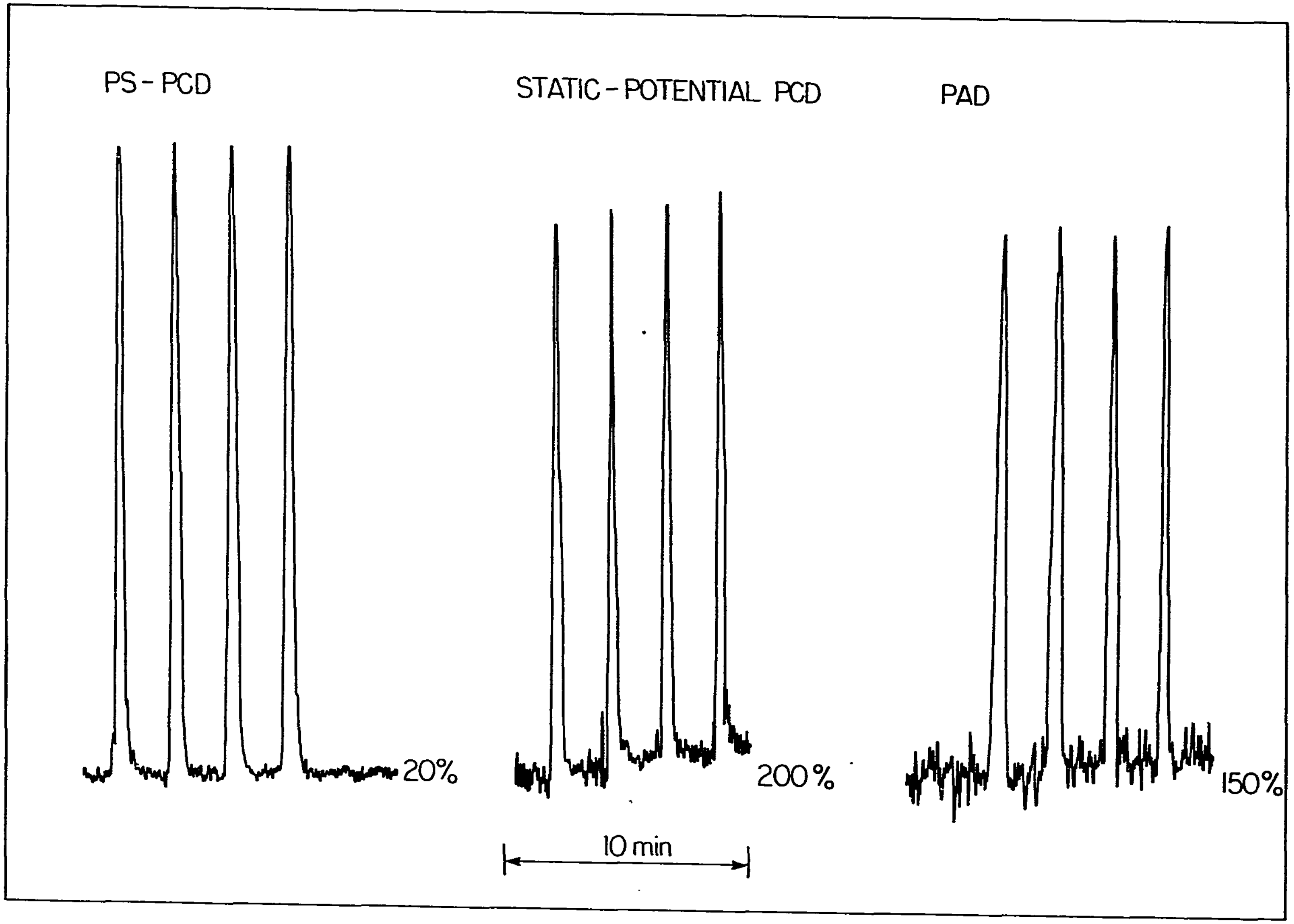

I)
A
B
II)
A
B
1μC
10 min
(2.0)
(1.9)
(1.8)
(1.6)

Figure X-15. Comparison of detectability of thiourea in 0.25 M NH_4NO_3 at a Au electrode for PS-PCD, static-potential PCD and PAD

PS-PCD waveform (1B):	E_1 = 0.15 V (t_d = 100 ms, t_1 = 300 ms) E_2 = 1.2 V (t_2 = 400 ms) E_3 = -0.60 V (t_3 = 500 ms)
SP-PCD waveform:	E_1 = 1.0 V (t_d = 1 μs, t_1 = 400 ms) E_2 = 1.2 V (t_2 = 300 ms) E_3 = -0.6 V (t_3 = 500 ms)
PAD waveform:	E_1 = 1.0 V (t_1 = 400 ms) E_2 = 1.2 V (t_2 = 300 ms) E_3 = -0.60 V (t_3 = 500 ms)
Conditions:	0.50 mL min^{-1} flow rate 100 μL sample injected


PS - PCD
STATIC - POTENTIAL PCD
PAD
20%
200 %
150%
10 min

constant detection potential. The decrease in detectability for static-potential PCD as compared to PS-PCD is a result of the large background from the formation of surface oxides.

E. Conclusions

The design of the waveforms for PS-PCD can virtually eliminate the large background signal observed for PAD and PCD which results from formation of surface oxides at the detection potential. The constancy and near-zero value of the baseline for PS-PCD results in lower detection limits for sulfur compounds as compared to PCD with a static detection potential. Furthermore, long-term baseline drift observed in PAD and PCD due to the gradual increase in true surface area, is eliminated. With appropriate selection of waveform parameters, the background of swept-potential PCD is immune to changes of pH and the technique is recommended for chromatographic systems employing pH-gradient or pH-step elution.

Several inherent advantages exist with the use of PS-PCD in comparison to PAD at a constant detection potential. As noted, the rejection of background shifts from pH gradients or steps, and elimination of background drift resulting from surface reformation processes. Additional advantages include: 1) A great reduction in the background signal resulting from the formation of surface oxides on noble metal electrodes and the passage of charging current, thus eliminating the need for exotic offset circuitry, and providing an overall improvement in the observed S/N; 2) The minimization of errors due to variation in the degree of surface oxide coverage of the noble metal electrode as a function of bulk analyte concentration; 3) Compensation for the alteration in voltammetric response as a function of bulk analyte concentration, i.e., the variation of potential of maximum current with bulk analyte concentration, or the variation of electrochemical response for specific compounds in a defined class; 4) Rapid equilibration of baseline response after physical or chemical perturbations; 5) The ability to separate reversible and irreversible processes, i.e., the ability to determine exactly the charge passed for oxidation (or reduction) of an irreversible process (absorption and subsequent irreversible oxidation of an analyte) in a potential region where a reversible process may occur.

F. Acknowledgement

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XI. PULSED COULOMETRIC DETECTION OF ELECTRODEPOSITED METALS AT A GOLD ELECTRODE FOR FLOW INJECTION ANALYSIS AND LIQUID CHROMATOGRAPHY

A. Abstract

A new technique is described for the detection of metal ions which can be electrodeposited at Au electrodes in flow-injection and liquid chromatographic systems. Underpotential deposition effects observed at Au electrodes increases the number of metals which can be analyzed. Although the technique was designed primarily for use as a universal and quantitative chromatographic detector some selectivity may be obtained by judicious design of the potential waveform. Absolute detection limits (S/N = 2) for Hg(I), Hg(II), Cu(II), Bi(III), Pb(II), Cd(II), Ni(II), Zn(II) and Tl(III) are in the range 15-750 pmoles.

B. Introduction

Electroanalytical detectors are becoming more popular for use in monitoring liquid chromatographic effluents and flow-injection carrier streams. However, detectors designed for use in flow-injection analysis (FIA) may not be applicable as a detectors for liquid chromatography, primarily due to the time constraints of signal measurement. Conventional voltammetric stripping analysis for the determination of trace metals has recently been introduced for use in FIA[1-11] but has not been applied for chromatographic detection owing to the relatively long times necessary for electrodeposition. Excellent detection limits have been reported for the determination of electroactive metals with ASV in both batch and FIA systems, but are attributed to the selection of large deposition times, commonly 1-5 min.

Although much effort has been placed on anodic stripping at mercury electrodes it is slowly being replaced by methods which are more reliable and by methods which require less hazardous materials handling. In addition, the applicability of polarographic methods for on-line detection is still in question, owing to the interferences from dissolved oxygen and difficulties resulting from surface tension phenomena. The former problem has been resolved in this laboratory with the introduction of reverse pulse amperometry[12] and constant potential pulse polarography,[13] and others have resolved the problem by removal of dissolved oxygen.[14,15] The latter problem is commonly associated with difficulties of "hanging" a drop. Here, capillary plugging or streaming is typically observed and the obstacle is not easily rectified. Methods which do not involve electrode renewal are in general not suitable for on-line detection due to relatively slow diffusion of amalgam forming ions within the bulk Hg, which results in a constantly drifting baseline.[16] Many of difficulties commonly associated with polarographic methods can be eliminated with the use of solid electrodes.

Described within is a method which takes advantage of the metal ion deposition phenomena at Au electrodes. Metals which theoretically are not reduced at potentials anodic of hydrogen evolution may in fact be deposited owing to underpotential deposition (UPD) effects. Initial investigations of UPD were reported by Hevesy,[17,18] Paneth and Hevesy,[19-21] Herzfeld,[22] Haissinsky[23] and Rogers *et al.*[24] Since then much effort has been spent on the oxidative "catalysis" of organic molecules by submonolayer deposits of metal atoms on polycrystalline and single crystal electrode substrates.[25-30] Compilations of the underpotential shifts observed for a variety of adatoms on several electrode substrates have recently appeared in the literature.[31,32] These observed UPD shifts have resulted in an increase in the number of metals which may be determined, and eliminated the need for deposition potentials negative of solvent decomposition, where electrogenerated H_2 would interfere.

With the observed underpotential and bulk deposition effects of many metal ions on Au electrodes it is possible to define a potentiodynamic waveform for anodic detection. However, attention must be drawn to the rapid stripping of the metal deposit from the electrode surface, thus rendering chronoamperometric experiments, similar to pulsed amperometric detection,[33-45] as being insensitive. For the case of a short delay time between the potential step and sampling of current, the S/N is poor due to the relatively large background.

Similar results are obtained for the case of long delay times, but the poor S/N is now a result of the low signal. In comparison to the stripping of amalgam forming metals from Hg, the stripping of nonalloy forming metals from solid electrodes is much more rapid owing to surface preconcentration; hence, waveforms commonly used for amperometric detection with Hg electrodes are not applicable because of the relatively long delay times before current measurement.

For improved sensitivity and detectability, chronocoulometric methods may be employed which allow for very short delay times before current sampling, and because of the relatively long sampling times, the S/N is greatly improved. The waveform used for pulsed coulometric detection (PCD) is shown in Fig. XI-1, and is different than those previously described[46-47] for use in the detection of organic compounds at noble metal electrodes. Here, the metal is deposited at E_2 for a period t_2 before detection at E_1. The signal is integrated for a period t_i at E_1 following a delay time t_d, with the total time at E_1 defined as t_1. At the end of the integration cycle, the signal is sampled and output to a recording device, such as a strip chart recorder. Ideally, the period t_1 is defined as $t_d + t_i$, however, owing to instrumental limitations t_1 may be greater than this sum, with the additional time added after current integration and before the beginning of the next cycle.

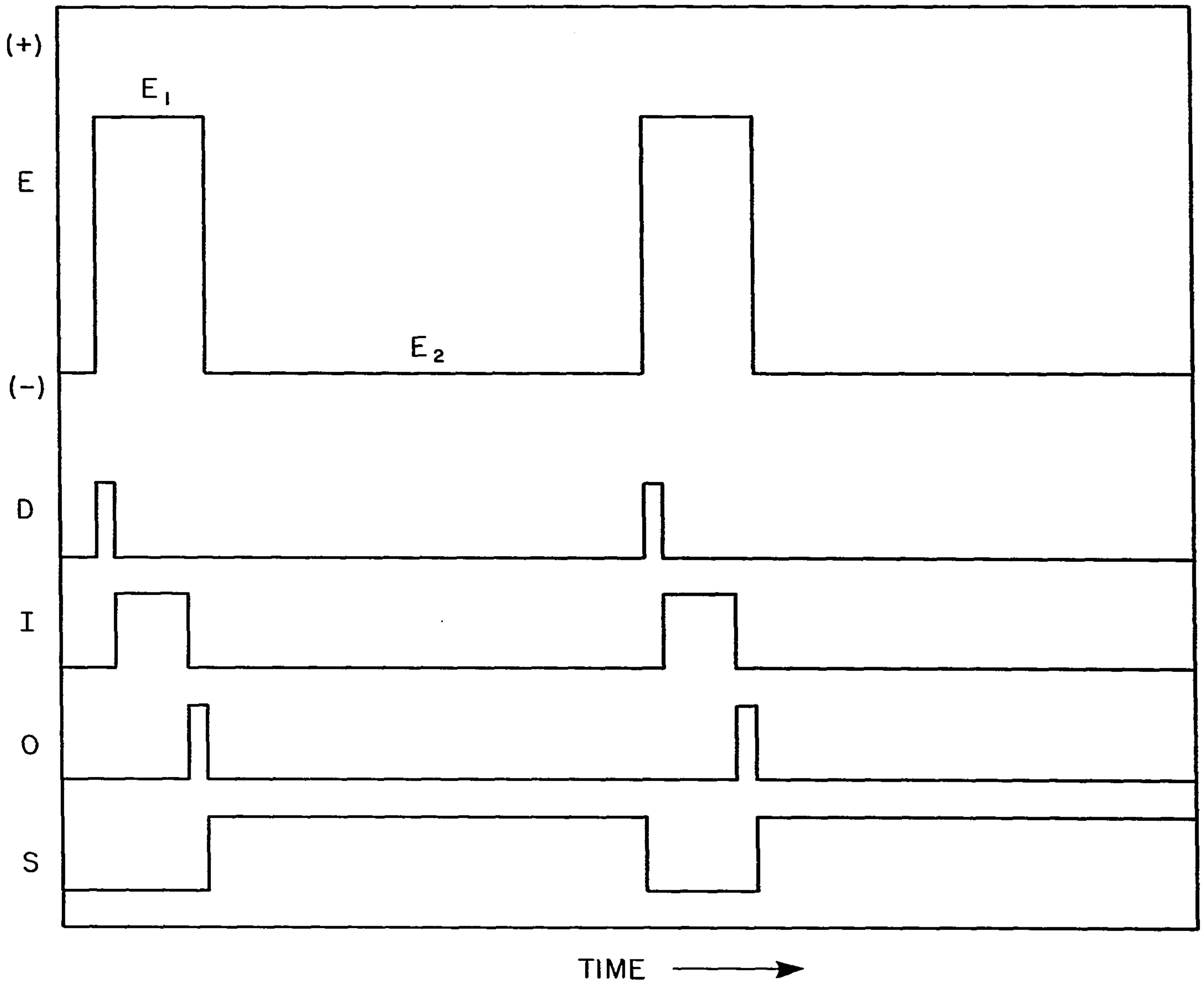
Figure XI-1. Pulsed coulometric waveform for electrodeposited metal ions

Timing parameters: (D) delay time before integration;

(I) integration time;

(O) sampling time for signal output;

(S) shorting time of integrator.


(+)
E₁
E
E₂
(-)
D
I
O
S
TIME

C. Experimental

1. *Instrumentation*

All staircase voltammograms were obtained with a specially designed computer system (Hewlett Packard, Palo Alto, CA) interfaced to a PAR 174A potentiostat (EG&G Princeton Applied Research, Princeton, NJ).[9] The waveform consisted of 18 ms steps with current integration for the last 16.67 ms and potential scan reversal at the specified limits. The waveforms were applied to a gold rotated disk electrode (RDE, 0.005 cm^2; Pine Instrument Co., Grove City, PA). The rotator was a Model MSR (Pine Instrument Co.) and rotation speed was controlled via the computer system. All potentials are referenced to the SCE.

All flow-injection studies were performed with a Dionex UEM detector (Dionex Corporation, Sunnyvale, CA), a microprocessor based potentiostat. In order to perform these experiments the software and hardware were slightly modified to allow for integration time variation and background offset compensation.

The FIA system was based on a low-pressure peristaltic pump with computer controlled injection and has been described.[34] The flow-through detector cell[34] for FIA studies (Dionex Corp.) was of the sandwich-type and contained a Au working (0.05 cm^2), glassy carbon counter, and SCE reference electrode.

2. *Chemicals*

Solutions were prepared with reagent grade chemicals (Fisher Scientific, Fair Lawn, NJ) and triply distilled water. All metal ion solutions were made with nitrate salts and the supporting electrolyte was 0.2 M HNO_3. Where noted, dissolved oxygen was removed by purging with reagent grade nitrogen (99.99%, Cooks Inc., Algona, IA).

D. Results and Discussion

To establish a general PCD waveform for the metal ions of interest it was necessary to determine their electrochemical behavior, i.e., the UPD half-wave potentials and stripping peak potentials, in an electrolyte which prohibits precipitation. For our studies, Hg(II) and Bi(III) were chosen as model analytes. Staircase voltammograms are shown in Figs. XI-2 and XI-3 for these metals. For all metals tested, the reduction waves appear negative of the oxide stripping peak for Au, indicating that deposition does not occur on the oxide surface. With the exception of Hg(II) reductions for all metals tested occur at ca. 0.3 V or less, but values are specific for each species. Stripping of the metal is also distinctive, but regions are less well defined, with some metals having two or more peaks (e.g., Bi(III)) resulting from multilayer deposition. For all metals used in this study, it was observed that they are stripped from the surface before Au oxide formation supporting the observation that deposition

Figure XI-2. Current-potential curves for Hg(II) in nitrogen saturated 0.20 M HNO_3

Pulse amplitude (ΔE): 20 mV

Scan rate (ϕ): 2.4 V min^{-1}

Electrode rotation rate (ω): 900 rev min^{-1}

Curves:
[A] residual;
[B] 1.0 mM Hg(II);

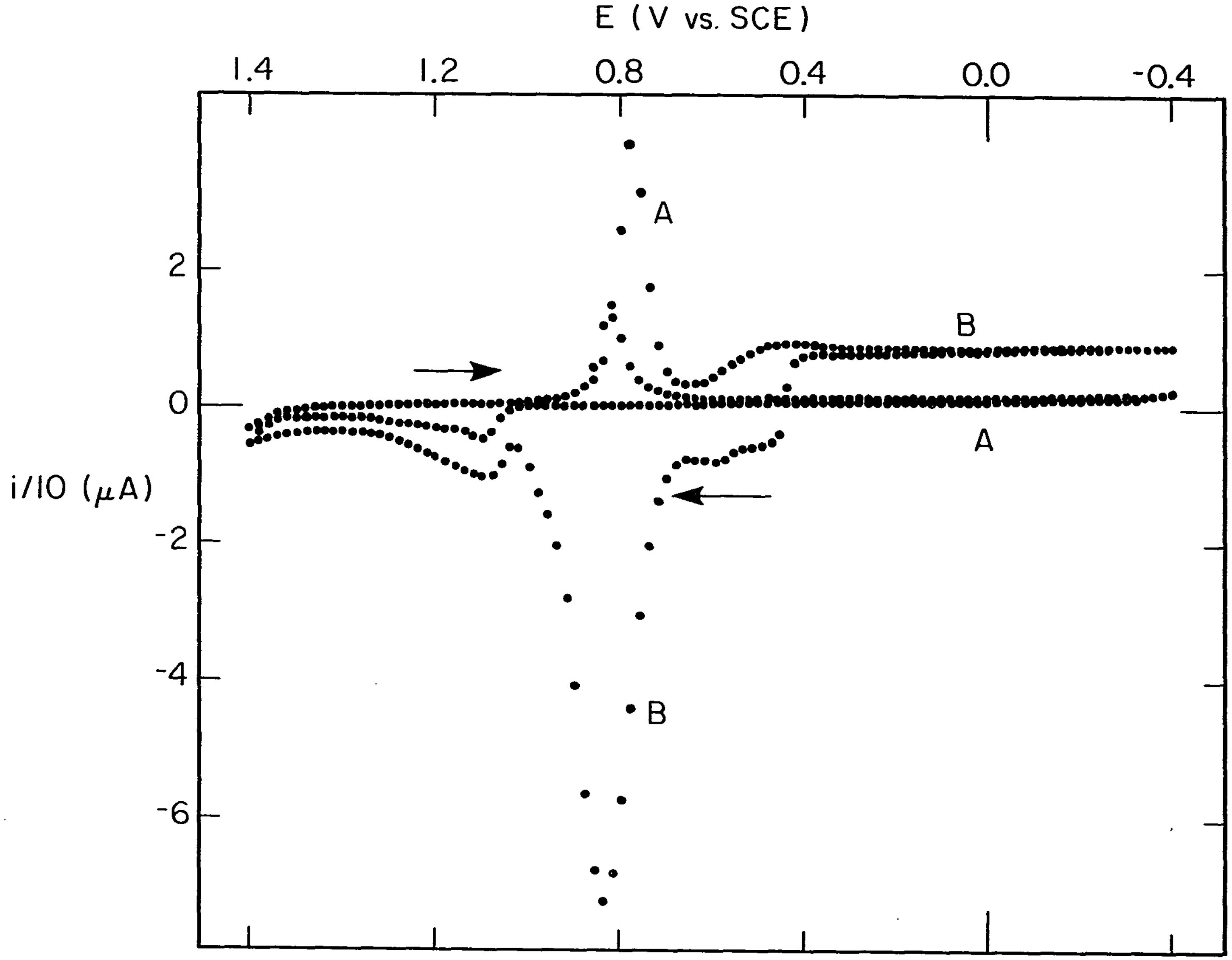
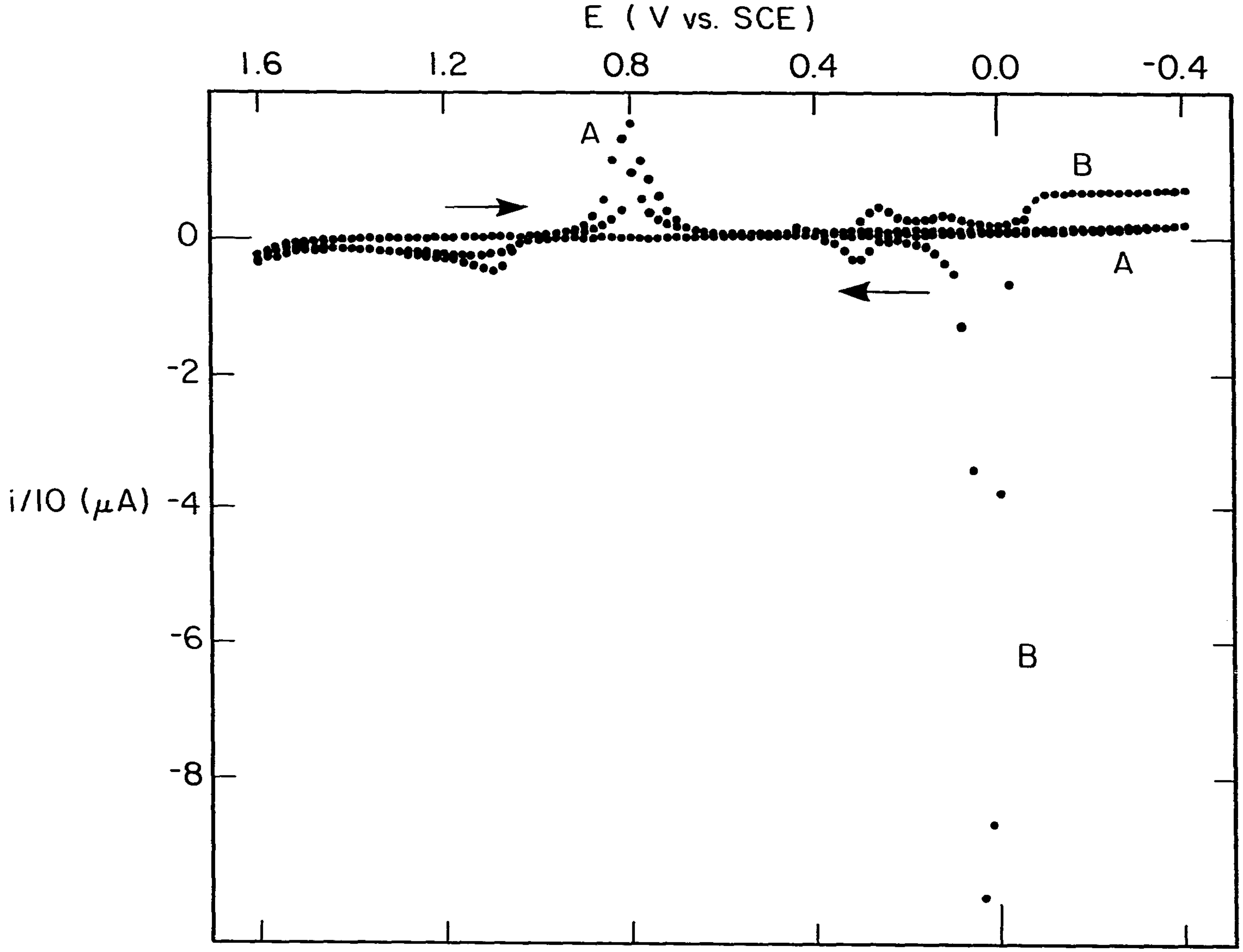

E (V vs. SCE)
1.4
1.2
0.8
0.4
0.0
-0.4
i/10 (μA)
2
0
-2
-4
-6
A
B
B
A
A
B

Figure XI-3. Current-potential curves for Bi(III) in nitrogen saturated 0.20 M HNO_3

Pulse amplitude (ΔE):	20 mV
Scan rate (ϕ):	2.4 V min^{-1}
Electrode rotation rate (ω):	900 rev min^{-1}
Curves:	[A] residual; [B] 1.0 mM Bi(III).


E (V vs. SCE)
1.6
1.2
0.8
0.4
0.0
-0.4
i/10 (μA)
0
-2
-4
-6
-8
A
B
A
B

does not occur on oxide films.

Knowing the behavior of the metals on Au, it is possible to construct a general and tentative waveform from the staircase voltammograms. Since all deposition processes for the metal ions of interest begin at potentials positive of ca. -0.3 V, the deposition potential, E_2, may be selected as any value equal to or negative of this potential, with the cathodic limit set at solvent decomposition, i.e., ca. -0.45 V. For the general case, the stripping potential, E_1, is selected to be a potential positive of the most anodic stripping peak for the metal ions in the mixture. However, due to the interference effects from dissolved oxygen, this potential is limited to potentials positive of ca. 0.7 V. For the analysis of solutions containing Hg(II), this potential would not be sufficiently positive and would result in exceptionally tailed peaks and a slow baseline drift, owing to the sluggish removal of the deposited metal from the electrode surface.

With the rate of deposition limited by mass transport, and the realization that the stripping process is rapid compared to deposition, an unsymmetric square-wave waveform results, where $t_2 >> t_1$. Methods for waveform optimization have been described elsewhere[34] and correspond simply to the variation of all parameters of the waveform to obtain a maximum signal-to-background ratio. With essentially no upper limit for deposition times, limitations on waveform frequency must rest on the minimum frequency necessary to resolve the most poorly resolved chromatographic peaks. In our laboratory, this minimum has been arbitrarily set at ca. 1 Hz.

With the waveform of E_2 = -0.3 V (t_2 = 800 ms), E_1 = 0.9 V for Bi(III) and 1.05 V for Hg(II) (t_1 = 200 ms; t_i = 167 ms, t_d = 4 ms), calibration plots were obtained and are shown in Fig. XI-4. The response is linear for the ranges indicated, but is expected to deviate at higher concentrations. Detection limits for several ions are shown in Table 1. The average limit of detection is on the order of 1 $\mu\underline{M}$ for 50 μL injected. A noteworthy exception is Hg(II) which is ca. one order of magnitude lower.

The lower detection limit for Hg(II) is primarily due to the alternate waveform used. In this case, the detection potential was selected to be just positive of the observed stripping peak (i.e., ca. 200 mV positive of E_p) as compared to a minimum of ca. 400 mV for the other metals. For the best S/N, i.e., the ratio of peak current to peak-to-peak background noise, the potential should be selected to be just positive of E_p, with the upper limit of E_1 defined by the onset of Au oxide formation (Figs. XI-2 and 3) which inadvertently would lead to large background charge. This suggests that the detection limits for metals reported in Table 1, with the exception of Hg(II), may be improved by selective positioning of E_1.

To demonstrate the variation of E_1 while holding all

Figure XI-4. Calibration plots for Hg(II) and Bi(III)

Waveform:	E_1 = 0.9 V for Bi(III) (t_1 = 200 ms), E_1 = 1.05 V for Hg(II) (t_1 = 200 ms), E_2 = -0.3 V (t_2 = 800 ms), t_i = 167 ms, t_d = 4 ms.
Curves:	[●] Hg(II) [▲] Bi(III)
Volume injected:	50 μL
Carrier stream:	0.20 M KNO_3 at 0.5 mL min^{-1}
Dispersion coefficient ($D_p = C_p/C^b$):	0.56

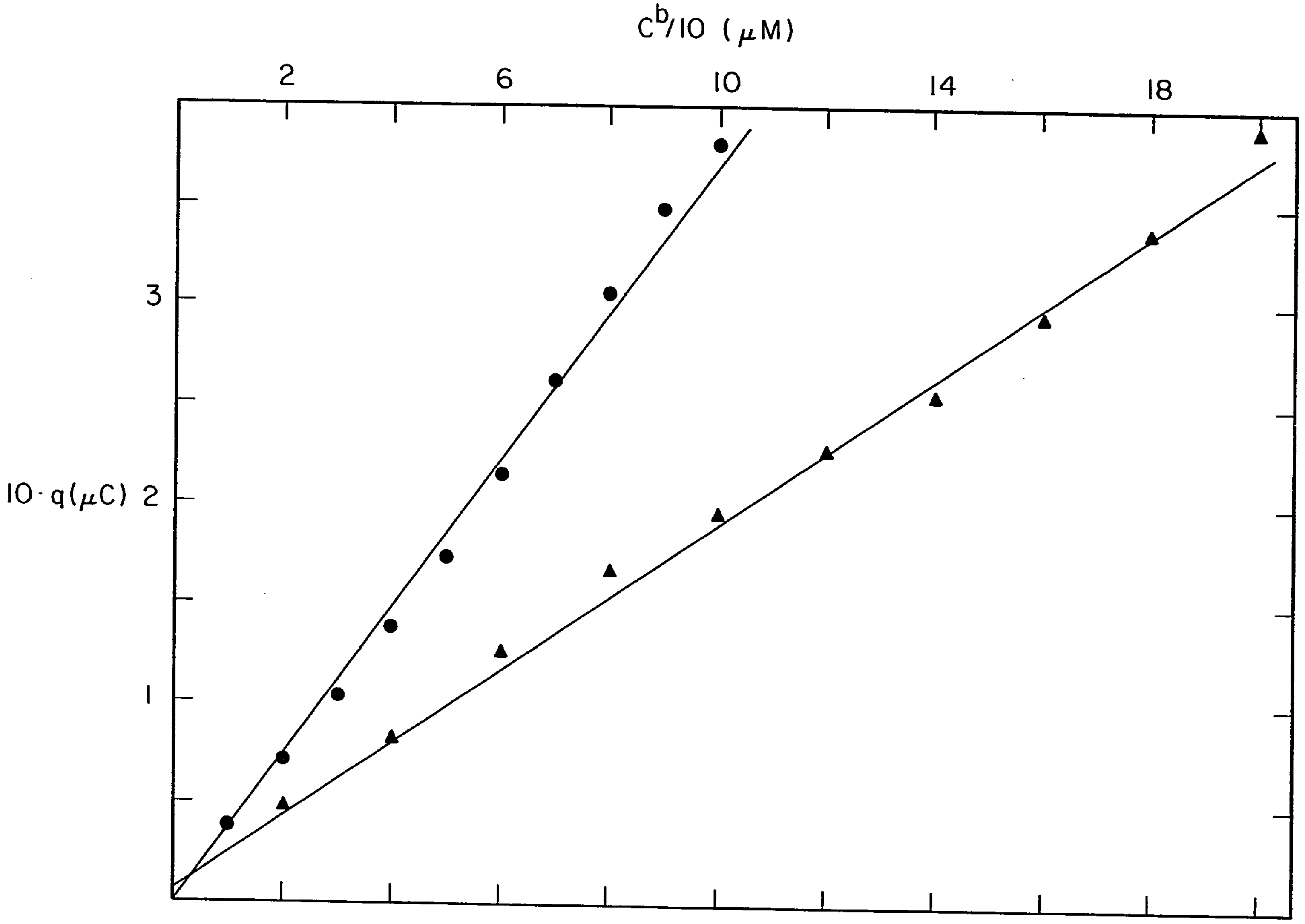

C^b/10 (μM)
2
6
10
14
18
10·q(μC)
1
2
3

Table XI-I. Detection limits of metals obtained with FI-PCD[a] at a Au electrode with the waveform E_1 = 0.90 V (t_i = 167 ms, t_d = 4 ms, t_1 = 200 ms), E_2 = -0.30 V (t_2 = 800 ms). Nitrate salts were used for all metal ion solutions unless otherwise noted

Metal ion	C^b (μM)	Amount injected (pmoles)	ΔE_p (V)[b]
Hg(I)[c]	0.3	15	0.43
Hg(II)[c]	0.3	15	0.43
Cu(II)	3	150	0.21
Bi(III)	4	200	0.25
Pb(II)	12	600	0.40
Cd(II)	8	400	0.50
Ni(II)	15	750	--
Zn(II)	8	400	--
Tl(III)[d]	0.7	35	0.68

[a] Volume injected: 50 μL
Carrier stream: 0.20 $\underline{M}$ KNO_3 at 0.5 mL min^{-1}
Dispersion coefficient ($D_p = C_p/C^b$): 0.56.

[b] Reprinted from Ref. 31.

[c] E_1 = 1.05 V.

[d] Sulfate salt.

other parameters constant Cu(II) was substituted for Hg(II) in this study because of the inability to vary this potential for the latter without producing substantial amounts of gold oxide; the results are shown in Fig. XI-5. As E_1 approaches E_p, i.e., shifting to more cathodic potentials, the peak height is seen to increase, until E_1 is approximately equal to, or more negative than E_p, where the peak height decreases and eventually becomes negative due to reduction of the metal ion. It is seen that the peak height may increase as much as an order of magnitude, resulting in a decrease in the observed detection limit by an equivalent amount. This increase in peak height is attributed to the slower kinetics associated with oxidation of the metal deposit at potentials nearer, yet anodic, of the stripping peak, and is not a result of oxygen reduction since this is compensated for in the baseline determination. However, we feel the values in Table 1 are more valid unless special precautions are taken either to remove dissolved oxygen, or to keep its concentration constant in the carrier and the injected samples.

Although the technique was originally designed to be used for universal chromatographic detection some selectivity may be gained by proper selection of E_2; the variation of this potential is demonstrated with the FI-PCD of Hg(II) and Bi(III) in the presence of several other metals (Fig. XI-6). Each set of multiple peaks, I, II, and III, correspond to the definition of E_2 as 0.60, 0.25, and -0.30 V, respectively.

Figure XI-5. Variation of E_1 in PCD waveform for Bi(III) and Cu(II)

Waveform: E_1 varied (t_1 = 200 ms),
E_2 = −0.3 V (t_2 = 800 ms).
t_i = 167 ms,
t_d = 4 ms.

Conditions: Same as Fig. XI-4.

Curves: [●] 100 $\mu\underline{M}$ Bi(III),
[▲] 100 $\mu\underline{M}$ Cu(II).

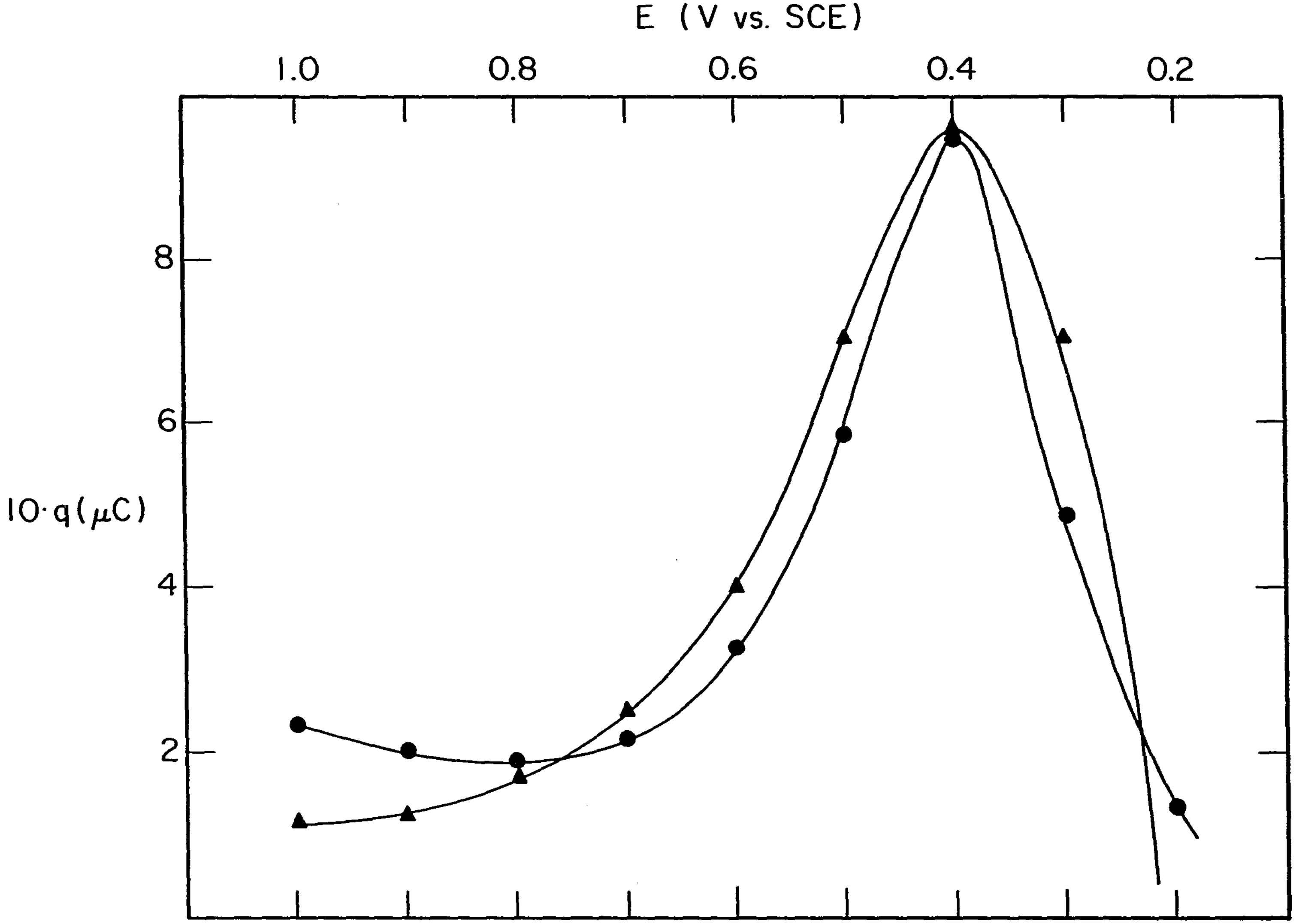

E (V vs. SCE)
1.0
0.8
0.6
0.4
0.2
8
6
4
2
10·q(μC)

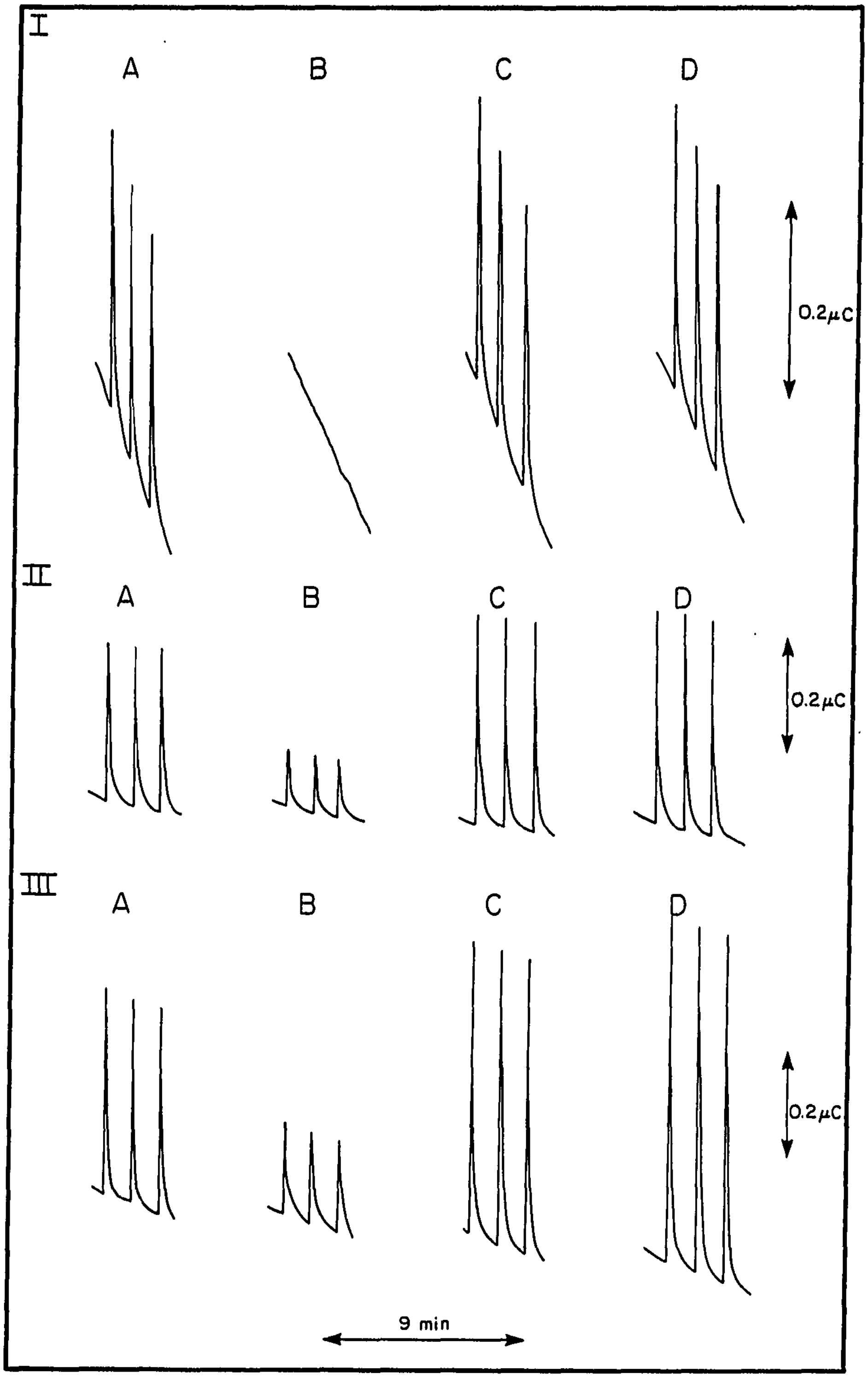
Figure XI-6. Selective detection of Hg(II) and Bi(III) by variation of E_2 in PCD waveform

Waveform: $E_1 = 1.05$ V ($t_1 = 200$ ms),
E_2 varied ($t_2 = 800$ ms),
$t_i = 167$ ms,
$t_d = 4$ ms.

Conditions: Same as Fig. 4.

Injection Peaks:
[I] $E_2 = 0.60$ V,
[II] $E_2 = 0.25$ V,
[III] $E_2 = -0.30$ V.

[A] 50 $\mu\underline{M}$ Hg(II);
[B] 100 $\mu\underline{M}$ Bi(III);
[C] 50 $\mu\underline{M}$ Hg(II) and 100 $\mu\underline{M}$ Bi(III);
[D] 50 $\mu\underline{M}$ Hg(II), 100 $\mu\underline{M}$ Bi(III), 100 $\mu\underline{M}$ Cd(II), 100 $\mu\underline{M}$ Cu(II), and 100 $\mu\underline{M}$ Zn(II).


I
A
B
C
D
0.2μC
II
A
B
C
D
0.2μC
III
A
B
C
D
0.2μC
9 min

Each subset of three peaks, A - D, correspond to the solutions analyzed. For example, the subset IIC corresponds to the FI-PCD analysis of a solution containing Hg(II) and Bi(III) at $E_2 = 0.25$ V, and IIIB corresponds to the analysis of a solution containing Bi(III) only at $E_2 = -0.30$ V. For $E_2 = 0.60$ V (subsets IA-D), only Hg(II) is detected even for solutions containing several ions. For $E_2 = 0.25$ V (subsets IIA-D), both Hg(II) and Bi(III) are detected; however, the sensitivity is greatly reduced for the latter owing to the relatively large deposition potential. Again, no other ions in the mixture are detected, denoted by the equivalent peaks heights for subsets IIC and IID. For $E_2 = -0.30$ V (subsets IIIA-D), all ions are detected and the method is considered universally applicable. Experiments employing variation in E_1 are not considered as selective due to overlapping stripping peaks for many of the metals.

E. Conclusions

The initial experiments for the bulk and underpotential deposition of metal ions at Au electrodes indicate that the method of PCD is a viable technique for the determination of trace metal ions. The method is applicable for the determination of many metals now determined with polarographic methods, and with the added advantages of nontoxic material handling and the ease of application to flow-injection and chromatographic analyses makes it an alternative source for the determination of heavy metals.

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XII. SUMMARY

Techniques have been presented for the electrochemical detection of electroactive elements and compounds utilizing pulsed waveforms in flow-injection and liquid chromatographic systems. Particular emphasis has been placed on the optimization of waveforms for the rejection of common interferants, and the enhancement of signal-to-noise with a concomitant increase in sensitivities and decrease in detection limits.

Constant potential pulse polarography has been presented as an alternate polarographic technique for the determination of reversible electroactive ions, such as Cd(II), Cu(II) and Pb(II), in the presence of dissolved oxygen with no apparent interferences. Particular emphasis was placed on the development of CPPP for use in on-line flow-injection analysis with large sample sizes, ca. 2-mL, for qualitative as well as quantitative identification.

The advantages of using a gold electrode over platinum with a three-step pulsed amperometric waveform have been presented with special emphasis on the detection of carbohydrates in alkaline solutions. For optimum sensitivities and detection limits, pulsed amperometric detection of carbohydrates with a platinum electrode requires the selection of a detection potential where dissolved oxygen is reduced. As a result background currents are very large and the superimposed noise limits the detectability. However, the oxidation of simple carbohydrates on a gold electrode occurs in a region of zero background resulting in a five-fold increase in detectability.

Methods for detecting carbohydrates with ***pulsed amperometric detection*** are extended with the addition of an asymmetric two-step waveform at a gold electrode. The addition of a two-step waveform extends the application of PAD to potentiostats capable of performing an asymmetric square waveform, that is, instruments capable of performing normal pulse voltammetry. Detection limits are equivalent to previous three-step methods at a gold electrode and are represented by detection limits of 35 and 50 $\mu\underline{M}$ for glucose and sucrose, respectively, in 0.20 $\underline{M}$ NaOH.

In an attempt to increase the overall linear range for the detection of carbohydrates with pulsed waveforms, the method of ***pulsed coulometric detection*** was developed. This approach takes advantage of the observed linear i vs. C response, for low C, in PAD, which implies that linearization may be accomplished with the increase in detectability. This increase is obtained by increasing the signal-to-noise through integration of the transient signal at a fixed detection potential. Detection limits are lowered by over an order of magnitude, and are represented by limits of detection of 1.0 and 2.5 $\mu\underline{M}$ for glucose and sucrose, respectively.

Pulse coulometric methods were also developed which would automatically reduce background signals, by virtue of their design, and reduce the need for design of special offset compensation circuitry. In addition, these waveforms virtually eliminated background drift due to electrode surface reconstruction; a result of the charge involved in the formation of surface oxide is equivalent to the charge passed with the stripping of the oxide layer. The waveforms were also designed for the minimization of pH effects which would be encounter in ion chromatography utilizing pH gradients. Emphasis is placed on the development of such waveforms for the detection of carbohydrates and sulfur containing compounds. Detection limits for the carbohydrates were comparable to previous pulsed coulometric methods stated above.

Pulsed coulometric detection was developed also for the analysis of heavy metal ions which are reduced and deposited at cathodic potentials on a gold electrode, and subsequently stripped at more anodic potentials. Limits of detection for most metals, such as Hg(II), Bi(III), Pb(II), Cd(II), etc., are 0.1-10 $\mu\underline{M}$ for a two-step waveform applied with a frequency of 1 Hz.

XIII. FUTURE WORK

An endless number of waveforms may be created for the electrochemical detection of electroactive and electroinactive compounds in FIA and LC. Future research should center around the development of more universal waveforms applicable for the detection of a wide variety of analytes on a variety of electrodes. Additional work should also be performed on the development of more selective detection, perhaps in conjunction with other electroanalytical methods. Both of these areas will require, however, the development of a multi-programmable low noise potentiostat, and may also require interfacing nonelectrochemical instrumentation.

The power of future LC detectors will be in the development of AI instruments. Few electrochemical detectors can resist or compensate for changes in background variations. For example, the variation of eluent pH or composition will cause a severe base line drift for most detectors. Detectors must be developed to automatically compensate for these background variations but not at the expense of sensitivity or detectability.

It is also necessary that the detector be able to provide some qualitative information. For more complex samples it becomes difficult to attempt to identify each constituent by simple peak assignments through sample "spiking" with known standards and it becomes necessary that information be available, preferably in a large data base, that would reduce the amount of time necessary for qualitative identification. Although it is certainly questionable whether electrochemical detectors could provide qualitative information equivalent to MS or NMR, methods have been developed sufficiently for distinguishing between different compounds in a specific class.

As a final note, it is apparent that current and future detectors must be involved in the separation process. This is an extension of detector specificity, however, it may also provide for the "deconvolution" of overlapping peaks due to an inefficient separation on the chromatographic column. With the increasing complexity of sample matrices, and the reduction in sample work-up, it becomes more and more difficult to develop analytically useful chromatographic schemes which will effect complete separation of all sample constituents. Clearly, "separation" of overlapping components by the detector must be based on different molecular properties than the chromatographic separation.

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XVIII. SUBJECT INDEX

XVI. AUTHOR INDEX

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XVIII. APPENDIX

A. Extended Bibliography for Underpotential Deposition Summary

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B. Program Listings

Since most of the data presented in this dissertation were obtained by software written entirely by this author, it is felt that they are as important, if not more important, than any chapter appearing in this dissertation--without these programs there would be no data and, hence, no dissertation. However, only those programs which have been extensively used are included. Several other programs are available, e.g., for performing polarographic experiments, and modifying data sets, but have not been included because of their limited use, and the large amount of time necessary for converting them to the format of this dissertation. Before these programs are duplicated in the following pages, a very brief summary of each will follow; however, because of the complexity of many of the programs, due primarily to the versatility in their writing, a detailed discussion of their workings or operation will not be included. Additionally, these programs are not considered to be totally error free; this is a result of the versatility of the programs, which imposed severe limitations on the minimal time necessary for debugging. Therefore, a unique application can give erroneous results because it is, in fact, unique, and has not been tested by this author. Users of this system can assume that no errors exist in the predefined waveforms, such as those which exist in the program *Triple Step*, and calculations, such as equations used for conversion of volts to current or charge.

Array Create is used to combine individual files obtained from *PAD i-t Decays* or *Triple Step*. Either the entire files can be added as separate columns in the new array file created by *Array Create*, or parts (sections) of these files can be added in any user defined combination, thus allowing for a wide variety curves which can be plotted by *Array Plot*. For example, PAD voltammograms obtained by *Triple Step* for varying rotation speeds, can be combined into a single array file where these files are added as separate columns in the new array file.

Array Plot is used solely to plot array files created by *Array Create*. Any subset of the data within the array file can be plotted by selecting the desire columns and rows. For the example of an array containing voltammograms obtained at different electrode rotation speeds, one can select a subset of the voltammograms by specifying the desired rows (i.e., potentials) and the rotation rates by specifying the desired columns. In addition there are a variety of built-in mathematical functions which can be used to modify the data set before plotting. Note, that due to memory limitations of the microcomputer, once the data set has been mathematically manipulated the original data set can be reviewed or manipulated in a different fashion only by "re-entering the array file."

PAD i-t Decays is used to obtain transient responses where a S/H circuit is not used. *PAD Plot* is the corresponding plotting program for *PAD i-t Decays*; however, *Array Create* can be used to create an array file for *Array Plot* where this file can contain a group of files initially created with *PAD i-t Decays*.

Since it would be difficult to use analog methods in conjunction with the digital sampling programs, the program *Staircase* was created to simulate cyclic voltammetry. This program uses a standard staircase waveform with scan reversal at the potential extremes. Up to five files created with *Staircase* can be superimposed with the use of the program *Staircase Plot*. The graphical output uses current-potential axes which conform to the "Midwest" convention of voltammetric representations.

The most widely used program, and the most versatile, is *Triple Step* which applies multi-potential step waveforms for PAD and PCD. In addition, any parameter(s) of the waveform can be varied, with specified precedence for variation of several waveform parameters. Thus, this program can be used for FIA or LC as well as for batch studies. At present, there are five predefined waveforms which can be selected, four of these waveforms are kept in separate files which are merged with the program when needed. A group listing of these waveforms can be found in *Waveforms* which has been included here as the last "program".

Note that the file structure is kept essentially the same between programs so that it is possible transfer files between several programs. It is best to experiment to determine the files (actually, file types) which can be read by the plotting programs. Also, provisions have been made in all of the data acquisition programs to allow for automatic electrode rotation speed control.

1. Array Create

```
10      GOTO beginning
20      !
30      Y(U+T*(L-1),V)=Y(U+T*(L-1),V)/(CONC(X)*DIVIDE) @ RETURN
40      Y(U+T*(L-1),V)=Y(U+T*(L-1),V)/(POT(Y)*DIVIDE) @ RETURN
50      Y(U+T*(L-1),V)=Y(U+T*(L-1),V)/DIVIDE @ RETURN
60      Y(U+T*(L.1),V)=Y(U+T*(L-1),V)/(POT(Y)*CONC(X)*DIVIDE) @ RETURN
70      !
80      beginning:
90      !
100     DIM Y(150,60),POT(150),CONC(150),
        PREFILE$[10],FILE$(150)[10],T$[60]
110     DIM ARRAYFILE$[10],J1$[5],J2$[5],C1$[5],C2$[5],CUR(20)
120     ON ERROR GOSUB 1770
130     CLEAR @ DISP @ DISP "A) Run program ARRAY CREATE" @
        DISP "B) Chain Autost"
140     DISP @ DISP @ INPUT T$ @ IF LEN (T$)=0 THEN 160
150     IF T$[1,1]="A" OR T$[1,1]="a" THEN 160 ELSE CHAIN "Autost"
160     CLEAR @ DISP "Enter the file prefix." @ INPUT PREFILE$
170     CLEAR @
        DISP "Enter file names Individually or by Limits <I,L> [I] :"
180     INPUT T$ @ IF LEN (T$)=0 THEN 430
190     IF T$[1,1]="I" OR T$[1,1]="i" THEN 430
200     CLEAR @ DISP @ DISP "Enter the lower row limit ,";@ INPUT I1$
210     DISP @ DISP "Enter the upper row limit ,"; @ INPUT I2$
220     DISP @ DISP "Enter the lower column limit,"; @ INPUT J1$
230     DISP @ DISP "Enter the upper column limit,"; @ INPUT J2$
240     DISP @ DISP "Read Rows or Columns first <R,C> [R]"
250     DISP "For reading whole files the variable read FIRST is placed
        in adjacent columns"
260     DISP "with each successive increment in the second variable. For
        reading parts of"
270     DISP "files whatever is varied first is read into the first
        column and the columns"
280     DISP "are filled with each successive increment in the second
        variable."
290     INPUT T$ @ INC=0 @ IF LEN (T$)=0 THEN TYPE=1 @ GOTO 310
300     IF T$[1,1]="r" OR T$[1,1]="R" THEN TYPE=1 ELSE TYPE=2 @ GOTO 370
310     FOR J=VAL (J1$) TO VAL (J2$)
320     FOR I=VAL (I1$) TO VAL (I2$)
330     INC=INC+1 @ FILE$(INC)=VAL$ (I)&VAL$ (J)
340     NEXT I
350     NEXT J @ NF=INC
360     GOTO 420
370     FOR I=VAL (I1$) TO VAL (I2$)
380     FOR J=VAL (J1$) TO VAL (J2$)
390     INC=INC+1 @ FILE$(INC)=VAL$ (I)&VAL$ (J)
400     NEXT J
410     NEXT I @ NF=INC
```

```
420     GOTO 470
430     CLEAR @ DISP "Enter the file names (numbers)." @ DISP "Press <END
        LINE> when all have been entered."
440     FOR J=1 TO 60 @ INPUT FILE$(J)
450     IF LEN (FILE$(J))=0 THEN NF=J-1 @ GOTO 470
460     NEXT J
470     CLEAR @ DISP "Drive number <0,1> [1]" @ INPUT DRIVE$
480     IF LEN (DRIVE$)=0 THEN DRIVE$="1"
490     IF VAL (DRIVE$)=0 OR VAL (DRIVE$)=1 THEN 500 ELSE 470
500     CLEAR @ DISP "Eat the Whole file or just Parts <W,P> [W] :" @
        INPUT T$
510     IF LEN (T$)=0 THEN PARTS=0 @ GOTO 760
520     IF T$[1,1]="W" OR T$[1,1]="w" THEN PARTS=0 @ GOTO 760 ELSE
        PARTS=1
530     CLEAR @ DISP "Which current elements do you want <1,N> :"
540     FOR I=1 TO 50
550     INPUT T$
560     IF LEN (T$)=0 THEN TOTCUR=I-1 @ GOTO 590 ELSE CUR(I)=VAL (T$) @
        GOTO 580
570     GOTO 550
580     NEXT I
590     PTYPE,CFLAG,RFLAG,KFLAG=0 @ DIVIDE=1
600     CLEAR @ DISP "Divide all elements by Column or Row values or a
        Konstant <C,R,K> [K] :"
610     PTYPE=0 @ INPUT T$ @ IF LEN (T$)=0 THEN PTYPE=3 @ GOTO 760
620     IF T$[1,1]=" " THEN 660
630     IF T$[1,1]="C" THEN CFLAG=1 @ GOTO 660
640     IF T$[1,1]="R" THEN RFLAG=1 @ GOTO 660
650     IF T$[1,1]="K" THEN KFLAG=1
660     IF LEN (T$)>1 THEN T$=T$[2,LEN (T$)] @ GOTO 620
670     IF CFLAG=0 AND RFLAG=0 AND KFLAG=0 THEN 600
680     IF CFLAG=1 THEN PTYPE=1
690     IF RFLAG=1 THEN PTYPE=2
700     IF KFLAG=1 THEN PTYPE=3
710     IF CFLAG=1 AND RFLAG=1 THEN PTYPE=4
720     IF CFLAG=1 AND KFLAG=1 THEN PTYPE=5
730     IF RFLAG=1 AND KFLAG=1 THEN PTYPE=6
740     IF CFLAG=1 AND RFLAG=1 AND KFLAG=1 THEN PTYPE=7
750     IF PTYPE=1 OR PTYPE=2 OR PTYPE=4 THEN 810
760     DISP @
        DISP "Enter the constant divisor <any non-zero value> [1] :"
770     INPUT T$ @ IF LEN (T$)=0 THEN DIVIDE=1 @ GOTO 810 ELSE DIVIDE=VAL
        (T$) @ GOTO 790
780     GOTO 760
790     IF DIVIDE=0 THEN 770
800 !
810     CLEAR @ DISP "Enter the minimum row header, e.g., beginning
        potential."
820     INPUT T$ @ IF LEN (T$)=0 THEN 810 ELSE RMIN=VAL (T$) @ GOTO 840
830     GOTO 810
```

```
840     DISP @ DISP @ DISP "Enter the maximum row header, e.g., final
        potential."
850     INPUT T$ @ IF LEN (T$)=0 THEN 840 ELSE RMAX=VAL (T$) @ GOTO 870
860     GOTO 840
870     DISP @ DISP @ DISP "Enter the row header increment, e.g.,
        potential increment."
880     INPUT T$ @ IF LEN (T$)=0 THEN 870 ELSE RINC=VAL (T$) @ GOTO 900
890     GOTO 870
900     T=(RMAX-RMIN)/RINC+1 @ IF PARTS=1 THEN 910 ELSE 940
910     IF T<T*TOTCUR THEN INC=1 @ GOTO 920 ELSE 940
920     INC2=0 @ FOR J=INC TO INC+T @ INC2=INC2+1 @
        POT(J)=RMIN+RINC*(INC2-1) @ NEXT J @ INC=INC+T
930     IF INC<T*TOTCUR THEN 920 ELSE 950
940     FOR J=1 TO T @ POT(J)=RMIN+RINC*(J-1) @ NEXT J
950     CLEAR @ DISP "Enter tbe minimum column header, e.g., conc.,
        w(1/2), etc."
960     INPUT T$ @ IF LEN (T$)=0 THEN 950 ELSE CMIN=VAL (T$) @ GOTO 980
970     GOTO 950
980     DISP @ DISP "Enter the maximum column header, e.g., conc.,
        w(1/2), etc."
990     INPUT T$ @ IF LEN (T$)=0 THEN 980 ELSE CMAX=VAL (T$) @ GOTO 1010
1000    GOTO 980
1010    DISP @ DISP "Enter the column header increment, e.g., conc.,
        w(1/2), etc."
1020    INPUT T$ @ IF LEN (T$)=0 THEN 1010 ELSE CINC=VAL (T$) @ GOTO 1040
1030    GOTO 1010
1040    T=(CMAX-CMIN)/CINC+1 @ IF PARTS=0 THEN 1050 ELSE 1080
1050    IF T<NF THEN INC=1 @ GOTO 1060 ELSE 1080
1060    INC2=0 @ FOR J=INC TO INC+T @ INC2=INC2+1 @
        CONC(J)=CMIN+CINC*(INC2-1) @ NEXT J @ INC =INC+T
1070    IF INC<NF THEN 1060 ELSE 1090
1080    FOR J=1 TO NF @ CONC(J)=CMIN+CINC*(J-1) @ NEXT J
1090    CLEAR @ DISP "Enter the array file name" @ INPUT ARRAYFILE$
1100    F$=":D70"&DRIVE$
1110    IF PARTS=0 THEN 1430
1120    ON TYPE GOTO 1130,1280
1130    INC=0 @ T=VAL (I2$)-VAL (I1$)+1
1140    FOR J=1 TO VAL (J2$)-VAL (J1$)+1
1150    FOR I=1 TO VAL (I2$)-VAL (I1$)+1
1160    INC=INC+1
1170    ASSIGN# 1 TO PREFILE$&FILE$(INC)&F$
1180    DI$P "Reading";PREFILE$&FILE$(INC)
1190    FOR L=1 TO TOTCUR
1200    READ# 1,20+CUR(L)*2 ; Y(I+T*(L-1),J)
1210    X=J @ Y=I @ U=I @ V=J
1215    DISP CONC(X),POT(Y)
1220    ON PTYPE GOSUB 30,40,50,60,30,40,60
1230    NEXT L
1240    ASSIGN# 1 TO *
1250    NEXT I
1260    NEXT J
```

```
1270    N=TOTCUR*(VAL (I2$)-VAL (I1$)+1) @ NF=VAL (J2$)-VAL (J1)+1 @
        GOTO 1510
1280    INC=0 @ T=VAL (J2$)-VAL (J1$)+1
1290    FOR I=1 TO VAL (I2$)-VAL (I1$)+1
1300    FOR J=1 TO VAL (J2$)-VAL (J1$)+1
1310    INC=INC+1
1320    ASSIGN# 1 TO PREFILE$&FILE$(INC)&F$
1330    DISP "Reading";PREFILE$&FILE$(INC)
1340    FOR L=1 TO TOTCUR
1350    READ# 1,20+CUR(L)*2 ; Y(J+T*(L-1),I)
1360    X=I @ Y=J @ U=J @ V=I
1365    DISP CONC(X),POT(Y)
1370    ON PTYPE GOSUB 30,40,50,60,30,40,60
1380    NEXT L
1390    ASSIGN# 1 TO *
1400    NEXT J
1410    NEXT I
1420    N=TOTCUR*(VAL (J2$)-VAL (J1$)+1) @ NF=VAL (I2$)-VAL (I1$)+1 @
        GOTO 1510
1430    FOR J=1 TO NF
1440    ASSIGN# 1 TO PREFILE$&FILE$(J)&F$
1450    READ# 1 ; A,A,A A,A,A,A,A$,A,A,A$,N,A,A,A,A,A,A,A,A
1460    DISP "Reading";PREFILE$&FILE$(J),N
1470    FOR I=1 TO N @ READ# 1 ; Y(I,0),Y(I,J)
1480    Y(I,J)=Y(I,J)/DIVIDE @ NEXT I
1490    ASSIGN# 1 TO *
1500    NEXT J
1510    DISP @ DISP "Place correct disk in drive and press <END LINE>." @
        INPUT T$
1515    IF SGN (RINC)=-1 THEN TEMP=RMIN @ RMIN=RMAX @ RMAX=TEMP
1520    DISP @ DISP "Writing";ARRAYFILE$
1530    CREATE ARRAYFILE$&F$,20+(N+3)*(NF+3),10
1540    ASSIGN# 1 TOARRAYFILE$&F$
1550    PRINT# 1 ; RMIN,RMAX
1560    PRINT# 1 ; 0,0
1570    PRINT# 1 ; 0,0
1580    PRINT# 1 ; 0,"milli",0
1590    PRINT# 1 ; 0,0
1600    PRINT# 1 ; "NULL",RINC
1610    PRINT# 1 : NF,N,0,0,0,0,0
1620    PRINT# 1 ; 1
1630    FOR J=1 TO NF @ PRINT# 1 ; CONC(J) @ NEXT J
1640    PRINT# 1 ; 0,0
1650    FOR I=1 TO N
1660    PRINT# 1 ; POT(I)
1670    FOR J=1 TO NF
1680    PRINT# 1 ; Y(I,J)
1690    NEXT J
1700    PRINT# 1 ; 1,NF
1710    NEXT I
```

```
1720    PRINT# 1 ; 0 @ FOR J=1 TO NF @ PRINT# 1 ; 1 @ NEXT J @
        PRINT# 1 ; 0 @ PRINT# 1 ; 0
1730    PRINT# 1 ; 0 @ FOR J=1 TO NF @ PRINT# 1 ; N @ NEXT J @
        PRINT# 1 : 0 @ PRINT# 1 ; 0
1740    ASSIGN# 1 TO *
1750    GOTO 130
1760    END
1770    RETURN
```

2. Array Plot

```
1       CLEAR @ DISP "Number of columns 1) less than 30, 2) greater than
        30 <1,2> [2] :"
2       DISP "If you use more than 30 columns the row size is limited to
        100." @ INPUT ZZZ$
10      GOTO beginning
20  !
30      FOR I=1 TO 14 @ ON KEY# I GOTO menu @ NEXT I @ RETURN
40      T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128)
        @ NEXT L
50      RETURN
60  !
70      ASSIGN# 1 TO"CHARSET"
80      FOR I=1 TO 46
90      READ# 1 ; CHAR$(I)
100     NEXT I @ ASSIGN# 1 TO *
110     RETURN
120 !
130 !   dat$ assignment
140 !
150     DAT$(1),DAT$(2),DAT$(3),DAT$(4),DAT$(5),
        DAT$(6),DAT$(7),DAT$(8) =""
160     DAT$(9)=DSPFLAG$ @ DAT$(10)=FILE2$ @ DAT$(11)=DATADRIVE$
170     DAT$(12)=GRAPHDRIVE$ @ DAT$(13)=VAL$ (DRIVE)
180     DAT$(14),DAT$(15),DAT$(16),DAT$(17),DAT$(18),DAT$(19),DAT$(20)=""
190     DAT$(21)=FILE$&LOCK$&" <"&FILETYPE$&">" @ DAT$(22)=""
200     DAT$(23)=VAL$ (YMIN)&" , "&VAL$ (YMAX)
210     DAT$(24)=VAL$ (XMIN)&" , "&VAL$ (XMAX)
220     DAT$(25),DAT$(26)=""
230     DAT$(27)=DSPCRT$ @ DAT$(28)="N/A" @ DAT$(29)=DSPXY$
240     DAT$(30)=SCALING$ @ DAT$(31)=PENSWITCH$ @ DAT$(32)=PLOTAXES$
250     DAT$(33)=PLOTLABEL$ @ DAT$(34)=VAL$ (XCLICK) @
        DAT$(35)=VAL$ (YCLICK)
260     DAT$(36)=TYPE$ @ DAT$(37),DAT$(38)="" @  DAT$(39)=ZPRINT$
270     DAT$(40),DAT$(41)=""
280     RETURN
290 !
300 !   Inputs
310 !
320     IF DSPCRT$="YES" THEN DSPCRT$="NO" ELSE DSPCRT$="YES"
330     GOTO menu
340     IF DSPFLAG$="YES" THEN DSPFLAG$="NO" ELSE DSPFLAG$="YES"
350     GOTO menu
360     IF DSPXY$="YES" THEN DSPXY$="NO" ELSE DSPXY$="YES"
370     GOTO menu
380     CLEAR @ DISP "Enter storage file name <10 characters> [TEST] :" @
        INPUT FILE2$
390     IF LEN (FILE2$)=0 THEN FILE2$="TEST"
400     GOTO menu
```

```
410      CLEAR @ DISP "Enter the minimum on X <-100,100> [0] :" @ INPUT T$
         @ IF LEN (T$)=0 THEN XMIN=0 ELSE XMIN=VAL (T$)
420      IF YMIN<-100 OR YMIN>100 THEN 410
430      DISP @ DISP @ DISP "Enter the maximum on X <-100,100> [0] :" @
         INPUT T$ @ IF LEN (T$)= 0 THEN XMAX=0 ELSE XMAX=VAL (T$)
440      IF XMAX<-100 OR XMAX>100 THEN 430 ELSE GOTO menu
450      CLEAR @ DISP "Enter the minimum on Y <-100,100> [0] :" @ INPUT T$
         @ IF LEN (T$)=0 THEN YMIN=0 ELSE YMIN=VAL (T$)
460      IF YMIN<-100 OR YMIN>100 THEN 450
470      DISP @ DISP @ DISP "Enter the maximum on Y <-100,100> [0] :" @
         INPUT T$ @ IF LEN (T$)= 0 THEN YMAX=0 ELSE YMAX=VAL (T$)
480      IF YMAX<-100 OR YMAX>100 THEN 470 ELSE GOTO menu
490      CLEAR @ DISP "Enter the drive number <0,1 or Both--data read
         only> [B] :" @ INPUT T$
500      IF LEN (T$)=0 THEN T$="B" @ GOTO 540
510      IF T$[1,1]="B" OR T$[1,1]="b" THEN T$="B" @ GOTO 530
520      IF VAL (T$)=0 OR VAL (T$)=1 THEN 530 ELSE 490
530      IF CRSR=5 AND T$[1,1]="B" THEN 490
540      IF CRSR=4 THEN DATADRIVE$=T$[1,1] ELSE GRAPHDRIVE$=T$[1,1]
550      GOTO menu
560      CLEAR @ DISP "Enter the file name" @ INPUT T$
570      IF LEN (T$)=0 THEN FILE$="NULL" @ LOCK$="" @ GOTO 630
580      FILE$=T$
590      GOSUB fileinput @ LOCK$=""
600 !   Row NR+1 is minimun or NR(1,J) for each column, row NR+2 is
         maximum or  NR(2 ,J) for each column.
610 !   A similar assignment is also made for NC+1 and NC+2 columns.
620      IF Y(0,0)=0 THEN FILETYPE$="time base"
         ELSE FILETYPE$="conc. base"
630      GOTO menu
640      CLEAR @ DISP "Drive number <0,1> [1]" @ INPUT T$
650      IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 670
660      DRIVE=VAL (T$) @ IF DRIVE=0 OR DRIVE=1 THEN 670 ELSE 640
670      CLEAR @ CAT ":D70"&VAL$ (DRIVE)
680      DISP "Press <END LINE> to continue," @ INPUT T$
690      GOTO menu
700      IF ZPRINT$="NO" THEN ZPRINT$="YES" @ PRINTER IS 705,90 ELSE
         ZPRINT$="NO" @ PRINTER IS 1
710      GOTO menu
720      IF PLOTAXES$="NO" THEN PLOTAXES$="YES" ELSE PLOTAXES$="NO"
730      GOTO menu
740 !
750      IF SCALING$="Man" THEN SCALING$="Auto" ELSE SCALING$="Man"
760      GOTO menu
770      IF PENSWITCH$="Man" THEN PENSWITCH$="Auto" ELSE PENSWITCH$="Man"
780      GOTO menu
790      IF PLOTLABEL$="NO" THEN PLOTLABEL$="YES" ELSE PLOTLABEL$="NO"
800      GOTO menu
810      CLEAR @ DISP "Enter the x-axis labels as literal strings <10 max>
         :"
```

```
820      FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN XCLICK=I-1 @ GOTO
         840
830      XCLICK(I)=VAL (T$) @ NEXT I @ XCLICK=10
840      GOTO menu
850      CLEAR @
         DISP "Enter the y-axis Iabels as literal strings <10 max> :"
860      FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN YCLICK=I-1 @
         GOTO 880
870      YCLICK(I)=VAL (T$) @ NEXT I @ YCLICK=10
880      GOTO menu
890 !
900 fileinput:
910 !
920      IF DATADRIVE$="B" OR DATADRIVE$="b" THEN DRIVE$=VAL$ (1) ELSE
         DRIVE$=DATADRIVE$
930      ASSIGN# 1 TO FILE$&":D70"&DRIVE$
940      READ# 1 ; E1,E2 ! beginning detection pot., ending detection pot.
950      READ# 1 ; E3,E4 ! anodic limit, cathodic limit
960      READ# 1 ; T1,T2 ! beginning detection time, ending detection time
970      READ# 1 ; I_RANGE,I_TYPE$,V_RANGE
980      READ# 1 ; T3,T4 ! cleaning time, adsorption time
990      READ# 1 ; EXTDATA$,T5
1000     READ# 1 ; NC,NR,A,A,A,A,A
1010     FOR I=0 TO NR+2
1020     FOR J=0 TO NC+2
1030     READ# 1 ; Y(I,J)
1040     NEXT J
1050     NEXT I
1060     ASSIGN# 1 TO *
1070     RETURN
1080 !
1090 calculations:
1100 !
1110     IF FILE$="NULL" THEN CLEAR @ DISP "No master file on board" @
         DISP "Press <END LINE> to continue." @ INPUT T$ @ GOTO menu
1120     IF CAL=1 AND LOCK$="*" THEN RETURN
1130     IF CAL=0 AND LOCK$="*" THEN menu
1140     CLEAR @ AWRITE 10,33,"calculating"
1150     ON TYPE GOSUB
         4850,4860,4900,5040,5140,5290,5150,5220,5360,4970,5430 @
         LOCK$="*"
1160     IF CAL=1 THEN RETURN
1170     GOTO menu
1180 !
1190 plotting:
1200 !
1210 ! Graphics routine
1220 !
1230     CAL=1 @ GOSUB calculations @ CAL=0
1240     IF DSPCRT$="NO" AND DSPXY$="NO" THEN 2810
1250     CLEAR @ AWRITE 10,33,"Plotting"
```

```
1260     MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
1270     PFLAG=0 @ IF PLOTTYPE=2 THEN 1380
1280     FOR I=1 TO NR @ IF ROW(I)=0 THEN 1360
1290     IF Y(I,0)<MINX THEN MINX=Y(I,0)
1300     IF Y(I,0)>MAXX THEN MAXX=Y(I,0)
1310     FOR J=1 TO NC @ IF COL(J)=0 THEN 1350
1320     PFLAG=1
1330     IF Y(I,J)<MINY THEN MINY=Y(I,J)
1340     IF Y(I,J)>MAXY THEN MAXY=Y(I,J)
1350     NEXT J
1360     NEXT I
1370     GOTO 1470
1380     FOR J=1 TO NC @ IF COL(J)=0 THEN 1460
1390     IF Y(0,J)<MINX THEN MINX=Y(0,J)
1400     IF Y(0,J)>MAXX THEN MAXX=Y(0,J)
1410     FOR I=1 TO NR @ IF ROW(I)=0 THEN 1450
1420     PFLAG=1
1430     IF Y(I,J)<MINY THEN MINY=Y(I,J)
1440     IF Y(I,J)>MAXY THEN MAXY=Y(I,J)
1450     NEXT I
1460     NEXT J
1470     IF PFLAG<> 0 THEN 1500
1480     AWRITE 20,0,"Improper boundary selection" @
         AWRITE 21,0,"Press <END LINE> to continue ." @ AWRITE 22,0,""
1490     RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD @ GOTO menu
1500     IF DSPCRT$ <> "YES" THEN 1770
1510     GRAPHALL @ FRAME
1520     LOCATE 30,200,25,95
1530     XEXP=ABS ((MAXX-MINX)/200 @ YEXP=ABS ((MAXY-MINY)/20)
1540     IF PLOTTYPE=2 THEN SCALE MINX-XEXP,MAXX+XEXP,MINY-YEXP,MAXY+YEXP
         ELSE SCALE MAXX+XEXP,MINX-XEXP,MINY-YEXP,MAXX.YEXP
1550     FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
1560     LAXES -((MAXX-MINX)/60),(MAXY-MINY)/4/5,0,0,10,5,3
1570     MOVE MINX,MINY
1580     LORG 4 @ X$=CHR$ (46)
1590     IF PLOTTYPE=2 THEN 1660
1600     FOR J=1 TO NC @ IF COL(J)=0 THEN 1640
1610     FOR I=1 TO NR @ IF ROW(I)=0 THEN 1630
1620     MOVE Y(I,0),Y(I,J) @ LABEL X$
1630     NEXT I
1640     NEXT J
1650     GOTO 1710
1660     FOR I=1 TO NR @ IF ROW(I)=0 THEN 1700
1670     FOR J=1 TO NC @ IF COL(J)=0 THEN 1690
1680     MOVE Y(0,J),Y(I,J) @ LABEL X$
1690     NEXT J
1700     NEXT I
1710     CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
1720     LABEL "milliamps"
1730     LDIR 0 @ MOVE RATIO *100/2-10,15
1740     LABEL " "
```

```
1750    IF DSPFLAG$="YES" THEN GSTORE FILE2$&":D70"&GRAPHDRIVE$
1760    INPUT T$ @ ALPHALL
1770    IF DSPXY$ <> "YES" THEN 2810
1780 !
1790 !  Mechanical plotting routine
1800 !
1810    GOSUB label check
1820    XSCALE=8.5 @ YSCALE=7
1830    IF PLOTTYPE=1 THEN A=MINX @ MINX=MAXX @ MAXX=A
1840    XSCALING=XSCALE/(MAXX-MINX)
1850    YSCALING=YSCALE/(MAXY-MINY)
1860    XCENTER=MAXX-(MAXX-MINX)/2
1870    YCENTER=MAXY-(MAXY-MINY)/2
1880    OUTPUT 723 ;"GP"
1890    TAKE KEYBOARD
1900    CLEAR @ DISP "Set zero positions now !" @
        DISP "Press <END LINE> to continue"
1910    OUTPUT 723 ;"OP 7 OT OP 12 50T OP 14 50T"
1920    KYY=NUM (KEY$ ) @ IF NOT KYY THEN 1910
1930    WAIT 1000
1940    IF PLOTAXES$="NO" THEN 2510
1950    X=MINX*XSCALING-XCENTER*XSCALING+XSCALE/2
1960    Y=MAXY*YSCALING-YCENTER*YSCALING+YSCALE/2
1970    IF PLOTLABEL$="YES" THEN 2080
1980    OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 OT OP 14 50T"
1990    WAIT 2000
2000    OUTPUT 723 :"OP 7 7.0T OP 11 1500 14 50T WA .2T OP 7 ";X;"T OP 12
        50T"
2010    OUTPUT 723 ;"OP 7 0.0T OP 11 1500 14 50T"
2020    WAIT 3100
2030    OUTPUT 723 ;"OP 7 ";Y;"T OP 14 50T OP 7 ";0;"T OP 12 50T"
2040    WAIT 750
2050    OUTPUT 723 ;"OP 7 8.5T OP 11 1500 12 50T WA .2T OP 7 ";Y;"T OP 14
        50T"
2060    OUTPUT 723 ;"OP 7 0.0T OP 11 1500 12 50T"
2070    WAIT 3100
2080    Y=INT (Y*10000)/10000 @ X=INT (X*10000)/10000
2090    WAIT 1000
2100    XPOS=XSCALE/6
2110    YPOS=YSCALE/5
2120    IF Y-YSCALE/60<0 THEN Y1=0 ELSE Y1=Y-YSCALE/60
2130    IF Y+YSCALE/60>YSCALE THEN Y2=YSCALE ELSE Y2=Y+YSCALE/60
2140    Y1=INT (Y1*10000)/10000 @ Y2=INT (Y2*10000)/10000
2150    LXSCALING=550
2160    FOR I=1 TO XCLICK
2170    IF SCALING$ <> "Man" THEN 2190
2180    X1=XCLICK(I)*XSCALING-XCENTER*XSCALING+4.25 @ GOTO 2210
2190    X1=INT (I*(XSCALE/XCLICK)*10000)/10000
2200    IF X1>XSCALE THEN 2300
2210    Y3=INT ((Y2-Y1)*10000)/10000
2220    OUTPUT 723 ;"OP 7 ";X1;"T OP 12 50T OP 7 ";Y1;"T OP 14 50T"
```

```
2230    WAIT 1500
2240    OUTPUT 723 ;"OP 11 500 7 ";Y1+Y3;" 14 50T"
2250    WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (XCLICK(I)) @
        GOTO 2270
2260    LA$=VAL$ (INT (((MAXX-MINX)/XCLICK*I+MINX+.0001)*1000)/1000)
2270    XIN=X1-8.5/LXSCALING*LEN (LA$)*7/2
2280    YIN=7.25 @ GOSUB xylabel
2290    NEXT I
2300    IF X-XSCALE/73<0 THEN X1=0 ELSE X1=X-XSCALE/73
2310    IF X+XSCALE/73>XSCALE THEN X2=XSCALE ELSE X2=X+XSCALE/73
2320    X1=lNT (X1*10000)/10000 @ X2=INT (X2*10000)/10000
2330    FOR I=1 TO YCLICK
2340    IF SCALING$ <> "Man" THEN 2360
2350    Y1=YCLICK(I)*YSCALING-YCENTER*Y$CALING+3.5 @ GOTO 2390
2360    Y1=INT (I*(YSCALE/5)*10000)/10000
2370    IF Y1>YSCALE THEN 2510
2380    IF Y1=Y THEN 2470
2390    X3=INT ((X2-X1)*10000)/10000
2400    OUTPUT 723 ;"OP 7 ";Y1;"T OP 14 50T OP 7 ";X1;"T OP 12 50T"
2410    WAIT 1000
2420    OUTPUT 723 ;"OP 11 500 7 ";X1+X3;" 12 50T"
2430    WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (YCLICK(I)) @
        GOTO 2450
2440    LA$=VAL$ (INT ((MAXY-MINY)/5*I+MINY+.000001)*10000)/10000)
2450    XIN=8.75
2460    YIN=Y1+.12 @ GOSUB xylabel
2470    NEXT I
2480    IF PENSWITCH$="Auto" THEN 2510
2490    CLEAR @ DISP "Change pen color ?  Press <END LINE> to continue."
2500    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
2510    WAIT 1000
2520    PFLAG=0 @ IF PLOTTYPE=2 THEN 2670
2530    FOR J=1 TO NC @ IF COL(J)=0 THEN 2650
2540    FOR I=1 TO NR @ IF ROW(I)=0 THEN 2610
2550    PFLAG=1
2560    X=Y(I,0)*XSCALING-XCENTER*XSCALING+4.25
2570    Y=Y(I,J)*YSCALING-YCENTER*YSCALING+3.5
2580    OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
2590    IF PFLAG=2 THEN WAIT 1 ELSE PFLAG=2 @ WAIT 300
2600    OUTPUT 723 ;"OP 11 100T"
2610    NEXT I
2620    IF PENSWITCH$="Auto" THEN 2650
2630    CLEAR @ DISP "Change pen color ?  Press <END LINE> to continue."
2640    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
2650    NEXT J
2660    GOTO 2800
2670    FOR I=1 TO NR @ IF ROW(I)=0 THEN 2790
2680    FOR J=1 TO NC @ IF COL(J)=0 THEN 2750
2690    PFLAG=1
2700    X=Y(0,J)*XSCALING-XCENTER*XSCALING+4.25
2710    Y=Y(I,J)*YSCALING-YCENTER*YSCALING+3.5
```

```
2720    OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
2730    IF PFLAG=2 THEN WAIT 1 ELSE PFLAG=2 @ WAIT 300
2740    OUTPUT 723 ;"OP 11 100T"
2750    NEXT J
2760    IF PENSWITCH$="Auto" THEN 2790
2770    CLEAR @ DISP "Change pen color ?  Press <END LINE> to continue."
2780    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
2790    NEXT I
2800    GOSUB filelabel
2810    GOTO menu
2820 !
2830 beginning:
2840 !
2845    IF LEN (ZZZ$)=0 THEN ZZZ$="2"
2846    IF ZZZ$="1" OR ZZZ$="2" THEN 2847 ELSE ZZZ$="2"
2847    IF ZZZ$="2" THEN 2850 ELSE 2855
2850    DIM Y(102,60),COL(60),ROW(102),CODE(102),XCLICK(10),YCLICK(10)
2851    NRMAX=100 @ NCMAX=60
2853    GOTO 2860
2855    DIM Y(152,30),COL(30),ROW(152),CODE(152),XCLICK(10),YCLICK(10)
2856    NRMAX=150 @ NCMAX=30
2860    CLEAR
2870    DIM SCANS(10),DROPTYME(10),I_RANGE(10),I_TYPE$(10)[10],CODE$[150]
2880    DIM A$(45)[50],B$(45)[50],FILE$[15],DAT$(45)[25],FILETYPE$[10]
2890    DIM T$[150],T1$[150],PERIOD$[50],
        DATADRIVE$[5],GRAPHDRIVE$[5],DRIVE$[5]
2900    DIM DSPFLAG$[3],DSPCRT$[3],DSPXY$[3],
        CHAR$(46)[35],LA$[80],TYPE$[30]
2910    ON ERROR GOTO 3730 @ AWRITE 0,0
2920    DSPFLAG$="NO" @ FILE2$="TEST" @ DATADRIVE$="B" @ GRAPHDRIVE$="0"
        @ DRIVE=1
2930    FLAG=1 @ TOTAL=10 @ SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @
        YMIN,YMAX=0
2940    FILE$="NULL" @ E1,E4=0 @ PLOTTYPE=1 @ FILETYPE$="" @
        ZPRINT$="NO"
2950    LOCK$="" @ N=1 @ TYPE=5 @ CAL=0 @ PLOTAXES$="YES" @
        SCALING$="Auto
2960    PENSWITCH$="Man" @ PLOTLABEL$="NO" @ XCLICK=6 @ YCLICK=5 @
        TYPE2=1
2970    DSPCRT$="YES" @ DSPXY$="NO" @ TYPE$="i vs. x [j]" @ XMIN,XMAX=0
2980    FOR I=1 TO NRMAX @ ROW(I)=0 @ NEXT I
2990    FOR J=1 TO NCMAX @ COL(J)=0 @ NEXT J
3000    FOR I=1 TO 10 @ XCLICK(I),YCLICK(I)=10000000000 @ NEXT I
3010    TAKE KEYBOARD @ GOSUB 30 @ GOSUB 70
3020    A$(1)="Filer directory"
3030    A$(2)="Mass storage directory"
3040    A$(3)="Plotting directory"
3050    A$(4)="Start plotting"
3060    A$(5)="Chain Autost"
3070    A$(6)="End program"
3080    A$(7)="NULL"
```

```
3090    A$(8)="Exit to main menu"
3100    A$(9)="Store graph on disk"
3110    A$(10)="Graph storage file name"
3120    A$(11)="Numeric data drive number"
3130    A$(12)="Graphic data drive number"
3140    A$(13)="Catalog of disk"
3150    A$(14)="NULL"
3160    A$(15)="NULL"
3170    A$(16)="NULL"
3180    A$(17)="NULL"
3190    A$(18)="NULL"
3200    A$(19)="NULL"
3210    A$(20)="Exit to main menu"
3220    A$(21)="Master array file <type>"
3230    A$(22)="Re-enter master file"
3240    A$(23)="Set min and max for y-axis only"
3250    A$(24)="Set min and max for x-axis only"
3260    A$(25)="NULL"
3270    A$(26)="Exit to main menu"
3280    A$(27)="Plot on CRT"
3290    A$(28)="Plot on printer"
3300    A$(29)="Plot on X-Y recorder"
3310    A$(30)="Manual or Automatic scaling"
3320    A$(31)="Manual or Automatic pen switching"
3330    A$(32)="Plot axes (including labels)"
3340    A$(33)="Plot ticks and lables only"
3350    A$(34)="X-axis labels"
3360    A$(35)="Y-axis labels"
3370    A$(36)="Curves plotted"
3380    A$(37)="Set intervals for plotting"
3390    A$(38)="Least squares calculation"
3400    A$(39)="Activate printer"
3410    A$(40)="Do calculations"
3420    A$(41)="NULL"
3430    PERIOD$="..............................................."
3440    FOR I=1 TO 41 @ T$=A$(I) @ GOSUB 40 @ B$(I)=T1$ @ NEXT I
3450    SCRN=3 @ A1=1 @ A2=6
3460 menu: TAKE KEYBOARD @ GOSUB 130 @ PAGEFLAG=0
3470    CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$ (64+I.A1+1)&CHR$
        (41)&PERIOD$[1,4]&A$(I)&PERIOD$[1,40-LEN (A$(I))]&" "&DAT$(I) @
        NEXT I
3480    AWRITE 1,8,B$(A1) @ CRSR=1
3490    AWRITE 21,2,"Change any parameters ?" @ AWRITE 22,2,"Press the
        indicated letters or use the '.' and ',' keys for slewing "
3500    AWRITE 23,2,"Press '4' to change any parameters or to start
        experiment "
3510    TAKE KEYBOARD
3520    KYY=NUM (KEY$ ) @ IF NOT KYY THEN 3520
3530    IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @
        CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
3540    IF KYY<> 46 THEN 3570
```

```
3550    AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
        CR8R=A2-A1+1
3560    AWRITE CRSR,8,B$(A1+CRSR-1)
3570    IF KYY<> 44 THEN 3600
3580    AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @ IF CRSR>A2-A1+1 THEN
        CRSR=1
3590    AWRITE CRSR,8,B$(A1+CRSR-1)
3600    IF KYY<> 52 THEN 3510
3610    IF SCRN<> 3 THEN 3670
3620    IF CRSR=1 THEN SCRN=1 @ A1=20 @ A2=24 @ GOTO 3470
3630    IF CRSR=2 THEN SCRN=2 @ A1=8 @ A2=13 @ GOTO 3470
3640    IF CRSR=3 THEN SCRN=4 @ A1=26 @ A2=40 @ GOTO 3470
3650    IF CRSR=4 THEN 1190
3660    RELEASE KEYBOARD @ IF CRSR=5 THEN CHAIN "Autost" ELSE GOTO 3710
3670    PAGEFLAG=1 @ RELEASE KEYBOARD
3680    IF SCRN=1 THEN ON CRSR GOTO 3700,560,590,450,410
3690    IF SCRN=2 THEN ON CRSR GOTO 3700,340,380,490,490,640 ELSE ON CRSR
        GOTO 3700,320,3510,360,750,770,
        720,790,810,850,4470,5480,6060,700,1090
3700    TAKE KEYBOARD @ SCRN=3 @ A1=1 @ A2=6 @ GOTO 3470
3710    CLEAR @ END
3720 !
3730 ! Error trap subroutine
3740 !
3750    IF ERRN =71 THEN DISP "File read error" @ GOTO 3840
3760    IF ERRN =66 THEN DISP "File closed" @ GOTO 3840
3770    IF ERRN =11 THEN menu
3780    IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 3840
3790    IF ERRN =67 AND (DRIVE$="0" OR DRIVE$="1") THEN CLEAR @
        DISP "Place correct disk in drive" @ WAIT 5000 @ GOTO menu
3800    IF ERRN =67 AND (DATADRIVE$="B" OR DATADRIVE$="b") THEN
        DRIVE$=VAL$ (ABS (VAL (DRIVE$ )-1)) @ GOTO 930
3810    IF ERRN =130 AND DATADRIVE$="B" THEN
        DRIVE$=VAL$ (ABS (VAL (DRIVE$)-1)) @ GOTO 930
3820    IF ERRN =130 THEN BEEP 300,1000 @ RELEASE KEYBOARD @ CLEAR @
        DISP "Place disk in driv e and then press <END LINE>" @ INPUT T$
        @ TAKE KEYBOARD @ GOTO menu
3830    DISP ERRN,ERRL @ WAIT 5000
3840    GOTO menu
3850 !
3860 !
3870 xylabel:
3880 !
3890 !  Beginning of labeling subroutine
3900 !  Range of characters is defined by LXSCALING and should be within
       the
3910 !  interval 100 to 600 inclusive, where the larger the number the
       smaller
3920 !  the character.
3930 !  Inputs LA$,LXSCALING
3940    LRATIO=230/190 ! X/Y
```

```
 3950    LYSCALING=INT (LXSCALING/LRATIO*10000)/10000
 3960    IF LXSCALING>400 THEN LSPACE=2 ELSE LSPACE=1
 3970    LX=-((5+LSPACE)*8.5/LXSCALING)+XIN
 3980    OUTPUT 723 ;"OP 7 ";XIN;"T OP 12 50T OP 7 ";YIN;"T OP 14 50T"
 3990    WAIT 500
 4000    FOR LI=1 TO LEN (LA$)
 4010    LT=NUM (LA$[LI,LI])
 4020    IF LT=32 THEN LT=47
 4030    LY=YIN
 4040    LPOINT=0
 4050    LX=LX+(LSPACE+5)*8.5/LXSCALING
 4060    FOR LJ=1 TO 7
 4070    LY=INT ((LY-7/LYSCALING)*10000)/10000
 4080    LX1=LX
 4090    FOR LK=1 TO 5
 4100    LPOINT=LPOINT+1
 4110    LX2=INT ((LX1+LK*8.5/LXSCALING)*10000)/10000
 4120    IF CHAR$(LT-44)[LPOINT,LPOINT] <> "1" THEN 4170
 4130    OUTPUT 723 ;"OP 7 ";LX2;"T OP 12 50T OP 7 ";LY;"T OP 14 50T"
 4140    WAIT 200
 4150    OUTPUT 723 ;"OP 11 100T"
 4160    WAIT 200
 4170    NEXT LK
 4180    NEXT LJ
 4190    NEXT LI
 4200    RETURN
 4210 !
 4220 filelabel:
 4230 !
 4240    CLEAR @ DISP "Set zero positions now!" @
         DISP "Press <END LINE> to continue"
 4250    OUTPUT 723 ;"OP 7 OT OP 12 50 14 50T"
 4260    KYY=NUM (KEY$ ) @ IF NOT KYY THEN 4250
 4270    LXSCALING=550
 4280    LA$="FILES" @ XIN=0 @ YIN=0 @ GOSUB xylabel
 4290    LA$="-----" @ XIN=0 @ YIN=-.14 @ GOSUB xylabel
 4300    X=1
 4310    FOR I=1 TO TOTAL
 4320    IF FILE$="NULL" THEN 4410
 4330    X=X+1
 4340    LA$=UPC$ (FILE$)
 4350    FOR J=1 TO LEN (FILE$)
 4360    T$=FILE$[J,J]
 4370    IF T$="_" THEN LA$[J,J]="."
 4380    NEXT J
 4390    XIN=0 @ YIN=0-X*.1875
 4400    GOSUB xylabel
 4410    NEXT I
 4420    RETURN
 4430 !
 4440 !
```

```
4450 ! Plotting type
4460 !
4470     IF FILE$="NULL" THEN CLEAR @ DISP "No master file on board" @
         DISP "Press <END LINE> to Continue." @ INPUT T$ @ GOTO menu
4480     CLEAR @ DISP "Enter number corresponding to type of curve
         plotted" 4490 DIsP "Note, 'j' refers to rows, 'k' refers to
         columns;"
4500     DISP "i.e., j implies that the data is ploted vs. to zeroeth
         column,"
4510     DISP "Whereas, k implies that the data is ploted vs. to zeroeth
         row."
4520     AWRITE 8,20,"1) i vs. x  [k]"
4530     AWRITE 9,20,"2) i vs. 1/x  [k]"
4540     AWRITE 10,20,"3) ln(i) vs. ln(x)  [k]"
4550     AWRITE 11,20,"4) d(i)/d(1/y) vs. x  [j]"
4560     AWRITE 12,20,"5) i vs. x  [j]"
4570     AWRITE 13,20,"6) 1/i vs. 1/x  [k]"
4580     AWRITE 14,20,"7) i(o)/i vs. x  [k]"
4590     AWRITE 15,20,"8) (1-i/i(o))/i) vs. x  [k]"
4600     AWRITE 16,20,"9) 1/i vs. 1/x  [j]"
4610     AWRITE 17,19,"10) ln(i) vs. ln(x)  [j]"
4620     AWRITE 18,19,"11) i vs. sqr(x)  [j]"
4630     AWRITE 20,2,"" @ INPUT T$
4640     IF LEN (T$)=0 THEN menu ELSE TYPE=VAL (T$) @ GOTO 4660
4650     GOTO 4470
4660     IF TYPE<1 OR TYPE>11 THEN 4470
4670     IF TYPE=4 OR TYPE=5 OR TYPE=9 OR TYPE=10 OR TYPE=11 THEN TYPE2=1
         ELSE TYPE2=2
4680     IF TYPE2=1 THEN PLOTTYPE=1 ELSE PLOTTYPE=2
4690     ON TYPE GOSUB
         4710,4720,4730,4740,4750,4780,4760,4770,4790,4800,4810
4700     GOTO menu
4710     TYPE$="i vs. x [k]" @ RETURN
4720     TYPE$="i vs. 1/x [k]" @ RETURN
4730     TYPE$="ln(i) vs. ln(x) [k]" @ RETURN
4740     TYPE$="d(i)/d(1/y) vs. x [j]" @ RETURN
4750     TYPE$="i vs. x [j]" @ RETURN
4760     TYPE$="1/R vs. x [k]" @ RETURN
4770     TYPE$="1-R/R vs. x [k]" @ RETURN
4780     TYPE$="1/i vs. 1/x [k]" @ RETURN
4790     TYPE$="1/i vs. 1/x [j]" @ RETURN
4800     TYPE$="ln(i) vs. ln(x) [j]" @ RETURN
4810     TYPE$="i vs. sqr(x) [j]" @ RETURN
4820 !
4830 !   Calculations as per type selected for plotting
4840 !
4850     RETURN
4860     FOR J=1 TO NC
4870     Y(0,J)=1/Y(0,J)
4880     NEXT J
4890     RETURN
```

```
4900    FOR I=0 TO NR
4910    FOR J=1 TO NC
4920    IF NOT Y(I,J) THEN 4940
4930    Y(I,J)=LOG (ABS (Y(I,J)))
4940    NEXT J
4950    NEXT I
4960    RETURN
4970    FOR I=1 TO NR
4980    FOR J=0 TO NC
4990    IF NOT Y(I,J) THEN 5010
5000    Y(I,J)=LOG (ABS (Y(I,J)))
5010    NEXT J
5020    NEXT I
5030    RETURN
5040    GOSUB 4860
5050    PLOTTYPE=2
5060    FOR I=1 TO NR @ IF ROW(I)=0 THEN 5100
5070    RLOW,RHGIH=I
5080    LSCAL=2 @ GOSUB leastsquares
5090    Y(I,I)=SLOPE
5100    NEXT I
5110    PLOTTYPE=1 @ CLOW,CHIGH=1
5120    FOR J=2 TO NC @ COL(J)=0 @ NEXT J @ COL(1)=1
5130    RETURN
5140    RETURN
5150    FOR I=1 TO NR
5160    FOR J=2 TO NC
5170    Y(I,J)=Y(I,1)/Y(I,J)
5180    NEXT J
5190    Y(I,1)=1
5200    NEXT I
5210    RETURN
5220    GOSUB 5150
5230    FOR I=1 TO NR
5240    FOR J=2 TO NC
5250    Y(I,J)=(1-Y(I,J))/Y(I,J)
5260    NEXT J
5270    NEXT I
5280    RETURN
5290    FOR I=0 TO NR
5300    FOR J=1 TO NC
5310    IF NOT Y(I,J) THEN 5330
5320    Y(I,J)=1/Y(I,J)
5330    NEXT J
5340    NEXT I
5350    RETURN
5360    FOR I=1 TO NR
5370    FOR J=0 TO NC
5380    IF NOT Y(I,J) THEN 5400
5390    Y(I,J)=1/Y(I,J)
5400    NEXT I
```

```
5410    NEXT I
5420    RETURN
5430    FOR I=1 TO NR
5440    Y(I,0)=SQR (Y(I,0))
5450    NEXT I
5460    RETURN
5470 !
5480 limits:
5490 !
5500 !  Setting limits
5510 !
5520    IF FILE$="NULL" THEN CLEAR @ DISP "No master file on board" @
        DISP "Press <END LINE> to continue." @ INPUT T$ @ GOTO menu
5530    CLEAR @ TAKE KEYBOARD @ AWRITE 1,2,"Are you setting "&CHR$
        (128+67)&"olumns or "&CHR$ (128+82)&"ows, or perhaps "&CHR$
        (128+69)&"xiting ?"
5540    KYY=NUM (KEY$ ) @ IF NOT KYY THEN 5540
5550    IF KYY=69 TBEN menu
5560    IF KYY=67 OR KYY=82 THEN 5570 ELSE 5540
5570    IF KYY=82 THEN 5670
5580    CLEAR @ AWRITE 1,0,"Column number(s) -- e.g., 1,2,3... , 1-10, *
        for all"
5590    RELEASE KEYBOARD @ AWRITE 2,2,"" @ LINPUT CODE$ @
        IF LEN (CODE$)=0 THEN 5530
5600    FOR J=1 TO NC @ COL(J)=0 @ NEXT J
5610    GOSUB decode @ IF error=1 THEN 5580
5620    CLEAR @ AWRITE 2,0,"Column numbers to be defined." @
        AWRITE 3,0,"" @ DISP
5630    FOR J=1 TO NC @ IF CODE(J)=1 THEN DISP J;",";
5640    NEXT J @ DISP
5650    FOR J=1 TO NC @ IF CODE(J)=1 THEN COL(J)=1
5660    NEXT J @ AWRITE 20,0,"Press <END LINE> to continue" @
        AWRITE 21,0,"" @ INPUT T$ @ GOTO 5530
5670    CLEAR @ AWRITE 1,0,"Row number(s) -- e.g., 1,2,3... , 1-10, * for
        all"
5680    RELEASE KEYBOARD @ AWRITE 2,2,"" @ LINPUT CODE$ @
        IF LEN (CODE$)=0 THEN 5530
5690    FOR I=1 TO NR @ ROW(I)=0 @ NEXT I
5700    GOSUB decode @ IF error=1 THEN 5670
5710    CLEAR @ AWRITE 2,0,"Row numbers to be defined." @ AWRITE 3,0,"" @
        DISP
5720    FOR I=1 TO NR @ IF CODE(I)=1 THEN DISP I;",";
5730    NEXT I @ DISP
5740    FOR I=1 TO NR @ IF CODE(I)=1 THEN ROW(I)=1
5750    NEXT I @ AWRITE 20,0,"Press <END LINE> to continue" @ AWRITE
        21,0,"" @ INPUT T$ @ GOTO 5530
5760 !
5770 decode:
5780 !
5785    IF KYY=82 THEN NDMAX=NRMAX ELSE NDMAX=NCMAX
```

```
5790    ON ERROR GOTO error3 @ error=0 @ FOR I=1 TO NDMAX @ CODE(I)=0 @
        NEXT I
5800    FOR I=1 TO LEN (CODE$) @ IF CODE$[1,1]=CHR$ (32) THEN
        CODE$=CODE$[2,LEN (CODE$)] @ GOTO 5800
5810    IF CODE$[1,1] <> "*" THEN 5830
5820    FOR I=1 TO NDMAX @ CODE(I)=1 @ NEXT I @ GOTO 5940
5830    T$="1"
5840    FOR I=0 TO 9 @ IF CODE$[1,1]=VAL$ (I) THEN T$="-1"
5850    NEXT I @ IF T$ <> VAL$ (-1) THEN CODE$=CODE$[2,LEN (CODE$)]
        ELSE 5870
5860    IF LEN (CODE$)=0 THEN error3 ELSE 5840
5870    T=VAL (CODE$) @ IF T<0 OR T>NDMAX THEN error2 ELSE CODE(T)=1
5880    IF LEN (VAL$ (T))=LEN (CODE$) THEN 5940
5890    CODE$=CODE$[1+LEN (VAL$ (T)),LEN (CODE$)] @ IF LEN (CODE$)=0 THEN
        CODE(T)=1 @ GOTO 5940
5900    T$=CODE$[1,1] @ CODE$=CODE$[2,LEN (CODE$)] @ IF T$="," OR T$="-"
        THEN 5910 ELSE error1
5910    T1=VAL (CODE$) @ IF T1<0 OR T1>NDMAX THEN T=T1 @ GOTO error2
5920    IF T$="," THEN CODE(T1)=1 @ GOTO 5870
5930    FOR I=T+1 TO T1 @ CODE(I)=1 @ NEXT I @ GOTO 5870
5940    ON ERROR GOTO 3730 @ RETURN
5950 !
5960 error1: error=1
5970    DISP "Character ";T$;" not allowed." @ DISP @
        DISP "Press <END LINE> to continue." @  INPUT T$ @ RETURN
5980 !
5990 error2: error=1
6000    DISP "The value ";T;" is to large." @ DISP @
        DISP "Press <END LINE> to continue." @ I NPUT T$ @ RETURN
6010 !
6020 error3: error=1
6030    DISP "String does not follow syntax." @ DISP @
        DISP "Press <END LINE> to continue." @  INPUT T$ @ RETURN
6040 !
6050 !
6060 ls_select:
6070 !
6080    IF FILE$="NULL" OR LOCK$="" THEN menu
6090    IF TYPE=4 THEN 6230
6100    IF TYPE2=1 THEN 6110 ELSE 6170
6110    CLEAR @ AWRITE 1,0,"Column number ?" @ AWRITE 2,0,""
6120    RELEASE KEYBOARD @ INPUT T$ @ IF LEN (T$)=0 THEN menu
6130    IF VAL (T$)<1 OR VAL (T$)>NC THEN 6110 ELSE 6150
6140    GOTO 6110
6150    CLOW,CHIGH=VAL (T$)
6160    LSCAL=1 @ GOSUB leastsquares @ GOTO 6110
6170    CLEAR @ AWRITE 1,0,"Row number ?" @ AWRITE 2,0,""
6180    RELEASE KEYBOARD @ INPUT T$ @ IF LEN (T$)=0 THEN menu
6190    IF VAL (T$)<1 OR VAL (T$)>NR THEN 6170 ELSE 6210
6200    GOTO 6170
6210    RLOW,RHIGH=VAL (T$)
```

```
6240 !
6250 leastsquares:
6260 ! Linear least squares subroutine
6270 !
6280    CLEAR @ AWRITE 10,22,Least squares calculation" @ AWRITE 11,1,""
6290    DISP @ DISP
6300    SUMX,SUMY,SUMXSQRD,SUMYSQRD,SUMXY,VARIANCE,N=0
6310    IF TYPE2=2 THEN 6370
6320    FOR I=1 TO NR @ IF ROW(I)=0 THEN N=N-1 @ GOTO 6340
6330    SUMX=SUMX+Y(I,0) @ SUMY=SUMY+Y(I,CLOW) @ SUMXSQRD=SUMXSQRD+
        Y(I,0)^2 @ SUMYSQRD=SUMYSQRD+Y(I,CLOW)^2 @
        SUMXY=SUMXY+Y(I,0)*Y(I,CLOW)
6340    NEXT I
6350    N=NR+N
6360    GOTO 6410
6370    FOR J=1 TO NC @ IF COL(J)=0 THEN N=N-1 @ GOTO 6390
6380    SUMX=SUMX+Y(0,J) @ SUMY=SUMY+Y(RLOW,J) @ SUMXSQRD=SUMXSQRD+
        Y(0,J)^2 @ SUMYSQRD=SUMYSQRD+Y(RLOW,J)^2 @
        SUMXY=SUMXY+Y(0,J)*Y(RLOW,J)
6390    NEXT J
6400    N=NC+N
6410    CONSTANT=N*SUMXSQRD-SUMX^2 @ SLOPE=(N*SUMXY-SUMX*SUMY)/CONSTANT @
        INTERCEPT=(SUMXSQRD*SUMY-SUMX*SUMXY)/CONSTANT
6420    IF TYPE2=2 THEN 6470
6430    FOR I=1 TO NR @ IF ROW(I)=0 THEN GOTO 6450
6440    VARIANCE=VARIANCE+(Y(I,CLOW)-INTERCEPT-SLOPE*Y(I,0))^2
6450    NEXT I
6460    GOTO 6500
6470    FOR J=1 TO NC @ IF COL(J)=0 THEN 6490
6480    VARIANCE=VARIANCE+(Y(RLOW,J)-INTERCEPT-SLOPE*Y(0,J))^2
6490    NEXT J
6500    VARIANCE=VARIANCE/(N-2)
6510    SLOPESDERR=SQR (N*VARIANCE/CONSTANT)
6520    INTERCEPTSDERR=SQR (VARIANCE/N*(1+SUMX^2/CONSTANT))
6530    CORRCOEFF=SQR (SLOPE*((SUMXY-SUMX*SUMY/N)/(SUMYSQRD-SUMY^2/N)))
6540    IF LSCAL=2 THEN RETURN
6550    PRINT "CORRELATION COEFFICIENT= ";VAL$ (CORRCOEFF)
6560    PRINT "SLOPE = ":SLOPE @ PRINT " Y_INTERCEPT = ";INTERCEPT
6570    PRINT "SD ERROR IN SLOPE IS = ";SLOPESDERR
6580    PRINT "SD ERROR IN Y_INTERCEPY = ";INTERCEPTSDERR
6590    DISP @ DISP @ DISP "Press <END LINE> to continue " @ INPUT T$
6600    IF LSCAL=1 THEN RETURN
6610    RETURN
6620 !
6630 label_error:
6640    DISP @ DISP "Assigned labels for plotting out of data range"
6650    DISP "Re-enter values via menu" @ DISP "Press <END LINE> to
        continue."
6660    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD @ GOTO menu
6670 !
```

```
6680 label_check:
6690    IF SCALING$="Auto" THEN RETURN
6700    FOR I=1 TO XCLICK @ IF XCLICK(I)<MINX OR XCLICK(I)>MAXX THEN
        label_error
6710    NEXT I
6720    FOR I=1 TO YCLICK @ IF YCLICK(I)<MINY OR YCLICK(I)>MAXY THEN
        label_error
6730    NEXT I
6740    RETURN
```

3. PAD i-t Decays

```
10      GOTO beginning
20      OUTPUT 723 :"OP 13 ";ROT(ROT)+INTEGRATE;"T" @ RETURN
30      OUTPUT 723 ;"OP 13 ";INTEGRATE;"T" @ RETURN
40 experiment:
50      CLEAR
60      E6=E1 @ T9=T4 @ E8=E4 @ SCANS=1 @ COUNTER=0
70      IF E1<> E5 THEN N2=ABS (INT ((E5-E1)/INCPOT))+1 ELSE N2=1
80 experiment2: CLEAR 723 @ WAIT 4000 @ OUTPUT 723 ;"GP" @ N=INT (T1/T5)
90      OUTPUT 723 ;"CC 2,3,4T"
100     OUTPUT 723 :"SF 2,3,1,.005 12,4,3,1,.005,12T"
110     OUTPUT 723 ;"MI 2 ";N+1;"T"
120     OUTPUT 723 ;"WF 3.0 ";N+1:"T WF 11.2 1T"
130     INTEGRATE=8 @ GOSUB 20
140     PTYME=T5/2
150     IF STATIC$="YES" THEN STATIC=8 @ STATIC2=32768 ELSE
        STATIC=8+ROT(ROT) @ STATIC2=32768+ ROT(ROT)
160     FOR I=1 TO T6
170     OUTPUT 723 ;"OP 7 ";E3;" 14 ";T3;"T OP 7 ";E2;" 14 ";T2;"T"
180     NEXT I
190     OUTPUT 723 ;"OP 7 ";E8;" 14 ";T9;" 13 ";STATIC;"T OP 7 ";E6;" 11
        ";PTYME;" 13 ";STATIC 2;"T"
200     INTEGRATE=32768
210     DISP "Waiting";"";SCANS;"  ";T9;"  ";E8;"";E6
220     WAIT T6*(T2+T3+100)+T1+T9+100
230     DISP "Continuing"
240     OUTPUT 723 ;"WF 11.2 OT"
250     INTEGRATE=8 @ GOSUB 20
260 !
270 ! Input data from memory cards
280 !
290     SEND 7 ; UNL MLA TALK 23 SCG 5
300     FOR I=0 TO N
310     ENTER 7 USING "#,K" ; TEMP(I)
320     NEXT I
330 !
340     IF SCANS=1 THEN 360
350     FOR I=0 TO N @ Y(I)=Y(I)+TEMP(I) @ NEXT I @ GOTO 370
360     FOR I=0 TO N @ Y(I)=TEMP(I) @ NEXT I
370     SCANS=SCANS+1 @ IF SCANS<TOTALSCANS+1 THEN GOTO experiment2
380     COUNTER=COUNTER+1
390 !
400     FOR I=0 TO INT (N/SAMPLE)
410     X(I)=T5*I*SAMPLE
420     Y(I)=Y(I*SAMPLE)/TOTALSCANS
430     NEXT I
440     N=INT (N/SAMPLE)
445     DISP Y(1),Y(N)
450     IF COULOMB$="q" THEN 500
```

```
460      FOR I=1 TO N
470      Y(I)=-(Y(I)/10*ADVOLTAGE*I_RANGE/V_RANGE)
480      NEXT I
490      GOTO 540
500      FOR I=1 TO N
510      Y(I)=-(1000000*2*.000001*Y(I)/ADVOLTAGE*I_RANGE/(V_RANGE*100))
520      NEXT I
530 !
540      SCANFLAG=1 @ GOSUB datastore @ SCANFLAG=0 @ IF T4=T7 THEN 580
550      T9=T9+T8 @ IF T9>T7 THEN T9=T4 @ GOTO 580
560      SCANS=1 @ GOTO experiment2
570 !
580      IF E4=E7 THEN 630
590      E8=E8+INCPOT2 @ IF E8>E7 THEN E8=E4 @ GOTO 630
600      SCANS=1 @ GOTO experiment2
610 !
620 !
630      IF E1=E5 THEN 665
640      E6=E6+INCPOT @ IF E6>E5 TREN E6=E1 @ GOTO 665
650      SCANS=1 @ GOTO experiment2
660 !
665      IF STATIC$="YES" THEN 710
670      IF ROTMIN=0 THEN 710
680      ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN @ GOSUB 20 @ GOTO 710
690      GOSUB 20 @ SCANS=1 @ GOTO experiment2
700 !
710      IF PLOTFIG$="NO" THEN menu
720 !
730 plotter:     ! Graphics routine
740 !
750      LOW=1 @ HIGH=N
760      MINX=0 @ MAXX=0 @ MINY=YMIN @ MAXY=YMAX
770      IF X(N)>X(0) THEN MAXX=X(N) @ MINX=X(0) ELSE MAXX=X(0) @
         MINX=X(N)
780      FOR I=LOW TO HIGH
790      IF Y(I)<MINY THEN MINY=Y(I)
800      IF Y(I)>MAXY THEN MAXY=Y(I)
810      NEXT I
820      GRAPHALL @ FRAME
830      LOCATE 30,200,25,95
840      SCALE MINX,MAXX,MINY,MAXY
850      FRAME @ CSIZE 4 @ FXD 0,4 @ LINE TYPE 1
860      LAXES -((MAXX-MINX)/50),(MAXY-MINY)/4/5,0,0,10,5,3
870      MOVE MINX,MINY
880      LORG 4 @ X$=CHR$ (46)
890      FOR I=LOW TO HIGH
900      MOVE X(I),Y(I)
910      LABEL X$
920      NEXT I
930      CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
940      LABEL I TYPE$&"amps"
```

```
950     LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "time (msec)"
960     GOTO 1140
970 !
980 !  Store data on disk
990 !
1000    FD$=":D70"&VAL$ (FIGUREDRIVE)
1010    IF FIGSTORE$="YES" THEN GSTORE FIGUREFILE$&FD$ @ GOTO 1030 ELSE
        1030
1020    GSTORE FIGUREFILE$&FD$
1030 datastore: IF DATASTORE$="YES" THEN 1040 ELSE 1130
1040    DD$=VAL$ (COUNTER)&":D70"&VAL$ (DATADRIVE)
1050    PURGE DATAFILE$&DD$
1060    CREATE DATAFILE$&DD$,20+N*2,10
1070    ASSIGN# 1 TO DATAFILE$&DD$
1080    PRINT# 1 ; E6,E2,E3,E4,T1,T2,I_RANGE
1090    PRINT# 1 ; I_TYPE$[1,5],T3,T4,VAL$ (T7)&VAL$ (T8)
1100    PRINT# 1 ; N,T5,E5,E7,E8,V_RANGE,ADVOLTAGE,TOTALSCANS,T9
1110    FOR I=1 TO N @ PRINT# 1 : X(I),Y(I) @ NEXT I
1120    ASSIGN# 1 TO *
1130    IF SCANFLAG=1 THEN RETURN
1140    WAIT 1000 @ RELEASE KEYBOARD @ INPUT T$ @ ALPHALL @ GOTO menu
1160 ! inputs
1170 !
1180    CLEAR @ DISP "Enter the beginning detection potential <-10,+10>
        [0.80] :"
1190    INPUT T$ @ IF LEN (T$)=0 THEN E1=.8 @ GOTO 1210 ELSE E1=VAL (T$)
        @ GOTO 1210
1200    GOTO 1180
1210    IF E1<-10 OR E1>10 THEN 1180
1220    GOTO menu
1230 !
1240    CLEAR @
        DISP "Enter the anodic cleaning potential <-10,+10> [1.3] :"
1250    INPUT T$ @ IF LEN (T$)=0 THEN E2=1.3 @ GOTO 1270 ELSE E2=VAL (T$)
        @ GOTO 1270
1260    GOTO 1240
1270    IF E2<-10 OR E2>10 THEN 1240
1280    GOTO menu
1290 !
1300    CLEAR @ DISP "Enter the beginning reduction/adsorption potential
        <-10,10> [0.2] :"
1310    INPUT T$ @ IF LEN (T$)=0 THEN E4=.2 @ GOTO 1330 ELSE E4=VAL (T$)
        @ GOTO 1330
1320    GOTO 1300
1330    IF E4<-10 OR E4>10 THEN 1300
1340    GOTO menu
1350 !
1360    CLEAR @ DISP "Enter the detection time <0,600000 msec> [200] :" @
        INPUT T$
1370    IF LEN (T$)=0 THEN T1=200 @ GOTO 1390 ELSE T1=VAL (T$) @
        GOTO 1390
```

```
1380    GOTO 1360
1390    IF T1<0 OR T1>600000 THEN 1360
1400    IF T1=0 THEN T1=.001
1410    GOTO menu
1420 !
1430    CLEAR @ DISP "Enter the anodic cleaning time <0,600000 msec>
        [200] :"
1440    INPUT T$ @ IF LEN (T$)=0 THEN T2=200 @ GOTO 1460 ELSE T2=VAL (T$)
        @ GOTO 1460
1450    GOTO 1430
1460    IF T2<0 OR T2>600000 THEN 1430
1470    IF T2=0 THEN T2=.001
1480    GOTO menu
1490 !
1500    CLEAR @ DISP "Enter the initial reduction/adsorption time
        <0,600000> [500] :"
1510    INPUT T$ @ IF LEN (T$)=0 THEN T4=500 @ GOTO 1530 ELSE T4=VAL (T$)
        @ GOTO 1530
1520    GOTO 1500
1530    IF T4<0 OR T4>600000 THEN 1500
1540    IF T4=0 THEN T4=.001
1550    GOTO menu
1560 !
1570    CLEAR @ DISP "Enter the data file name <7 characters> [PADTEST]
        "
1580    INPUT T$ @ IF LEN (T$)=0 THEN DATAFILE$="PADTEST" ELSE
        DATAFILE$=T$
1590    IF LEN (T$)<8 OR DATAFILE$="PADTEST" THEN 1630
1600    DISP @ DISP @ DISP "File name is longer than 7 characters."
1610    DISP "Do you wish to change it?  <Y,N> [N] ;" @ INPUT T$
1615    IF LEN (T$)=0 THEN menu
1620    IF T$[1,1]="Y" OR T$[1,1]="y" THEN 1570
1630    GOTO menu
1640 !
1650    CLEAR @ DISP "Enter the figure file name <10 characters>
        [TEST_PAD] :"
1660    INPUT T$ @ IF LEN (T$)=0 THEN FIGUREFILE$="TEST_PAD" ELSE
        FIGUREFILE$=T$
1670    IF LEN (T$)<11 OR FIGUREFILE$="TEST_PAD" THEN 1710
1680    DISP @ DISP @ DISP "File name ";T$;" is longer than 10
        characters."
1690    DISP "Do you wish to change it?  <Y,N> [N] :" @ INPUT T$
1695    IF LEN (T$)=0 THEN menu
1700    IF T$[1,1]="Y" OR T$[1,1]="y" THEN 1650
1710    GOTO menu
1720 !
1730    IF DATADRIVE=1 THEN DATADRIVE=0 ELSE DATADRIVE=1
1740    GOTO menu
1750 !
1760    IF STATIC$="YES" THEN STATIC$="NO" ELSE STATIC$="YES"
1770    GOTO menu
```

```
1780 !
1790     IF FIGUREDRIVE=1 THEN FIGUREDRIVE=0 ELSE FIGUREDRIVE=1
1800     GOTO menu
1810 !
1820     IF DATASTORE$="YES" THEN DATASTORE$="NO" ELSE DATASTORE$="YES"
1830     GOTO menu
1840 !
1850     IF FIGSTORE$="YES" THEN FIGSTORE$="NO" ELSE FIGSTORE$="YES"
1860     GOTO menu
1870 !
1880     IF COULOMB$="i" THEN COULOMB$="q" ELSE COULOMB$="i"
1890     GOTO menu
1900 !
1910     CLEAR @ DISP "Enter the drive number <0,1> [1] :" @ INPUT T$
1920     IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 1940 ELSE DRIVE=VAL (T$) @
         GOTO 1940
1930     GOTO 1910
1940     IF DRIVE=0 OR DRIVE=1 THEN 1950 ELSE 1910
1950     CAT ":D70"&VAL$ (DRIVE)
1960     DISP "Press <END LINE> to continue :" @ INPUT T$
1970     GOTO menu
1980 !
1990     IF PLOTFIG$="YES" THEN PLOTFIG$="NO" ELSE PLOTFIG$="YES"
2000     GOTO menu
2010 !
2020     CLEAR @ DISP "Enter the cathodic cleaning potential <-10,+10>
         [-0.25] :"
2030     INPUT T$ @ IF LEN (T$)=0 THEN E3=-.25 @ GOTO 2050 ELSE E3=VAL
         (T$) @ GOTO 2050
2040     GOTO 2020
2050     IF E3<-10 OR E3>10 THEN 2020
2060     GOTO menu
2070 !
2080     CLEAR @ DISP "Enter the cathodic cleaning time <0,600000 msec>
         [200] :"
2090     INPUT T$ @ IF LEN (T$)=0 THEN T3=200 @ GOTO 2110 ELSE T3=VAL (T$)
         @ GOTO 2110
2100     GOTO 2080
2110     IF T3<0 OR T3>600000 THEN 2080
2120     IF T3=0 THEN T3=.001
2130     GOTO menu
2140 !
2150     CLEAR @ DISP "Enter the sampling time for i vs. t <0.1,600000
         msec> [2] :"
2160     INPUT T$ @ IF LEN (T$)=0 THEN T5=2 @ GOTO 2180 ELSE T5=VAL (T$) @
         GOTO 2180
2170     GOTO 2150
2180     IF T5<.1 OR T5>600000 THEN 2150
2190     GOTO menu
2200     CLEAR @ DISP "Enter the minimum on Y <-50,max Y> [0] :" @ INPUT
         T$
```

```
2210    IF LEN (T$)=0 THEN YMIN=0 @ GOTO 2230 ELSE YMIN=VAL (T$) @
        GOTO 2230
2220    GOTO 2200
2230    IF YMIN<-50 OR YMIN>50 THEN 2200
2240    DISP @ DISP @ DISP @
        DISP "Enter the maximum on Y <min Y, 50> [0] :"
2250    INPUT T$ @ IF LEN (T$)=0 THEN YMAX=0 @
        GOTO 2270 ELSE YMAX=VAL (T$) @ GOTO 2270
2260    GOTO 2240
2270    IF YMAX<YMIN OR YMAX>50 THEN 2240
2280    GOTO menu
2290    CLEAR @ DISP "Enter the current range <0.02, 10> [5] :" @ INPUT
        T$
2300    IF LEN (T$)=0 THEN I_RANGE=5 @ GOTO 2320 ELSE I_RANGE=VAL (T$) @
        GOTO 2320
2310    GOTO 2290
2320    IF I_RANGE<.02 OR I_RANGE>10 THEN 2290
2330    DISP @ DISP
2340    DISP "Enter the scale <milliamps (m,M), microamps (u,U)> [M] :" @
        INPUT T$
2350    IF LEN (T$)=0 THEN I_TYPE$="milli" @ GOTO 2380 ELSE I_TYPE$=T$
2360    IF T$[1,1]="M" OR T$[1,1]="m" THEN I_TYPE$="milli" @ GOTO 2380
2370    IF T$[1,1]="U" OR T$[1,1]="u" THEN I_TYPE$="micro" @ GOTO 2380
        ELSE 2340
2380    DISP @ DISP @ DISP I_RANGE;" ";I_TYPE$;"amps, per what voltage
        range <0, 5000> [10] ," @ INPUT T$
2390    IF LEN (T$)=0 THEN V_RANGE=10 @ GOTO 2410 ELSE V_RANGE=VAL (T$) @
        GOTO 2410
2400    GOTO 2380
2410    IF V_RANGE<0 OR V_RANGE>5000 THEN 2380
2420    GOTO menu
2430    CLEAR @ DISP "Total number of cleaning pulses <1,--> [5] :"
2440    INPUT T$ @ IF LEN (T$)=0 THEN T6=5 @ GOTO 2460 ELSE T6=VAL (T$) @
        GOTO 2460
2450    GOTO 2430
2460    IF T6<1 THEN 2430
2470    GOTO menu
2480    CLEAR @ DISP "Enter the sampling frequency <1,100> [1] :" @ INPUT
        T$
2490    IF LEN (T$)=0 THEN SAMPLE=1 @ GOTO 2510 ELSE SAMPLE=INT (VAL
        (T$)) @ GOTO 2510
2500    GOTO 2480
2510    IF SAMPLE<1 OR SAMPLE>100 OR SAMPLE>T1/T5 THEN 2480
2520    GOTO menu
2530    CLEAR @ DISP "Enter the ending detection potential <-10,+10>
        [0.80] :"
2540    INPUT T$ @ IF LEN (T$)=0 THEN E5=.8 @ GOTO 2560 ELSE E5=VAL (T$)
        @ GOTO 2560
2550    GOTO 2530
2560    IF E5<-10 OR E5>10 THEN 2530
2570    GOTO menu
```

```
2580    CLEAR @ DISP "Enter the potential increment, E-d <-2, 2 [.005
        min]> [0.05] :"
2590    INPUT T$ @ IF LEN (T$)=0 THEN INCPOT=.05 @ GOTO 2660 ELSE
        INCPOT=VAL (T$) @ GOTO 2610
2600    GOTO 2580
2610    IF INCPOT>ABS (E5-E2) THEN 2580
2620    IF INCPOT>-.005 AND INCPOT<0 THEN 2580
2630    IF INCPOT<.005 AND INCPOT>0 THEN 2580
2640    IF INCPOT<-2 OR INCPOT>2 THEN 2580
2650    IF INT (INCPOT*1000)/.005<> INCPOT*1000/.005 THEN 2580
2660    GOTO menu
2670    CLEAR @ DISP "Enter the A/D voltage range <1, 10> [10] :" @
        INPUT T$
2680    IF LEN (T$)=0 THEN ADVOLTAGE=10 @
        GOTO 2710 ELSE ADVOLTAGE=VAL (T$) @ GOTO 2700
2690    GOTO 2670
2700    IF ADVOLTAGE=10 OR ADVOLTAGE=1 THEN 2710 ELSE 2670
2710    GOTO menu
2720    CLEAR @
        DISP "Enter the number of signal averaged scans <1, --> [1] :"
2730    INPUT T$ @ IF LEN (T$)=0 THEN TOTALSCAN$=1 @ GOTO 2750 ELSE
        TOTALSCANS=VAL (T$) @ GOTO 2750
2740    GOTO 2720
2750    TOTALSCANS=INT (TOTALSCANS)
2760    IF TOTALSCANS<1 THEN 2720
2770    GOTO menu
2780    CLEAR @ DISP "Enter the final reduction/adsorption time
        <0,600000> [500] :"
2790    INPUT T$ @ IF LEN (T$)=0 THEN T7=500 @ GOTO 1530 ELSE T7=VAL (T$)
        @ GOTO 2810
2800    GOTO 2780
2810    IF T7<0 OR T7>600000 THEN 2780
2820    IF T7=0 THEN T7=.001
2830    GOTO menu
2840    CLEAR @ DISP "Enter the reduction/adsorption time increment
        <0,600000> [0] :"
2850    INPUT T$ @ IF LEN (T$)=0 THEN T8=0 @ GOTO 1530 ELSE T8=VAL (T$) @
        GOTO 2870
2860    GOTO 2840
2870    IF T8<0 OR T8>600000 THEN 2840
2880    IF T8=0 THEN T8=.001
2890    GOTO menu
2900    CLEAR @ DISP "Enter the potential increment, E-r/a <-2, 2 [.005
        min]> [0.05] :"
2910    INPUT T$ @ IF LEN (T$)=0 THEN INCPOT2=.05 @ GOTO 2980 ELSE
        INCPOT2=VAL (T$) @ GOTO 2930
2920    GOTO 2900
2930    IF INCPOT2>ABS (E5-E2) THEN 2900
2940    IF INCPOT2>-.005 AND INCPOT2<0 THEN 2900
2950    IF INCPOT2<.005 AND INCPOT2>0 THEN 2900
2960    IF INCPOT2<-2 OR INCPOT2>2 THEN 2900
```

```
2970     IF INT (INCPOT2*1000)/.005<> INCPOT2*1000/.005 THEN 2900
2980     GOTO menu
2990     CLEAR @ DISP "Enter the ending reduction/adsorption potential
         <-10,10> [0.2] :"
3000     INPUT T$ @ IF LEN (T$)=0 THEN E7=.2 @ GOTO 3020 ELSE E7=VAL (T$)
         @ GOTO 3020
3010     GOTO 2990
3020     IF E7<-10 OR E7>10 THEN 2990
3030     GOTO menu
3040     CLEAR @ AWRITE 1,0,"Rotation speed(s) -- e.g., 1,2,3... , 1-5, *
         for all"
3050     FOR I=1 TO 10 @ AWRITE I+7,12,VAL$ (I)&")"&PERIOD$[1,5-LEN (VAL$
         (I))]&ROT$(I)&ROT1$(I) @ NEXT I
3060     FOR I=1 TO 7 @ AWRITE I+7,30,VAL$ (I+10)&")"&
         PERIOD$[1,3]&ROT$(I+10)&ROT1$(I+10) @ NEXT I
3070     AWRITE 20,2,"" @ LINPUT CODE$ @ IF LEN (CODE$)=0 THEN menu
3080     GOSUB decode @ IF error=1 THEN 3040
3090     FOR I=1 TO 17 @ ROT1$(I)="" @ IF CODE(I)<> 0 THEN ROT1$(I)="*"
3100     NEXT I @ J=1 @ FOR I=1 TO 17 @ IF ROT$(I)="*" THEN
         ROT(J)=ROT2(I) @ J=J+1
3110     NEXT I @ ROTMAX=J-1 @ IF ROTMAX=0 THEN ROTMIN=0 @ ROT=0 ELSE
         ROTMIN=1 @ ROT=1
3120     GOTO 3040
3130     IF ZPRINT$="NO" THEN ZPRINT$="YES" @ PRINTER IS 705,90 ELSE
         ZPRINT$="NO" @ PRINTER IS 1
3140     GOTO menu
3150 !
3160 beginning:
3170     CLEAR
3180     DIM Y(3000),X(3000),TEMP(3000)
3190     DIM A$(50)[50],B$(50)[50],DAT$(50)[25],
         DATAFILEE$[20],FIGUREFILE$[20]
3200     DIM T$[50],T1$[50],PERIOD$[50],DATASTORE$[10],FIGSTORE$[10]
3210     DIM PLOTFIG$[10],I_TYPE$[5],FD$[15],DD$[15]
3220     DIM CODE(20),ROT(20),ROT2(20),ROT1$(20)[1],ROT$(20)[4]
3230     ON ERROR GOSUB 4720 @ AWRITE 0,0
3240     E1,E5=.8 @ E2=1.3 @ E4,E7=.2 @ T1,T2,T3=200 @ T4,T7=500 @ T6=5 @
         SAMPLE=1
3250     T5=2 @ T8=0 @ DATAFILE$="PADTEST" @ FIGUREFILE$="TEST_PAD" @
         DATADRIVE=1
3260     FIGUREDRIVE=1 @ DATASTORE$="YES" @ FIGSTORE$="NO" @ DRIVE=1 @
         E3=-.25
3270     ROT,ROT(0),ROTMAX,ROTMIN=0 @ ZPRINT$="NO" @ PRINTER IS 1 @
         INTEGRATE=8
3280     PLOTFIG$="YES" @ YMIN,YMAX=0 @ I_RANGE=5 @ I_TYPE$="milli" @
         INCPOT=.05
3290     SCANFLAG=0 @ ADVOLTAGE=10 @ TOTALSCANS=1 @ V_RANGE=10 @
         INCPOT2=.05
3300     FOR I=1 TO 10 @ ROT$(I)=VAL$ (I*500) @ ROT1$(I),ROT1$(I+10)="" @
         NEXT I
```

```
3310      ROT$(3)="1400" @ FOR I=10 TO 70 STEP 10 @
          ROT$(I/10+10)=VAL$ (I^2) @ NEXT I
3320      FOR I=1 TO 17 @ READ T @ ROT2(I)=T @ ROT(I)=0 @ NEXT I
3330      COULOMB$="i" @ STATIC$="YES"
3340      GOSUB 4140 @ TAKE KEYBOARD
3350      A$(1)="Experimental directory"
3360      A$(2)="Mass storage directory"
3370      A$(3)="Plotting directory"
3380      A$(4)="Begin experiment"
3390      A$(5)="Chain Autost"
3400      A$(6)="End program"
3410      A$(7)="Exit to main menu"
3420      A$(8)="Beginning detection potential, E1...*"
3430      A$(9)="Ending detection potential, E5...*"
3440      A$(10)="Potential increment,E-d...*"
3450      A$(11)="Anodic cleaning potential, E2"
3460      A$(12)="Cathodic cleaning potential, E3"
3470      A$(13)="Beginning adsorption potential, E4...**"
3480      A$(14)="Ending adsorption potential, E7...**"
3490      A$(15)="Potential increment,E-r/a...**"
3500      A$(16)="Detection time (msec), Tl"
3510      A$(17)="Anodic cleaning time (msec), T2"
3520      A$(18)="Cathodic cleaning time (msec), T3"
3530      A$(19)="Sampling time (msec), T5"
3540      A$(20)="Cleaning pulses, T6"
3550      A$(21)="Continuance of experimental directory"
3560      A$(22)="Exit to previous experimental menu"
3570      A$(23)="Beginning adsorption time (msec), T4...***"
3580      A$(24)="Ending adsorption time (msec), T7...***"
3590      A$(25)="Adsorption time increment (msec), T8...***"
3600      A$(26)="Samling frequency"
3610      A$(27)="Current range"
3620      A$(28)="A/D voltage range"
3630      A$(29)="Number of signal averaged decays"
3640      A$(30)="Rotation speeds"
3650      A$(31)="Converting to current or charge"
3660      A$(32)="Static electrode at detection"
3670      A$(33)="NULL"
3680      A$(34)="Exit to main menu"
3690      A$(35)="Data file name"
3700      A$(36)="Figure file name"
3710      A$(37)="Data file drive number"
3720      A$(38)="Figure file drive number"
3730      A$(39)="Store data on disk"
3740      A$(40)="Store figure on disk"
3750      A$(41)="Catalog of disk"
3760      A$(42)="NULL"
3770      A$(43)="Exit to main menu"
3780      A$(44)="Plot raw data curve"
3790      A$(45)="Enter max and min on Y only"
3800      A$(46)="Activate printer"
```

```
3810     PERIOD$="..............................................."
3820     FOR I=1 TO 46 @ T$=A$(I) @ GOSUB 4170 @ B$(I)=T1$ @ NEXT I
3830     SCRN=1 @ A1=1 @ A2=6
3840 menu: TAKE KEYBOARD @ GOSUB 4190
3850     CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$ (64+I-A1+1)&CHR$
         (41)&PERIOD$[1,4]&A$(I)&PERIOD$[1,45-LEN (A$(I))]&" "&DAT$(I) @
         NEXT I
3860     AWRITE 1,8,B$(A1) @ CRSR=1
3870     AWRITE 20,2,"Change any parameters ?" @ AWRITE 21,2,"Press the
         indicated letters or use the the '.' and ',' keys for slewing "
3880     AWRITE 22,2,"Press '4' to change any parameters or to start
         experiment "
3890     AWRITE 23,2,"Asterisks indicate precedence, * being the
         highest."
3900     TAKE KEYBOARD
3910     KYY=NUM (KEY$ ) @ IF NOT KYY THEN 3910
3920     IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @
         CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
3930     IF KYY<> 46 THEN 3960
3940     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
         CRSR=A2-A1+1
3950     AWRITE CRSR,8,B$(A1+CRSR-1)
3960     IF KYY<> 44 THEN 3990
3970     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @ IF CRSR>A2-A1+1 THEN
         CRSR=1
3980     AWRITE CRSR,8,B$(A1+CRSR-1)
3990     IF KYY<> 52 THEN 3900
4000     IF SCRN<> 1 THEN 4060
4010     IF CRSR=1 THEN SCRN=2 @ A1=7 @ A2=21 @ GOTO 3850
4020     IF CRSR=2 THEN SCRN=3 @ A1=34 @ A2=41 @ GOTO 3850
4030     IF CRSR=3 THEN SCRN=4 @ A1=43 @ A2=46 @ GOTO 3850
4040     IF CRSR=5 THEN RELEASE KEYBOARD @ CHAIN "Autost"
4050     IF CRSR=4 THEN experiment ELSE RELEASE KEYBOARD @ GOTO 4130
4060     PAGEFLAG=1 @ RELEASE KEYBOARD
4070     IF SCRN=2 THEN ON CRSR GOTO 4100,1180,2530,2580,1240,2020,1300,
         2990,2900,1360,1430,2080,2150,2430,4110
4080     IF SCRN=5 THEN ON CRSR GOTO
         4120,1500,2780,2840,2480,2290,2670,2720,3040,1880,1760
4090     IF SCRN=3 THEN ON CRSR GOTO
         4100,1570,1650,1730,1790,1820,1850,1910
         ELSE ON CRSR GOTO 4100,1990,2200,3130
4100     TAKE KEYBOARD @ SCRN=1 @ A1=1 @ A2=6 @ GOTO 3850
4110     TAKE KEYBOARD @ SCRN=5 @ A1=22 @ A2=32 @ GOTO 3850
4120     TAKE KEYBOARD @ SCRN=2 @ A1=7 @ A2=21 @ GOTO 3850
4130     CLEAR @ END
4140     FOR I=1 TO 14 @ ON KEY# I GOTO menu @ NEXT I
4150     ON KEY# 4 GOSUB 4710 @ ON KEY# 5 GOSUB 4390 @ ON KEY# 6 GOSUB 30
4160     RETURN
4170     T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128)
         @ NEXT L
4180     RETURN
```

```
4190     DAT$(1),DAT$(2),DAT$(3),DAT$(4),DAT$(5),DAT$(6),DAT$(7)=""
4200     DAT$(8)=VAL$ (E1) @ DAT$(9)=VAL$ (E5) @ DAT$(10)=VAL$ (INCPOT)
4210     DAT$(11)=VAL$ (E2) @ DAT$(12)=VAL$ (E3) @ DAT$(13)=VAL$ (E4)
4220     DAT$(14)=VAL$ (E7) @ DAT$(15)=VAL$ (INCPOT2)
4230     DAT$(16)=VAL$ (T1) @ DAT$(17)=VAL$ (T2)
4240     DAT$(18)=VAL$ (T3) @ DAT$(19)=VAL$ (T5) @ DAT$(20)=VAL$ (T6) @
         DAT$(21)=""
4250     DAT$(22)="" @ DAT$(23)=VAL$ (T4) @ DAT$(24)=VAL$ (T7) @
         DAT$(25)=VAL$ (T8)
4260     DAT$(26)=VAL$ (SAMPLE)
4270     DAT$(27)=VAL$ (I_RANGE)&" "&I_TYPE$[1,5]&"amps"&"/ "&
         VAL$ (V_RANGE)&"V"
4280     DAT$(28)=VAL$ (ADVOLTAGE)
4290     DAT$(29)=VAL$ (TOTALSCANS) @ DAT$(30)="" @ DAT$(31)=COULOMB$
4300     DAT$(32)=STATIC$ @ DAT$(33),DAT$(34)=""
4310     DAT$(35)=DATAFILE$ @ DAT$(36)=FIGUREFILE$ @ DAT$(37)=VAL$
         (DATADRIVE)
4320     DAT$(38)=VAL$ (FIGUREDRIVE) @ DAT$(39)=DATASTORE$
4330     DAT$(40)=FIGSTORE$ @ DAT$(41)=VAL$ (DRIVE) @ DAT$(42)=""
4340     DAT$(43)="" @ DAT$(44)=PLOTFIG$ @ DAT$(45)=VAL$ (YMIN)&", "&VAL$
         (YMAX)
4350     DAT$(46)=ZPRINT$
4360     RETURN
4370 !
4380 !
4390     ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN
4400     GOSUB 20 @ RETURN
4410     ROT=0 @ GOSUB 20 @ RETURN
4420 decode:
4430 !
4440     ON ERROR GOTO error2 @ error=0 @ FOR I=1 TO 20 @ CODE(I)=0 @
         NEXT I
4450     FOR I=1 TO LEN(CODE$) @ IF CODE$[1,1]=CHR$(32) THEN CODE$=
         CODE$[2,LEN(CODE$)] @ GOTO 4450
4460     IF CODE$[1,1] <> "*" THEN 4480
4470     FOR I=1 TO 100 @ CODE(I)=1 @ NEXT I @ GOTO 4590
4480     T$="1"
4490     FOR I=0 TO 9 @ IF CODE$[1,1]=VAL$ (I) THEN T$="-1"
4500     NEXT I @ IF T$ <> VAL$ (-1) THEN CODE$=CODE$[2,LEN (CODE$)]
         ELSE 4520
4510     IF LEN (CODE$)=0 THEN error3 ELSE 4490
4520     T=VAL (CODE$) @ IF T<0 OR T>99 THEN error2 ELSE CODE(T)=1
4530     IF LEN (VAL$ (T))=LEN (GODE$) THEN 4590
4540     CODE$=CODE$[1+LEN (VAL$ (T)),LEN (CODE$)] @ IF LEN (CODE$)=0 THEN
         CODE(T)=1 @ GOTO 4590
4550     T$=CODE$[1,1] @ CODE$=CODE$[2,LEN (CODE$)] @ IF T$="," OR T$="-"
         THEN 4560 ELSE errorl
4560     t1=VAL (CODE$) @ IF t1<0 OR t1>99 THEN T=t1 @ GOTO error2
4570     IF T$="," THEN CODE(t1)=1 @ GOTO 4520
4580     FOR I=T+1 TO t1 @ CODE(I)=1 @ NEXT I @ GOTO 4520
4590     ON ERROR GOSUB 4720 @ RETURN
```

```
4600 !
4610 error1: error=1
4620    DISP "Character ";T$;" not allowed." @ DISP @
        DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
4630 !
4640 error2: error=1
4650    DISP "The value ";T;" is to large." @ DISP @
        DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
4660 !
4670 error3: error=1
4680    DISP "String does not follow syntax." @ DISP @
        DISP "Press <END LINE> to continue." @  INPUT T$ @ RETURN
4690    DATA
        48,80,112,160,256,304,336,560,576,1040,16,32,64,128,256,512,1024
4700 ! Display results on 'printer is' default
4710    PRINT CHR$ (12) @ FOR K=1 TO 44 @ PRINT CHR$ (64+K)&CHR$
        (41)&PERIOD$[1,4]&A$(K)&PERIOD$[1,45-LEN (A$(K))]&" "&DAT$(K) @
        NEXT K @ PRINT CHR$ (12) @ RETURN
4720 ! Error trap subroutine
4730    IF ERRN =67 OR ERRN =66 THEN 4780
4740    IF ERRN =11 THEN menu
4750    IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 4780
4760    IF ERRN =130 THEN BEEP 300,700 @ RELEASE KEYBOARD @ DISP "Place
        disk in drive and then press <END LINE>" @ INPUT T$ @ TAKE
        KEYBOARD @ GOTO 4780
4770    DISP ERRN,ERRL @ WAIT 2000
4780    RETURN
4790    END
```

4. PAD Plot

```
5       GOTO beginning
10      FOR I=1 TO 14 @ ON KEY# I GOTO menu @ NEXT I @ RETURN
15      T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128)
        @ NEXT L
20      RETURN
25 !
26      ASSIGN# 1 TO"CHARSET"
27      FOR I=1 TO 46
28      READ# 1 : CHAR$(I)
29      NEXT I @ ASSIGN# 1 TO * @ RETURN
30      DAT$(1),DAT$(2),DAT$(3),DAT$(4),
        DAT$(5),DAT$(6),DAT$(7),DAT$(8)=""
35      DAT$(9)=DSPFLAG$ @ DAT$(10)=FILE2$ @ DAT$(11)=DATADRIVE$
40      DAT$(12)=GRAPHDRIVE$ @ DAT$(13)=VAL$ (DRIVE) @ DAT$(14)=""
45      FOR I=15 TO 24
50      DAT$(I)=FILE$(I-14)&LOCK$(I-14)&" ("&VAL$ (E1(I-14))&") <"&VAL$
        (E4(I-14))&">"
55      NEXT I
60      DAT$(25),DAT$(26),DAT$(27)=""
62      DAT$(28)=VAL$ (YMIN)&" , "&VAL$ (YMAX) @
        DAT$(29)=VAL$ (XMIN)&" , "&VAL$ (XMAX)
65      DAT$(31)=DSPCRT$ @ DAT$(32)="N/A" @ DAT$(33)=DSPXY$ @
        DAT$(34)=TYPE$ 67 DAT$(35)="" @ DAT$(36)="" @ DAT$(30)=""
70      RETURN
75 !
80      CLEAR @ DISP "Plot on CRT <Y/N> [Y] :" @ INPUT T$ @ IF LEN (T$)=0
        THEN DSPCRT$="YES" @  GOTO 90
85      IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPCRT$="YES" ELSE
        DSPCRT$="NO"
90      GOTO menu
95      CLEAR @ DISP "Store graph on disk <Y/N> [Y]:" @ INPUT T$
100     IF LEN (T$)=0 THEN DSPFLAG$="YES"
105     IF T$[1,1]="N" OR T$[1,1]="n" THEN DSPFLAG$="NO" ELSE
        DSPFLAG$="YES"
110     GOTO menu
115     CLEAR @ DISP "Plot on X-Y recorder <Y/N> [N] :" @ INPUT T$ @
        IF LEN (T$)=0 THEN DSPXY$ ="NO" @ GOTO 125
120     IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPXY$="YES" ELSE DSPXY$="NO"
125     GOTO menu
130     CLEAR @ DISP "Enter storage file name <10 characters> [TEST] :" @
        INPUT FILE2$
135     IF LEN (FILE2$)=0 THEN FILE2$="TEST"
136     GOTO menu
138     CLEAR @ DISP "Enter the minimum on X <-100,100> [0] :" @
        INPUT T$ @ IF LEN (T$)=0 THEN XMIN=0 ELSE XMIN=VAL (T$)
139     IF YMIN<-100 OR YMIN>100 THEN 138
140     DISP @ DISP @ DISP "Enter the maximum on X <-100,100> [0] :" @
        INPUT T$ @ IF LEN (T$)= 0 THEN XMAX=0 ELSE XMAX=VAL (T$)
```

```
141      IF XMAX<-100 OR XMAX>100 THEN 140 ELSE GOTO menu
145      CLEAR @ DISP "Enter the minimum on Y <-100,100> [0] :" @ INPUT
         T$ @ IF LEN (T$)=0 THEN YMIN=0 ELSE YMIN=VAL (T$)
150      IF YMIN<-100 OR YMIN>100 THEN 145
155      DISP @ DISP @ DISP "Enter the maximum on Y <-100,100> [0] :" @
         INPUT T$ @ IF LEN (T$)= 0 THEN YMAX=0 ELSE YMAX=VAL (T$)
160      IF YMAX<-100 OR YMAX>100 THEN 155 ELSE GOTO menu
165      CLEAR @ DISP "Enter the drive number <0,1 or both--data read
         only> [0] :" @ INPUT T$
170      IF LEN (T$)=0 THEN T$="0" @ GOTO 190
175      IF T$[1,1]="B" OR T$[1,1]="b" THEN FLAG=0 @ GOTO 185
180      IF VAL (T$)=0 OR VAL (T$)=1 THEN 185 ELSE 165
185      IF CRSR=5 AND (T$[1,1]="B" OR T$[1,1]="b") THEN 165
190      IF CRSR=4 THEN DATADRIVE$=T$[1,1] ELSE GRAPHDRIVE$=T$[1,1]
195      GOTO menu
200      CLEAR @ DISP "Enter the file name" @ INPUT T$
205      IF LEN (T$)=0 THEN FILE$(CRSR-1)="NULL" @ LOCK$(CRSR-1)="" @
         LOW(CRSR-1),HIGH(CRSR-1)= 1 @ GOTO 235
210      FILE$(CRSR-1)=T$ @ LOCK$(CRSR-1)=""
215      J=CRSR-1 @ GOSUB fileinput
235      GOTO menu
240      CLEAR @ DISP "Drive number <0,1> [1]:" @ INPUT T$
245      IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 255
250      DRIVE=VAL (T$) @ IF DRIVE=0 OR DRIVE =1 THEN 255 ELSE 240
255      CLEAR @ CAT ":D70"&VAL$(DRIVE)
260      DISP "Press <END LINE> to continue:" @ INPUT T$
265      GOTO menu
270      CLEAR @ DISP "Enter the raw data filenames [10] :" @
         DISP "Press <END LINE> when the last name has been entered."
275      FOR J=1 TO TOTAL
280      INPUT FILE$(J)
282      N=J @ LOCK$(J)="" @ LOW(J),HIGH(J)=1
285      IF LEN (FILE$(J))=0 THEN FILE$(J)="NULL" @ LOCK$(J)="" @ N=J-1 @
         J=TOTAL
290      NEXT J
295      FOR J=1 TO N
300      GOSUB fileinput
305      NEXT J
345      GOTO menu
380 fileinput:
385      IF DATADRIVE$="B" OR DATADRIVE$="b" THEN DRIVE$=VAL$ (0) ELSE
         DRIVE$=DATADRIVE$
390      ASSIGN# 1 TO FILE$(J)&":D70"&DRIVE$
395      READ# 1 ; E1(J),E2(J),E3(J),E4(J),T1(J),T2(J),I_RANGE(J)
400      READ# 1 ; I_TYPE$(J),T3(J),T4(J),EXTDATA$(J),N(J)
405      READ# 1 ; T5(J),A,A,A,A,A,A,A
410      FOR I=1 TO N(J) @ READ# 1 ; X(I,J),Y(I,J) @ NEXT I
415      IF DATADRIVE$="B" OR DATADRIVE$="b" THEN FLAG=0
420      IF ERRN =67 OR ERRN =66 THEN 430
425      ASSIGN# 1 TO *
430      HIGH(J)=N(J) @ RETURN
```

```
435     FOR J=1 TO TOTAL
440     FILE$(J)="NULL" @ LOCK$(J)="" @ LOW(J),HIGH(J)=1 @ E1(J),E4(J)=0
445     NEXT J
450     GOTO menu
490     FOR J=1 TO TOTAL
495     LOCK$(J)="" @ LOW(J),HIGH(J)=1
500     IF FILE$(J)="NULL" THEN 510
505     GOSUB fileinput
510     NEXT J
520     GOTO menu
560 !
565 plotting:
570 !
575 !  Graphics routine
580 !
581     CLEAR @ AWRITE 10,33,"Calculating"
582     ON TYPE GOSUB 3800,3850,3900,3950,4000,4050
585     IF DSPCRT$="NO" AND DSPXY$="NO" THEN 1200
590     CLEAR @ AWRITE 10,33,"Plotting"
595     SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @ FACTOR=1
600     FOR J=1 TO TOTAL
605     IF FILE$(J)="NULL" THEN 615
610     IF I TYPE$(J)="milli" THEN SETMILLI=1 ELSE SETMICRO=1
615     NEXT J
620     IF SETMILLI=1 AND SETMICRO=1 THEN PRODUCT=1
625     MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
630     FOR J=1 TO TOTAL
635     IF FILE$(J)="NULL" THEN 720
640     IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE
        FACTOR=1
642     LOW=LOW(J) @ HIGH=HIGH(J)
650     IF X(LOW,J)>MAXX THEN MAXX=X(LOW,J)
655     IF X(HIGH,J)>MAXX THEN MAXX=X(HIGH,J)
660     IF X(LOW,J)<MINX THEN MINX=X(LOW,J)
665     IF X(HIGH,J)<MINX THEN MINX=X(HIGH,J)
675     FOR I=LOW TO HIGH
680     IF Y(I,J)*FACTOR<MINY THEN MINY=Y(I,J)*FACTOR
685     IF Y(I,J)*FACTOR>MAXY THEN MAXY=Y(I,J)*FACTOR
690     NEXT I
720     NEXT J
725     IF DSPCRT$ <> "YES" THEN 870
730     GRAPHALL @ FRAME
735     LOCATE 30,200,25,95
740     XEXP=ABS ((MAXX-MINX)/20) @ YEXP=ABS ((MAXY-MINY)/20)
745     SCALE MINX-XEXP,MAXX+XEXP,MINY-YEXP,MAXY+YEXP
750     FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
755     LAXES -((MAXX-MINX)/60),(MAXY-MINY)/4/5,0,0,10,5,3
760     MOVE MINX,MINY
765     LORG 4 @ X$=CHR$ (46)
770     FOR J=1 TO TOTAL
775     IF FILE$(J)="NULL" THEN 840
```

```
 780      IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE
          FACTOR=1
 782      LOW=LOW(J) @ HIGH=HIGH(J)
 795      FOR I=LOW TO HIGH
 800      MOVE X(I,J),Y(I,J)*FACTOR
 805      LABEL X$
 810      NEXT I
 840      NEXT J
 845      CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
 850      IF PRODUCT=1 THEN LABEL "microamps" ELSE LABEL I_TYPE$(1)&"amps"
 855      LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "time (msec)"
 860      IF DSPFLAG$="YES" THEN GSTORE FILE2$&":D70"&GRAPHDRIVE$
 865      INPUT T$ @ ALPHALL
 870      IF DSPXY$ <> "YES" THEN 1200
 875 !
 880 !  Mechanical plotting routine
 885 !
 890      XSCALE=8.5 @ YSCALE=7
 895      XSCALING=XSCALE/(MAXX-MINX)
 900      YSCALING=YSCALE/(MAXY-MINY)
 905      XCENTER=MAXX-(MAXX-MINX)/2
 910      YCENTER=MAXY-(MAXY-MINY)/2
 912      OUTPUT 723 ;"GP"
 913      CLEAR @ RELEASE KEYBOARD @ DISP "Plot axes <Y,N> [Y] :" @
          INPUT T$
 915      IF LEN (T$)=0 THEN T$="Y"
 916      TAKE KEYBOARD
 919      CLEAR @ DISP "Set zero positions now !" @
          DISP "Press <END LINE> to continue"
 920      OUTPUT 723 ;"OP 7 0T OP 12 50T OP 14 50T"
 925      KYY=NUM (KEY$ ) @ IF NOT KYY THEN 920
 929      WAIT 1000
 930      IF T$[1,1]="N" OR T$[1,1]="n" THEN 1095
 931      X=MINX*XSCALING-XCENTER*XSCALING+XSCALE/2
 933      OUTPUT 723 :"OP 7 ";X:"T OP 12 50T OP 7 0T OP 14 50T"
 934      WAIT 2000
 935      OUTPUT 723 ;"OP 7 7.0T OP 11 1500 14 50T WA .2T OP 7 ";X;"T OP 12
          50T"
 936      OUTPUT 723 ;"OP 7 0.0T OP 11 1500 14 50T"
 938      WAIT 3100
 939      Y=MAXY*YSCALING-YCENTER*YSCALING+YSCALE/2
 943      OUTPUT 723 ;"OP 7 ";Y;"T OP 14 50T OP 7 ";0;"T OP 12 50T"
 944      WAIT 750
 945      OUTPUT 723 ;"OP 7 8.5T OP 11 1500 12 50T WA .2T OP 7 ";Y;"T OP 14
          50T"
 946      OUTPUT 723 ;"OP 7 0.0T OP 11 1500 12 50T"
 947      WAIT 3100
 957      Y=INT (Y*10000)/10000 @ X=INT (X*10000)/10000
 960      WAIT 1000
 970      XPOS=XSCALE/6
 990      YPOS=YSCALE/5
```

```
1005    IF Y-YSCALE/60<0 THEN Y1=0 ELSE Y1=Y-YSCALE/60
1010    IF Y+YSCALE/60>YSCALE THEN Y2=YSCALE ELSE Y2=Y+YSCALE/60
1012    Y1=INT (Y1*10000)/10000 @ Y2=INT (Y2*10000)/10000
1013    LXSCALING=550
1015    FOR I=1 TO 6
1020    X1=INT (I*(XSCALE/6)*10000)/10000
1025    IF X1>XSCALE THEN 1050
1033    Y3=INT ((Y2-Y1)*10000)/10000
1034    OUTPUT 723 ;"OP 7 ";X1;"T OP 12 50T OP 7 ";Y1;"T OP 14  50T"
1035    WAIT 1500
1036    OUTPUT 723 ;"OP 11 500 7 ";Y1+Y3;" 14 50T"
1038    WAIT 550
1039    LA$=VAL$ (INT (((MAXX-MINX)/6*I+MINX+.0001)*1000)/1000)
1040    XIN=X1-8.5/LXSCALING*LEN (LA$)*7/2
1041    YIN=7.25 @ GOSUB xylabel
1045    NEXT I
1050    IF X-XSCALE/73<0 THEN X1=0 ELSE X1=X-XSCALE/73
1055    IF X+XSCALEE/73>XSCALE THEN X2=XSCALE ELSE X2=X+XSCALE/73
1057    X1=INT (X1*10000)/10000 @ X2=INT (X2*10000)/10000
1060    FOR I=1 TO 5
1065    Y1=INT (I*(YSCALE/5)*10000)/10000
1070    IF Y1>YSCALE THEN 1095
1075    IF Y1=Y THEN 1090
1078    X3=INT ((X2-X1)*10000)/10000
1080    OUTPUT 723 ;"OP 7 ";Y1;"T OP 14 50T OP 7 ";X1;"T OP 12  50T"
1081    WAIT 1000
1082    OUTPUT 723 ;"OP 11 500 7 ";X1+X3;" 12 50T"
1085    WAIT 550
1086    LA$=VAL$ (INT (((MAXY-MINY)/5*I+MINY+.000001)*10000)/10000)
1087    XIN=8.75
1088    YIN=Y1+.12 @ GOSUB xylabel
1090    NEXT I
1092    CLEAR @ DISP "Change pen color ?  Press <END LINE> to continue."
1093    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
1095    WAIT 1000
1100    FOR J=1 TO TOTAL
1110    IF FILE$(J)="NULL" THEN 1195
1115    IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE
        FACTOR=1
1117    LOW=LOW(J) @ HIGH=HIGH(J)
1130    FOR I=LOW TO HIGH
1135    X=X(I,J)*XSCALING-XCENTER*XSCALING+4.25
1140    Y=Y(I,J)*FACTOR*YSCALING-YCENTER*YSCALING+3.5
1145    OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
1146    IF I=LOW THEN WAIT 500 ELSE WAIT 150
1147    OUTPUT 723 ;"OP 11 100T"
1150    NEXT I
1185    CLEAR @ DISP "Change pen color ?  Press <END LINE> to contine."
1190    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
1195    NEXT J
1197    GOSUB filelabel
```

```
1200    GOTO menu
1205 !
1390 beginning:
1395    CLEAR
1400    DIM Y(300,10),X(300,10),EXPMT(10),INTPOT(10),FINPOT(10)
1405    DIM SCANS(10),DROPTYME(10),I_RANGE(10),I_TYPE$(10)[10]
1410    DIM INCPOT(10),PTYME1(10),EXTDATA$(10)[10],N(10)
1415    DIM A$(36)[50],B$(36)[50],FILE$(10)[15],FILE2$[15],DAT$(36)[25]
1420    DIM
        T$[50],T1$[50],PERIOD$[50],DATADRIVE$[5],GRAPHDRIVE$[5],DRIVE$[5]
1425    DIM
        DSPFLAG$[3],DSPCRT$[3],DSPXY$[3],CHAR$(46)[35],LA$[80],TYPE$[30]
1427    DIM LOW(10),HIGH(10),LOCK$(10)[1]
1430    SMOOTH=0 @ ON ERROR GOSUB 1715 @ AWRITE 0,0
1435    DSPFLAG$="NO" @ FILE2$="TEST" @ DATADRIVE$="B" @ GRAPHDRIVE$="0"
        @ DRIVE=1
1440    FLAG=1 @ TOTAL=10 @ SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @ YMIN=0
        @ YMAX=0
1445    FOR J=1 TO TOTAL @ FILE$(J)="NULL" @ E1(J),E4(J)=0
1447    LOW(J),HIGH(J)=1 @ LOCK$(J)="" @ NEXT J @ N(1)=1
1450    DSPCRT$="YES" @ DSPXY$="NO" @ TYPE=1 @ TYPE$="i vs. t" @
        XMIN,XMAX=0
1455    TAKE KEYBOARD @ GOSUB 10 @ GOSUB 26
1460    A$(1)="Filer directory"
1465    A$(2)="Mass storage directory"
1470    A$(3)="Plotting directory"
1475    A$(4)="Start plotting"
1477    A$(5)="Chain Autost"
1480    A$(6)="End program"
1482    A$(7)="NULL"
1485    A$(8)="Exit to main menu"
1490    A$(9)="Store graph on disk"
1495    A$(10)="Graph storage file name"
1500    A$(11)="Numeric data drive number"
1505    A$(12)="Graphic data drive number"
1510    A$(13)="Catalog of disk"
1515    A$(15)="File <detection potential> <ads. potential>"
1520    A$(25)="Enter all files"
1525    A$(26)="Re-enter all files"
1530    A$(27)="Clear all files"
1535    A$(28)="Set min and max for y-axis only"
1537    A$(29)="Set min and max for x-axis only"
1540    A$(30)="Exit to main menu"
1545    A$(31)="Plot on CRT"
1550    A$(32)="Plot on printer"
1555    A$(33)="Plot on X-Y recorder"
1557    A$(34)="Curves plotted"
1558    A$(35)="Set intervals for plotting"
1559    A$(36)="Least squares calculation"
1560    PERIOD$="............................................."
1565    FOR I=1 TO 13 @ T$=A$(I) @ GOSUB 15 @ B$(I)=T1$ @ NEXT I
```

```
1570     T$=A$(15) @ GOSUB 15 @ B$(15)=T1$ @ A$(14)=A$(8) @ B$(14)=B$(8)
1575     FOR I=16 TO 24 @ A$(I)=A$(15) @ B$(I)=B$(15) @ NEXT I
1580     FOR I=25 TO 36 @ T$=A$(I) @ GOSUB 15 @ B$(I)=T1$ @ NEXT I
1585     SCRN=3 @ A1=1 @ A2=6
1590 menu: TAKE KEYBOARD @ GOSUB 30 @ PAGEFLAG=0
1595     CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$ (64+I-A1+1)&CHR$
         (41)&PERIOD$[1,4]&A$(I)&PERIOD$[1,45-LEN (A$(I))]&" "&DAT$(I) @
         NEXT I
1600     AWRITE 1,8,B$(A1) @ CRSR=1
1605     AWRITE 21,2,"Change any parameters ?" @ AWRITE 22,2,"Press the
         indicated letters or use the the '.' and ',' keys for slewing "
1610     AWRITE 23,2,"Press '4' to change any parameters or to start
         experiment "
1615     TAKE KEYBOARD
1620     KYY=NUM (KEY$ ) @ IF NOT KYY THEN 1620
1625     IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @
         CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
1630     IF KYY<> 46 THEN 1645
1635     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @
         IF CRSR<1 THEN CRSR=A2-A1+1
1640     AWRITE CRSR,8,B$(A1+CRSR-1)
1645     IF KYY<> 44 THEN 1660
1650     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @
         IF CRSR>A2-A1+1 THEN CRSR=1
1655     AWRITE CRSR,8,B$(A1+CRSR-1)
1660     IF KYY<> 52 THEN 1615
1665     IF SCRN<> 3 THEN 1690
1670     IF CRSR=1 THEN SCRN=1 @ A1=14 @ A2=29 @ GOTO 1595
1675     IF CRSR=2 THEN SCRN=2 @ A1=8 @ A2=13 @ GOTO 1595
1680     IF CRSR=3 THEN SCRN=4 @ A1=30 @ A2=36 @ GOTO 1595
1685     IF CRSR=4 THEN 565
1687     RELEASE KEYBOARD @ IF CRSR=5 THEN CHAIN "Autost" ELSE GOTO 1710
1690     PAGEFLAG=1 @ RELEASE KEYBOARD
1695     IF SCRN=1 THEN ON CRSR GOTO
         1705,200,200,200,200,200,200,200,200,200,200,270,490,435,145,138
1700     IF SCRN=2 THEN ON CRSR GOTO 1705,95,130,165,165,240 ELSE ON CRSR
         GOTO 1705,80,1615,115,3500,4300,7500
1705     TAKE KEYBOARD @ SCRN=3 @ A1=1 @ A2=6 @ GOTO 1595
1710     CLEAR @ END
1715 ! Error trap subroutine
1720     IF ERRN =71 THEN 1775
1725     IF ERRN =66 OR ERRN =12 THEN 1775
1730     IF ERRN =11 THEN menu
1735     IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 1775
1740     IF FLAG=1 AND ERRN =67 AND (DATADRIVE$="B" OR DATADRIVE$="b")
         THEN FLAG=0 @ GOTO 390
1745     IF FLAG=1 AND ERRN =67 THEN CLEAR @ DISP "Place correct disk in
         drive and press <END LINE> ," @ RELEASE KEYBOARD @ INPUT T$ @
         TAKE KEYBOARD
1750     IF ERRN =67 AND (DATADRIVE$="B" OR DATADRIVE$="b") THEN
         DRIVE$=VAL$ (ABS (VAL (DRIVE$)-1)) @ FLAG=1 @ GOTO 390
```

```
1755     IF ERRN =130 THEN BEEP 300,1000 @ RELEASE KEYBOARD @ DISP "Place
         disk in drive and then press <END LINE>" @ INPUT T$ @ TAKE
         KEYBOARD
1760     IF ERRN=130 AND ERRL=390 THEN 390
1765     IF ERRN =130 AND ERRL =860 THEN 860
1770     DISP ERRN,ERRL @ WAIT 5000
1775     RETURN
3000 xylabel:
3010 ! Beginning of labeling subroutine
3075 ! Range of characters is defined by LXSCALING and should be within
       the
3080 ! interval 100 to 600 inclusive, where the larger the number the
       smaller
3085 ! the character.
3086 ! Inputs LA$,LXSCALING
3090     RATIO=230/190 ! X/Y
3095     LYSCALING=INT (LXSCALING/LRATIO*10000)/10000
3105     IF LXSCALING>400 THEN LSPACE=2 ELSE LSPACE=1
3110     LX=-((5+LSPACE)*8.5/LXSCALING)+XIN
3112     OUTPUT 723 ;"OP 7 ";XIN;"T OP 12 50T OP 7 ";YIN;"T OP 14 50T"
3113     WAIT 500
3115     FOR LI=1 TO LEN (LA$)
3120     LT=NUM (LA$[LI,LI])
3125     IF LT=32 THEN LT=47
3130     LY=YIN
3135     LPOINT=0
3140     LX=LX+(LSPACE+5)*8.5/LXSCALING
3145     FOR LJ=1 TO 7
3150     LY=INT ((LY-7/LYSCALING)*10000)/10000
3155     LX1=LX
3160     FOR LK=1 TO 5
3165     LPOINT=LPOINT+1
3170     LX2=INT ((LX1+LK*8.5/LXSCALING)*10000)/10000
3175     IF CHAR$(LT-44)[LPOINT,LPOINT] <> "1" THEN 3200
3180     OUTPUT 723 ;"OP 7 ";LX2;"T OP 12 50T OP 7 ";LY;"T OP 14 50T"
3185     WAIT 200
3190     OUTPUT 723 ;"OP 11 100T"
3195     WAIT 200
3200     NEXT LK
3205     NEXT LJ
3210     NEXT LI
3215     RETURN
3300 filelabel:
3302 !
3305     CLEAR @ DISP "Set zero positions now!" @
         DISP "Press <END LINE> to continue"
3310     OUTPUT 723 ;"OP 7 0T OP 12 50 14 50T"
3320     KYY=NUM (KEY$ ) @ IF NOT KYY THEN 3310
3325     LXSCALING=550
3330     LA$="FILES" @ XIN=0 @ YIN=0 @ GOSUB xylabel
3340     LA$="-----" @ XIN=0 @ YIN=-.14 @ GOSUB xylabel
```

```
3345    X=1
3350    FOR I=1 TO TOTAL
3360    IF FILE$(I)="NULL" THEN 3400
3362    X=X+1
3365    LA$=UPC$ (FILE$(I))
3370    FOR J=1 TO LEN (FILE$(I))
3372    T$=FILE$(I)[J,J]
3374    IF T$="_" THEN LA$[J,J]="."
3376    NEXT J
3380    XIN=0 @ YIN=0-X*.1875
3390    GOSUB xylabel
3400    NEXT I
3450    RETURN
3500    CLEAR @ DISP "Enter number corresponding to type of curve
        plotted"
3510    AWRITE 8,20,"1) i vs. t"
3520    AWRITE 9,20,"2) i vs. 1/t"
3530    AWRITE 10,20,"3) ln(i) vs. t"
3540    AWRITE 11,20,"4) ln(i) vs. 1/t"
3550    AWRITE 12,20,"5) 1/i vs. 1/t"
3552    AWRITE 13,20,"6) ln(i) vs. ln(t)"
3600    AWRITE 20,1,"number ?" @ INPUT T$
3610    IF LEN (T$)=0 THEN 3500 ELSE TYPE=VAL (T$) @ GOTO 3630
3620    GOTO 3500
3630    IF TYPE<1 OR TYPE>6 THEN 3500
3640    ON TYPE GOSUB 3700,3705,3710,3715,3720,3725
3645    GOTO menu
3700    TYPE$="i vs. t" @ RETURN
3705    TYPE$="i vs. 1/t" @ RETURN
3710    TYPE$="ln(i) vs. t" @ RETURN
3715    TYPE$="ln(i) vs. 1/t" @ RETURN
3720    TYPE$="ln(i) vs. t" @ RETURN
3725    TYPE$="ln(i) vs. ln(t)" @ RETURN
3800    RETURN
3850    FOR J=1 TO TOTAL
3855    IF FILE$(J)="NULL" OR LOCK$(J)="*" THEN 3885
3860    FOR I=1 TO N(J)
3865    X(I,J)=1/X(I,J)
3870    NEXT I
3875    LOCK$(J)="*"
3885    NEXT J
3890    RETURN
3900    FOR J=1 TO TOTAL
3905    IF FILE$(J)="NULL" OR LOCK$(J)="*" THEN 3930
3910    FOR I=1 TO N(J)
3915    Y(I,J)=LOG (Y(I,J))
3920    NEXT I
3925    LOCK$(J)="*"
3930    NEXT J
3940    RETURN
3950    FOR J=1 TO TOTAL
```

```
3955    IF FILE$(J)="NULL" OR LOCK$(J)="*" THEN 3980
3960    FOR I=1 TO N(J)
3965    Y(I,J)=LOG (ABS (Y(I,J))) @ X(I,J)=1/X(I,J)
3970    NEXT I
3975    LOCK$(J)="*"
3980    NEXT J
3990    RETURN
4000    FOR J=1 TO TOTAL
4005    IF FILE$(J)="NULL" OR LOCK$(J)="*" THEN 4030
4010    FOR I=1 TO N(J)
4015    Y(I,J)=1/Y(I,J) @ X(I,J)=1/X(I,J)
4020    NEXT I
4025    LOCK$(J)="*"
4030    NEXT J
4035    RETURN
4050    FOR J=1 TO TOTAL
4055    IF FILE$(J)="NULL" OR LOCK$(J)="*" THEN 4090
4060    FOR I=1 TO N(J)
4065    Y(I,J)=LOG (ABS (Y(I,J))) @ X(I,J)=LOG (X(I,J))
4070    NEXT I
4080    LOCK$(J)="*"
4090    NEXT J
4095    RETURN
4300    CLEAR @ DISP "Which file" @ DISP @ DISP @ DISP
4310    FOR J=1 TO TOTAL
4320    AWRITE J+8,20,CHR$ (J+64)&")...."&FILE$(J)&" <"&
        VAL$ (LOW(J))&"> <"&VAL$ (HIGH(J))&">"
4330    NEXT J
4340    AWRITE 19,20,CHR$ (64+TOTAL+1)&")....Interval for all files"
4345    AWRITE 20,20,CHR$ (64+TOTAL+2)&")....Exit to plotting menu"
4350    AWRITE 21,1,"" @ INPUT T$
4360    IF LEN (T$)=0 THEN menu
4370    T=NUM (T$)-64 @ IF T<1 OR T>TOTAL+2 THEN 4350
4380    IF T=TOTAL+2 THEN menu
4385    IF T=TOTAL+1 THEN CLEAR @ GOTO 4510
4390    IF FILE$(T)="NULL" THEN AWRITE 21,1,"File "&CHR$ (64+T)&" does
        not exist" @ WAIT 2000 @ GOTO 4300
4410    CLEAR @ AWRITE 10,20,"" @ DISP "Enter interval for "&FILE$(T)
4420    DISP @ DISP "Enter lower bound of interval <1,upper> [1] :"
        @ INPUT T$
4430    IF LEN (T$)=0 THEN LOW(T)=1 @ GOTO 4460 ELSE LOW(T)=VAL (T$) @
        GOTO 4450
4440    GOTO 4410
4450    IF LOW(T)>N(T)-3 THEN DISP "Value to large" @ GOTO 4420
4460    DISP "Enter upper bound of interval <lower, total> [total] :" @
        INPUT T$
4470    IF LEN (T$)=0 THEN HIGH(T)=N(T) @ GOTO 4600 ELSE HIGH(T)=VAL (T$)
        @ GOTO 4490
4480    GOTO 4460
4490    IF HIGH(T)<1 OR HIGH(T)<LOW(T) THEN 4460
4500    GOTO 4300
```

```
4510     CLEAR @ DISP @
         DISP "Enter lower bound of interval <1,upper> [1] :" @ INPUT T$
4520     IF LEN (T$)=0 THEN LOW=1 @ GOTO 4530 ELSE LOW=VAL (T$) @
         GOTO 4530
4525     GOTO 4510
4530     DISP "Enter upper bound of interval <lower, total> [total] :" @
         INPUT T$
4540     IF LEN (T$)=0 THEN HIGH=N(1) @ GOTO 4550 ELSE HIGH=VAL (T$) @
         GOTO 4550
4545     GOTO 4530
4550     FOR J=1 TO TOTAL
4560     IF FILE$(J) <> "NULL" THEN LOW(J)=LOW @ HIGH(J)=HIGH
4570     NEXT J
4600     GOTO 4300
7500     CLEAR @ DISP "Which file" @ DISP @ DISP @ DISP
7510     FOR J=1 TO TOTAL
7520     AWRITE J+8,20,CHR$ (J+64)&")...."&FILE$(J)
7530     NEXT J
7540     AWRITE 19,20,CHR$ (64+TOTAL+1)&")...."&"Exit to plotting menu"
7550     AWRITE 20,1,"File" @ INPUT T$
7560     IF LEN (T$)=0 THEN menu
7570     T=NUM (T$)-64 @ IF T<1 OR T>TOTAL+1 THEN 7550
7580     IF T=TOTAL+1 THEN menu
7590     IF FILE$(T)="NULL" THEN AWRITE 21,2,"File "&CHR$ (64+T)&" does
         not exist" @ WAIT 2000 @ GOTO 7550
7600     GOSUB lesstsquares
7610     GOTO 7500
7999 !
8000 leastsquares:  ! Linear least squares subroutine
8001 !
8005     CLEAR @ AWRITE 10,22,"Least squares calculation" @ AWRITE 11,1,""
8007     DISP @ DISP
8010     SUMX,SUMY,SUMXSQRD,SUMYSQRD,SUMXY,VARIANCE=0
8020     FOR I=LOW(T) TO HIGH(T)
8030     SUMX=SUMX+X(I,T) @ SUMY=SUMY+Y(I,T) @ SUMXSQRD=SUMXSQRD+X(I,T)^2
         @ SUMYSQRD=SUMYSQRD+Y(I,T)^2 @ SUMXY=SUMXY+X(I,T)*Y(I,T)
8040     NEXT I
8045     N=HIGH(T)-LOW(T)+1
8050     CONSTANT=N*SUMXSQRD-SUMX^2 @ SLOPE=(N*SUMXY-SUMX*SUMY)/CONSTANT @
         INTERCEPT=(SUMXSQRD*SUMY-SUMX*SUMXY)/CONSTANT
8060     FOR I=LOW(T) TO HIGH(T) @
         VARIANCE=VARIANCE+(Y(I,T)-INTERCEPT-SLOPE*X(I,T))^2 @ NEXT I
8070     VARIANCE=VARIANCE/(N-2)
8080     SLOPESDERR=SQR (N*VARIANCE/CONSTANT)
8090     INTERCEPTSDERR=SQR (VARIANCE/N*(1+SUMX^2/CONSTANT))
8100     CORRCOEFF=SQR (SLOPE*((SUMXY-SUMX*SUMY/N)/(SUMYSQRD-SUMY^2/N)))
8110     DISP "CORRELATION COEFFICIENT = ";VAL$ (CORRCOEFF)
8120     DISP "SLOPE = ":SLOPE @ DISP " Y-INTERCEPT = ";INTERCEPT
8130     DISP "SD ERROR IN SLOPE IS = ";SLOPESDERR
8140     DISP "SD ERROR IN Y-INTERCEPY = ";INTERCEPTSDERR
8150     DISP @ DISP @ DISP "Press <END LINE> to continue ," @ INPUT T$
8200     RETURN
```

5. Staircase

```
10      GOTO beginning
20      OUTPUT 723 ;"OP 13 ";ROT(ROT);"T" @ RETURN
30 !
40 !
50 experiment:
60 !
70      CLEAR @ AWRITE 10,36,"Working"
80      GOSUB calculate
90      GRAPHALL
100     CSIZE 4 @ FXD 0,4 @ LINE TYPE 1
110     MAXY=10 @ MINY=-10 @ X$=CHR$ (46)
120 !
130 experiment1:
140 !
150     CLEAR 723 @ WAIT 4000 @ SCALE E2,E3,MINY,MAXY @ COUNTER=1
160     GOSUB 20 @ XX=E2-(E2-E3)/2 @ YY=MINY+(MAXY-MINY)/20
170     FRAME @ AXES -.2,(MAXY-MINY)/2,0,0,2,1,3 @ I=1 @ SCANS=0 @ T3=T1
        @ TSCANS=0
180     OUTPUT 723 ;"OP 7 ";VOLT(I);"T OP 12 ";T3;"T OP 14 .03 12 18T IP
        4T"
190     SEND 7 ; UNL MLA TALK 23 SCG 1
200     ENTER 7 ; Y(I)
210     MOVE VOLT(I),-Y(I) @ LABEL X$
220     IF I<> N THEN I=I+1 @ GOTO 180
230     SCANS=SCANS+1 @ TSCANS=TSCANS+1 @ MOVE XX,YY @ PEN -1 @ LABEL
        VAL$ (TSCANS-1) @ MOVE XX,YY @ PEN 1 @ LABEL VAL$ (TSCANS)
240     IF TSCANS=TOTALSCANS THEN SCANFLAG=1 @ GOSUB calculation @
        SCANFLAG=0 @ ROT=ROTMIN @ GOSUB 20 @ GOTO menu
250     IF SCANS=INTSCAN THEN SCANFLAG=1 @ GOSUB calculation @ SCANFLAG=0
        ELSE I=1 @ GOTO 180
260     COUNTER=COUNTER+1 @ SCANS=0
270 !
280     ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN @ GOSUB 20 @ GOTO 300
        ELSE GOSUB 20 @ I=1 @  GOTO 180
290 !
300     IF T2=T1 THEN I=1 @ GOTO 180
310     T3=T3*INCTIME @ IF T3>T2 THEN ROT=ROTMIN @ GOSUB 20 @ GOTO menu
        ELSE I=1 @ GOTO 180
320 !
330 calculation:
340 !
350     FOR I=1 TO N
360     Y(I)=-(Y(I)/10*ADVOLTAGE*I_RANGE/V_RANGE)
370     NEXT I
38" @ INPUT T$ @ IF LEN (T$)=0 THEN DSPCRT$="YES" @  GOTO 90
85      IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPCRT$="YES" ELSE
        DSPCRT$="NO"
90      GOTO menu
```

```
95       CLEAR @ DISP "Store graph on disk <Y/N> [Y]:" @ INPUT T$
100      IF LEN (T$)=0 THEN DSPFLAG$="YES"
105      IF T$[1,1]="N" OR T$[1,1]="n" THEN DSPFLAG$="NO" ELSE
         DSPFLAG$="YES"
110      GOTO menu
115      CLEAR @ DISP "Plot on X-Y recorder <Y/N> [N] :" @ INPUT T$ @
         IF LEN (T$)=0 THEN DSPXY$ ="NO" @ GOTO 125
120      IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPXY$="YES" ELSE DSPINY,MAXY
560      FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
570      LAXES -((MAXX-MINX)/50),(MAXY-MINY)/4/5,0,0,10,5,3
580      MOVE MINX,MINY
590      LORG 4 @ X$=CHR$ (46)
600      FOR I=LOW TO HIGH
610      MOVE VOLT(I),Y(I)
620      LABEL X$
630      NEXT I
640      CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
650      LABEL I_TYPE$&"amps"
660      LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "volts (V)"
670 !
680 ! Store data on disk
690 !
700      IF FIGSTORE$="Y" THEN GSTORE FILE$&":D70"&VAL$ (FIGUREDRIVE) @
         GOTO 730 ELSE 730
710      GSTORE FILE$&"D70"&VAL$ (FIGUREDRIVE)
720 !
730 storedata:
740 !
750      IF DATASTORE$="Y" THEN 760 ELSE 850
760      DD$=DATAFILE$&VAL$ (COUNTER)&":D70"&VAL$ (DATADRIVE)
770      PURGE DD$ @ GOTO 780
780      CREATE DD$,20+N*2,10
790      ASSIGN# 1 TO DD$
800      PRINT# 1 ; E1,E2,E3,E4,T1,T2,I_RANGE
810      PRINT# 1 ; I_TYPE$[1,5],INCTIME,0,"NULL"
820      PRINT# 1 ; N,V_RANGE,ADVOLTAGE,INTSCAN,TOTALSCANS,0,0,0,0
830      FOR I=1 TO N @ PRINT# 1 ; VOLT(I),Y(I) @ NEXT I
840      ASSIGN# 1 TO *
850      IF SCANFLAG=1 THEN RETURN
860      IF PLOTCRT$="N" THEN 870 ELSE RELEASE KEYBOARD @ INPUT T$ @
         ALPHALL
870      GOSUB xyplot
880      GOTO menu
890 !
900 ! inputs
910 !
920      CLEAR @ DISP "Enter the beginning potential <-10,+10> [0.2] :" @
         INPUT T$
930      IF LEN (T$)=0 THEN E1=.2 @ GOTO 950 ELSE E1=VAL (T$) @ GOTO 950
940      GOTO 920
950      IF E1<-10 OR E1>10 THEN 920
```

```
960     IF FLAG=1 THEN RETURN
970     GOTO menu
980 !
990     CLEAR @ DISP "Enter the anodic potential limit <-10,+10> [1.3] :"
1000    INPUT T$ @ IF LEN (T$)=0 THEN E2=1.3 @ GOTO 1020 ELSE E2=VAL (T$)
        @ GOTO 1020
1010    GOTO 990
1020    IF E2<-10 OR E2>10 THEN 990
1030    IF E2<E3 THEN 990
1040    IF FLAG=1 THEN RETURN
1050    GOTO menu
1060 !
1070    CLEAR @ DISP "Enter the cathodic potential limit <-10,10> [-0.25]
        :"
1080    INPUT T$ @ IF LEN (T$)=0 THEN E3=-.25 @ GOTO 1100 ELSE
        E3=VAL (T$) @ GOTO 1100
1090    GOTO 1070
1100    IF E3<-10 OR E3>10 THEN 1070
1110    IF E3>E2 THEN 1070
1120    IF FLAG=1 THEN RETURN
1130    GOTO menu
1140 !
1150    CLEAR @ DISP "Enter the beginning current sampling delay time
        <0.001, 600000 msec> [0 .001] :" @ INPUT T$
1160    IF LEN (T$)=0 THEN T1=.001 @ GOTO 1180 ELSE T1=VAL (T$) @ GOTO
        1180
1170    GOTO 1150
1180    IF T1=0 THEN T1=.001
1190    IF T1<.001 OR T1>600000 THEN 1150
1200    GOTO menu
1210 !
1220 !
1230    CLEAR @
        DISP "Enter the data file name <7 characters> [DTESTSC] :"
1240    INPUT T$ @ IF LEN (T$)=0 THEN DATAFILE$="DTESTSC" ELSE
        DATAFILE$=T$
1250    IF LEN (T$)<8 OR DATAFILE$="DTESTSC" THEN 1300
1260    DISP @ DISP @ DISP "File name is longer than 7 characters."
1270    DISP "Do you wish to change it?  <Y,N> [N] :" @ INPUT T$
1280    IF LEN (T$)=0 THEN menu
1290    IF LEN (T$)<> 0 AND (T$[1,1]="Y" OR T$[1,1]="y") THEN 1230
1300    GOTO menu
1310 !
1320    CLEAR @
        DISP "Enter the figure file name <10 characters> [TEST_ SC] ,"
1330    INPUT T$ @ IF LEN (T$)=0 THEN FIGUREFILE$="TEST_SC" ELSE
        FIGUREFILE$=T$
1340    IF LEN (T$)<11 OR FIGUREFILE$="TEST_SC" THEN 1390
1350    DISP @ DISP @ DISP "File name ";T$; is longer than 10
        characters."
1360    DISP "Do you wish to change it?  <Y,N> [N] :" @ INPUT T$
```

```
1370    IF LEN (T$)=0 THEN menu
1380    IF LEN (T$)<> 0 AND (T$[1,1]="Y" OR T$[1,1]="y") THEN 1320
1390    GOTO menu
1400 !
1410    IF DATADRIVE=0 THEN DATADRIVE=1 ELSE DATADRIVE=0
1420    GOTO menu
1430 !
1440    IF FIGUREDRIVE=0 THEN FIGUREDRIVE=1 ELSE FIGUREDRIVE=0
1450    GOTO menu
1460 !
1470    IF DATASTORE$="Y" THEN DATASTORE$="N" ELSE DATASTORE$="Y"
1480    GOTO menu
1490 !
1500    IF FIGSTORE$="Y" THEN FIGSTORE$="N" ELSE FIGSTORE$="Y"
1510    GOTO menu
1520 !
1530    CLEAR @ DISP "Enter the drive number <0,1> [1] :" @ INPUT T$
1540    IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 1560 ELSE DRIVE=VAL (T$) @ GOTO
        1560
1550    GOTO 1530
1560    IF DRIVE=0 OR DRIVE=1 THEN 1570 ELSE 1530
1570    CAT ":D70"&VAL$ (DRIVE)
1580    DISP "Press <END LINE> to continue:" @ INPUT T$
1590    GOTO menu
1600 !
1610    IF PLOTFIG$="Y" THEN PLOTFIG$="N" ELSE PLOTFIG$="Y"
1620    GOTO menu
1630 !
1640    CLEAR @ DISP "Enter the potential increment, dE, <-10,+10> [0.01]
        :"
1650    INPUT T$ @ IF LEN (T$)=0 THEN E4=.01 @ GOTO 1670 ELSE E4=VAL (T$)
        @ GOTO 1670
1660    GOTO 1640
1670    IF E4<-10 OR E4>10 THEN 1640
1680    IF FLAG=1 THEN RETURN
1690    GOTO menu
1700 !
1710    CLEAR @ DISP "Enter the cathodic cleaning time <0,600000 msec>
        [200] :"
1720    INPUT T$ @ IF LEN (T$)=0 THEN T3=200 @ GOTO 1740 ELSE T3=VAL (T$)
        @ GOTO 1740
1730    GOTO 1710
1740    IF T3<0 OR T3>600000 THEN 1710
1750    IF T3=0 THEN T3=.001
1760    GOTO menu
1770 !
1780    IF AXIS$="Y" THEN AXIS$="N" ELSE AXIS$="Y"
1790    GOTO menu
1800 !
1810    CLEAR @ DISP "Enter the minimum on Y <-50,max Y> [0] :" @
        INPUT T$
```

```
1820    IF LEN (T$)=0 THEN YMIN=0 @ GOTO 1840 ELSE YMIN=VAL (T$) @
        GOTO 1840
1830    GOTO 1810
1840    IF YMIN<-50 OR YMIN>50 THEN 1810
1850    DISP @ DISP @ DISP @
        DISP "Enter the maximum on Y <min Y, 50> [0] :"
1860    INPUT T$ @ IF LEN (T$)=0 THEN YMAX=0 @
        GOTO 1880 ELSE YMAX=VAL (T$) @ GOTO 1880
1870    GOTO 1850
1880    IF YMAX<YMIN OR YMAX>50 THEN 1850
1890    GOTO menu
1900    CLEAR @ DISP "Enter the current range <0.02, 10> [1] :" @ INPUT
        T$
1910    IF LEN (T$)=0 THEN I_RANGE=1 @ GOTO 1930 ELSE I_RANGE=VAL (T$) @
        GOTO 1930
1920    GOTO 1900
1930    IF I_RANGE<.02 OR I_RANGE>10 THEN 1900
1940    DISP @ DISP
1950    DISP "Enter the scale <milliamps (m,M), microamps (u,U)> [M] :" @
        INPUT T$
1960    IF LEN (T$)=0 THEN I_TYPE$="milli" @ GOTO 1990 ELSE I_TYPE$=T$
1970    IF T$[1,1]="M" OR T$[1,1]="m" THEN I_TYPE$="milli" @ GOTO 1990
1980    IF T$[1,1]="U" OR T$[1,1]="u" THEN I_TYPE$="micro" @ GOTO 1990
        ELSE 1950
1990    DISP @ DISP @ DISP I_RANGE;" ";I_TYPE$;"amps, per what voltage
        range <1,100> [10] :" @ INPUT T$
2000    IF LEN (T$)=0 THEN V_RANGE=10 @ GOTO 2020 ELSE V_RANGE=VAL (T$) @
        GOTO 2020
2010    GOTO 1990
2020    IF V_RANGE<1 OR V_RANGE>100 THEN 1990
2030    IF FLAG=1 THEN RETURN
2040    GOTO menu
2050    CLEAR @ DISP "Enter the minimum on X <-50,max X> [0] :" @
        INPUT T$
2060    IF LEN (T$)=0 THEN XMIN=0 @ GOTO 2080 ELSE XMIN=VAL (T$) @
        GOTO 2080
2070    GOTO 2050
2080    IF XMIN<-50 OR XMIN>50 THEN 2050
2090    DISP @ DISP @ DISP @
        DISP "Enter the maximum on X <min X, 50> [0] :"
2100    INPUT T$ @ IF LEN (T$)=0 THEN XMAX=0 @ GOTO 2120 ELSE XMAX=VAL
        (T$) @ GOTO 2120
2110    GOTO 2090
2120    IF XMAX<XMIN OR XMAX>50 THEN 2090
2130    GOTO menu
2140 !
2150    IF ZPRINT$="NO" THEN ZPRINT$="YES" @ PRINTER IS 705,90 ELSE
        ZPRINT$="NO" @ PRINTER IS 1
2160    GOTO menu
2170 !
2180    IF PLOTCRT$="Y" THEN PLOTCRT$="N" ELSE PLOTCRT$="Y"
```

```
2190     GOTO menu
2200 !
2210     IF PLOTXY$="Y" THEN PLOTXY$="N" ELSE PLOTXY$="Y"
2220     GOTO menu
2230 !
2240     CLEAR @ DISP "Enter the A/D voltage range <1 & 10 only> [10] :" @
         INPUT T$
2250     IF LEN (T$)=0 THEN ADVOLTAGE=10 @
         GOTO 2270 ELSE ADVOLTAGE=VAL  (T$) @ GOTO 2270
2260     GOTO 2240
2270     IF ADVOLTAGE=1 OR ADVOLTAGE=10 THEN 2280 ELSE 2240
2280     GOTO menu
2290 calculate:
2300     N=INT (ABS ((E2-E1)/E4)+ABS ((E2-E3)/E4)+ABS ((E1-E3)/E4))+1
2310     VOLT(0)=E1-E4
2320     FOR I=1 TO N
2330     VOLT(I)=VOLT(I-1)+E4
2340     IF VOLT(I)>E2 THEN E4=-E4 @ VOLT(I)=VOLT(I)+2*E4
2350     IF VOLT(I)<E3 THEN E4=-E4 @ VOLT(I)=VOLT(I)+2*E4
2360     NEXT I
2370     RETURN
2380     CLEAR @ DISP "Enter the ending current sampling delay time <0.001
         ,600000 msec> [0.00 1] :" @ INPUT T$
2390     IF LEN (T$)=0 THEN T2=.001 @ GOTO 2410 ELSE T2=VAL (T$) @
         GOTO 2410
2400     GOTO 2380 .
2410     IF T2=0 THEN T2=.001
2420     IF T2<.001 OR T2>600000 THEN 2380
2430     GOTO menu
2440     CLEAR @ DISP "Enter the current sampling multiplicative factor
         <0.0001 ,100000 msec> [1] :" @ INPUT T$
2450     IF LEN (T$)=0 THEN INCTIME=1 @ GOTO 2470 ELSE INCTIME=VAL (T$) @
         GOTO 2470
2460     GOTO 2440
2470     IF INCTIME<.0001 OR INCTIME>100000 THEN 2440
2480     GOTO menu
2490     CLEAR @ DISP "Enter the number of scans per file <1,total
         scans--> [1] ""
2500     INPUT T$ @ IF LEN (T$)=0 THEN INTSCAN=1 @ GOTO 2520 ELSE
         INTSCAN=VAL (T$) @ GOTO 2520
2510     GOTO 2490
2520     IF INTSCAN<1 OR INTSCAN>TOTALSCANS THEN 2490
2530     GOTO menu
2540     CLEAR @ DISP "Enter the total number of scans <1,--> [100] :"

2550     INPUT T$ @ IF LEN (T$)=0 THEN TOTALSCANS=100 @ GOTO 2570
         ELSE TOTALSCANS=VAL (T$) @ GOTO 2570
2560     GOTO 2540
2570     IF TOTALSCANS<1 THEN 2540
2580     GOTO menu
2590     CLEAR @ AWRITE 1,0,"Rotation speed(s) -- e.g., 1,2,3... , 1-5, *
```

```
          for all"
2600      FOR I=1 TO 10 @ AWRITE I+7,12,VAL$ (I)&")"&PERIOD$[1,5-LEN (VAL$
          (I))]&ROT$(I)&ROT1$(I) @ NEXT I
2610      FOR I=1 TO 7 @ AWRITE I+7,30,VAL$
          (I+10)&")"&PERIOD$[1,3]&ROT$(I+10)&ROT1$(I+10) @ NEXT I
2620      AWRITE 20,2," @ LINPUT CODE$ @ IF LEN (CODE$)=0 THEN menu
2630      GOSUB decode @ IF error=1 THEN 2590
2640      FOR I=1 TO 17 @ ROT1$(I)=" @ IF CODE(I)<> 0 THEN ROT1$(I)="*"
2650      NEXT I @ J=1
2660      FOR I=1 TO 17 @ IF ROT1$(I)="*" THEN ROT(J)=ROT2(I) @ J=J+1
2670      NEXT I
2680      ROTMAX=J-1 @ IF ROTMAX=0 THEN ROTMIN=0 @ ROT=0 ELSE ROTMIN=1 @
          ROT=1
2690      GOTO 2590
2700 !
2710 beginning:
2720 !
2730      CLEAR
2740      DIM Y(1000),VOLT(1000),SMTHDATA(300)
2750      DIM A$(40)[50],B$(40)[50],FILE$[15],FILE2$[15],DAT$(40)[30]
2760      DIM
          T$[50],T1$[50],PERIOD$[50],DATADRIVE$[5],GRAPHDRIVE$[5],DRIVE$[5]
2770      DIM DSPFLAG$[3],DSPCRT$[3],AXIS$[3],PLOTCRT$[3],PLOTXY$[3]
2780      DIM CODE(20),ROT(20),ROT2(20),ROT1$(20)[1],ROT$(20)[4]
2790      ON ERROR GOSUB 4140 @ AWRITE 0,0
2800      FOR I=1 TO 10 @ ROT$(I)=VAL$ (I*500) @ ROT1$(I),ROT1$(I+10)="" @
          NEXT I
2810      ROT$(3)="1400" @ FOR I=10 TO 70 STEP 10 @
          ROT$(I/10+10)=VAL$ (I^ 2) @ NEXT I
2820      FOR I=1 TO 17 @ READ T @ ROT2(I)=T @ ROT(I)=0 @ NEXT I
2830      DATADRIVE=1 @ FIGUREDRIVE=1 @ DATAFILE$="DTESTSC" @
          FIGUREFILE$="TEST_SC"
2840      E1=.2 @ E2=1.3 @ E3=-.25 @ E4=.01 @ T1=.001 @ DATASTORE$="Y" @
          FIGSTORE$="N"
2850      PLOTFIG$="Y" @ I_RANGE=1 @ I_TYPE$="milli" @ FLAG=0 @ YMIN,YMAX=0
2860      XMIN,XMAX=0 @ PLOTCRT$="Y" @ PLOTXY$="N" @ AXIS$="Y" @ V_RANGE=10
2870      DRIVE=1 @ ADVOLTAGE=10 @ INCTIME=1 @ T2=T1 @ SCANFLAG=0 @
          INTSCAN=1
2880      TOTALSCANS=100 @ ROT,ROT(0),ROTMAX,ROTMIN=0 @ ZPRINT$="NO" @
          PRINTER IS 1
2890      TAKE KEYBOARD @ GOSUB 3770
2900      A$(1)="Experimental directory"
2910      A$(2)="Mass storage directory"
2920      A$(3)="Plotting directory"
2930      A$(4)="Begin experiment"
2940      A$(5)="Chain Autost"
2950      A$(6)="End program"
2960      A$(7)="NULL"
2970      A$(8)="Exit to main menu"
2980      A$(9)="Beginning potential, E1"
2990      A$(10)="Anodic limit, E2"
```

```
3000     A$(11)="Catbodic limit, E3"
3010     A$(12)="Potential increment,E"
3020     A$(13)="Beginning sampling delay time (msec), T1 **"
3030     A$(14)="Ending sampling delay time (msec), T2 **"
3040     A$(15)="Sampling delay time factor **"
3050     A$(16)="Current range and scale"
3060     A$(17)="A/D voltage range"
3070     A$(18)="Total number of scans"
3080     A$(19)="Interval of scans for storage"
3090     A$(20)="Min and Max on Y, only"
3100     A$(21)="Min and Max on X, only"
3110     A$(22)="Rotation speeds *"
3120     A$(23)="NULL"
3130     A$(24)="Exit to main menu"
3140     A$(25)="Data file name"
3150     A$(26)="Figure file name"
3160     A$(27)="Data file drive number"
3170     A$(28)="Figure file drive number"
3180     A$(29)="Store data on disk"
3190     A$(30)="Store figure on disk"
3200     A$(31)="Catalog of disk"
3210     A$(32)="NULL"
3220     A$(33)="Exit to main menu"
3230     A$(34)="Plot raw data curve"
3240     A$(35)="Plot on CRT"
3270     A$(38)="Activate printer"
3280     PERIOD$="................................................"
3290     FOR I=1 TO 38 @ T$=A$(I) @ GOSUB 3580 @ B$(I)=T1$ @ NEXT I
3300     SCRN=1 @ A1=1 @ A2=6
3310 menu: TAKE KEYBOARD @ GOSUB 3600 @ PAGEFLAG=0
3320     CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$ (64+I-A1+1)&CHR$
         (41)&PERIOD$[1,4]&A$(I)&PERIOD$[1,48-LEN (A$(I))]&" "&DAT$(I) @
         NEXT I
3330     AWRITE 1,8,B$(A1) @ CRSR=1
3340     AWRITE 21,2,"Change any parameters ?" @ AWRITE 22,2,"Press the
         indicated letters or use the '.' and ',' keys for slewing :"
3350     AWRITE 23,2,"Press '4' to change any parameters or to start
         experiment "
3360     AWRITE 24,2,"Asterisks indicate precedence, * being the highest"
3370     TAKE KEYBOARD
3380     KYY=NUM (KEY$ ) @ IF NOT KYY THEN 3380
3390     IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @
         CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
3400     IF KYY<> 46 THEN 3430

3410     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
         CRSR=A2-A1+1
3420     AWRITE CRSR,8,B$(A1+CRSR-1)
3430     IF KYY<> 44 THEN 3460
3440     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @
         IF CRSR>A2-A1+1 THEN CRSR=1
```

```
3450    AWRITE CRSR,8,B$(A1+CRSR-1)
3460    IF KYY<> 52 THEN 3370
3470    IF SCRN<> 1 THEN 3530
3480    IF CRSR=1 THEN SCRN=2 @ A1=8 @ A2=22 @ GOTO 3320
3490    IF CRSR=2 THEN SCRN=3 @ A1=24 @ A2=31 @ GOTO 3320
3500    IF CRSR=3 THEN SCRN=4 @ A1=33 @ A2=38 @ GOTO 3320
3510    IF CRSR=5 THEN RELEASE KEYBOARD @ CHAIN "Autost"
3520    IF CRSR=4 THEN experiment ELSE RELEASE KEYBOARD @ GOTO 3570
3530    PAGEFLAG=1 @ RELEASE KEYBOARD
3540    IF SCRN=2 THEN ON CRSR GOTO
        3560,920,990,1070,1640,1150,2380,2440,1900,2240,2540,2490
        ,1810,2050,2590
3550    IF SCRN=3 THEN ON CRSR GOTO
        3560,1230,1320,1410,1440,1470,1500,1530 ELSE ON CRSR GOTO
        3560,1610,2180,2210,1780,2150
3560    TAKE KEYBOARD @ SCRN=1 @ A1=1 @ A2=6 @ GOTO 3320
3570    CLEAR @ END
3580    T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128)
        @ NEXT L
3590    RETURN
3600    DAT$(1)="" @ DAT$(2)="" @ DAT$(3)="" @ DAT$(4)="" @ DAT$(5)=""
3610    DAT$(6)="" @ DAT$(7)="" @ DAT$(8)=""
3620    DAT$(9)=VAL$ (E1) @ DAT$(10)=VAL$ (E2) @ DAT$(11)=VAL$ (E3)
3630    DAT$(12)=VAL$ (E4) @ DAT$(13)=VAL$ (T1) @ DAT$(14)=VAL$ (T2)
3640    DAT$(15)=VAL$ (INCTIME) @ DAT$(17)=VAL$ (ADVOLTAGE)
3650    DAT$(16)=VAL$ (I_RANGE)&" "&I_TYPE$[1,5]&"amps/"&
        VAL$ (V_RANGE)&" V"
3660    DAT$(17)=VAL$ (ADVOLTAGE)
3670    DAT$(18)=VAL$ (TOTALSCANS) @ DAT$(19)=VAL$ (INTSCAN)
3680    DAT$(20)=VAL$ (YMIN)&" , "&VAL$ (YMAX)
3690    DAT$(21)=VAL$ (XMIN)&" , "&VAL$ (XMAX)
3700    DAT$(22),DAT$(23),DAT$(24)="" @ DAT$(25)=DATAFILE$
3710    DAT$(26)=FIGUREFILE$ @ DAT$(27)=VAL$ (DATADRIVE)
3720    DAT$(28)=VAL$ (FIGUREDRIVE) @ DAT$(29)=DATASTORE$ @
        DAT$(30)=FIGSTORE$
3730    DAT$(31)=VAL$ (DRIVE) @ DAT$(32)="" @ DAT$(33)="" @
        DAT$(34)=PLOTFIG$
3740    DAT$(35)=PLOTCRT$ @ DAT$(36)=PLOTXY$ @ DAT$(37)=AXIS$ @
        DAT$(38)=ZPRINT$
3750    RETURN
3760    !
3770    ON KEY# 1 GOTO 3920
3780    ON KEY# 2 GOTO 3930
3790    ON KEY# 3 GOTO 3940
3800    ON KEY# 4 GOTO 3950
3810    ON KEY# 5 GOTO 3970
3820    ON KEY# 6 GOTO 3990
3830    ON KEY# 7 GOTO 4010
3840    ON KEY# 8 GOTO 4020
3850    ON KEY# 9 GOTO 4040
3860    ON KEY# 10 GOSUB 4060
```

```
3870     ON KEY# 11 GOSUB 4080
3880     ON KEY# 12 GOSUB 4100
3890     ON KEY# 13 GOSUB 4120
3900     ON KEY# 14 GOSUB 4130
3910     RETURN
3920     ALPHALL @ GOTO menu
3930     GOTO calculation
3940     MAXY=MAXY/2 @ MINY=MINY/2 @ GCLEAR @ GOTO experiment1
3950     MAXY=MAXY*2 @ MINY=MINY*2
3960     GCLEAR @ GOTO experiment1
3970     ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1900
3980     TAKE KEYBOARD @ FLAG=0 @ GRAPHALL @ GOTO experiment1
3990     ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1640
4000     TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @ I=1 @
         GOTO experiment1
4010     GCLEAR @ GOTO experiment1
4020     ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 920
4030     TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @
         GOTO experiment1
4040     ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 990
4050     TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @
         GOTO experiment1
4060     ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1070
4070     TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @
         GOTO experiment1
4080     ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1470
4090     TAKE KEYBOARD @ FLAG=0 @ GRAPHALL @ GOTO experiment1
4100     ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=1
4110     OUTPUT 723 ;"OP 13 ";ROT(ROT);"T" @ RETURN
4120     OUTPUT 723 ;"OP 13 OT" @ RETURN
4130     PRINT CHR$ (12) @ FOR K=1 TO 37 @ PRINT CHR$ (64+K)&CHR$
         (41)&PERIOD$[1,4]&A$(K)&PERIOD$[1,45-LEN (A$(K))]&" "&DAT$(K) @
         NEXT K @ PRINT CHR$ (12) @ RETURN
4140   ! Error trap subroutine
4150     IF ERRN =67 OR ERRN =66 THEN 4200
4160     IF ERRN =11 THEN menu
4170     IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 4200
4180     IF ERRN =130 THEN BEEP 300,1000 @ RELEASE KEYBOARD @ DISP "Place
         disk in drive and then press <END LINE>" @ INPUT T$ @ TAKE
         KEYBOARD @ GOTO 4200
4190     DISP ERRN ,ERRL @ WAIT 2000
4200     RETURN
4210     END
4220 xyplot:
4230     IF PLOTXY$="N" THEN 4640
4240 !
4250 ! Mechanical plotting routine
4260 !
4270     RELEASE KEYBOARD
4280     CLEAR @ DISP "Press <END LINE> if all hardware is properly
         connected :"
```

```
4290    INPUT T$ @ TAKE KEYBOARD
4300    XSCALE=8.5 @ YSCALE=7
4310    XSCALING=XSCALE/(ABS (MAXX)+ABS (MINX))
4320    YSCALING=YSCALE/(ABS (MAXY)+ABS (MINY))
4330    XCENTER=MAXX-(MAXX-MINX)/2
4340    YCENTER=MAXY-(MAXY-MINY)/2
4350    OUTPUT 723 ;"GP"
4360    TAKE KEYBOARD
4370    CLEAR @ DISP "Set zero positions now !" @
        DISP "Press <END LINE> to continue"
4380    OUTPUT 723 ;"OP 7 0T OP 12 50T OP 14 50T"
4390    KYY=NUM (KEY$ ) @ IF NOT KYY THEN 4380
4400    WAIT 1000
4410    IF AXIS$="N" THEN 4560
4420    X=8.5-(-(XCENTER*XSCALING)+XSCALE/2)
4430    OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 0T OP 14 50T"
4440    WAIT 2000
4450    OUTPUT 723 ;"OP 7 7.0T OP 11 1500 14 50T WA .2T OP 7 ";X;"T OP 12
        50T"
4460    OUTPUT 723 ;"OP 7 0.0T OP 11 1500 14 50T"
4470    WAIT 3100
4480    Y=-(YCENTER*YSCALING)+YSCALE/2
4490    OUTPUT 723 ;"OP 7 ";Y;"T OP 14 50T OP 7 ";0;"T OP 12 50T"
4500    WAIT 750
4510    OUTPUT 723 ;"OP 7 8.5T OP 11 1500 12 50T WA .2T OP 7 ";Y;"T OP
        14 50T"
4520    OUTPUT 723 ;"OP 7 0.0T OP 11 1500 12 50T"
4530    WAIT 3100
4540    Y=INT (Y*10000)/10000 @ X=INT (X*10000)/10000
4550    WAIT 1000
4560 !
4570    FOR I=LOW TO HIGH
4580    X=8.5-(VOLT(I)*XSCALING-XCENTER*XSCALING+XSCALE/2)
4590    Y=Y(I)*YSCALING-YCENTER*YSCALING+3.5
4600    OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
4610    IF I=LOW THEN WAIT 500 ELSE WAIT 150
4620    OUTPUT 723 ;"OP 11 100T"
4630    NEXT I
4640    RETURN
4650 !
4660 decode:
4670 !
4680    ON ERROR GOTO error3 @ error=0 @ FOR I=1 TO 20 @ CODE(I)=0 @
        NEXT I

4690    FOR I=1 TO LEN (CODE$) @ IF CODE$[1,1]=CHR$ (32) THEN
        CODE$=CODE$[2,LEN (CODE$)] @ GOTO 4690
4700    IF CODE$[1,1] <> "*" THEN 4720
4710    FOR I=1 TO 100 @ CODE(I)=1 @ NEXT I @ GOTO 4830
4720    T$="1"
4730    FOR I=0 TO 9 @ IF CODE$[1,1]=VAL$ (I) THEN T$=""1"
```

```
4740     NEXT I @ IF T$ <> VAL$ (-1) THEN CODE$=CODE$[2,LEN (CODE$)]
         ELSE 4760
4750     IF LEN (CODE$)=0 THEN error3 ELSE 4730
4760     T=VAL (CODE$) @ IF T<0 OR T>99 THEN error2 ELSE CODE(T)=1
4770     IF LEN (VAL$ (T))=LEN (CODE$) THEN 4830
4780     CODE$=CODE$[1+LEN (VAL$ (T)),LEN (CODE$)] @ IF LEN (CODE$)=0 THEN
         CODE(T)=1 @ GOTO 4830
4790     T$=CODE$[1,1] @ CODE$=CODE$[2,LEN (CODE$)] @ IF T$="," OR T$="-"
         THEN 4800 ELSE error1
4800     t1=VAL (CODE$) @ IF t1<0 OR t1>99 THEN T=t1 @ GOTO error2
4810     IF T$="," THEN CODE(t1)=1 @ GOTO 4760
4820     FOR I=T+1 TO t1 @ CODE(I)=1 @ NEXT I @ GOTO 4760
4830     ON ERROR GOSUB 4140 @ RETURN
4840 !
4850 error1: error=1
4860     DISP "Character ";T$;" not allowed." @ DISP @
         DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
4870 !
4880 error2: error=1
4890     DISP "The value ";T;" is to large." @ DISP @
         DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
4900 !
4910 error3: error=1
4920     DISP "String does not follow syntax." @ DISP @
         DISP "Press <END LINE> to continue." @  INPUT T$ @ RETURN
4930     DATA
         48,80,112,160,256,304,336,560,576,1040,16,32,64,128,256,512,1024
```

6. Staircase Plot

```
10      GOTO beginning
20      FOR I=1 TO 14 @ ON KEY# I GOTO menu @ NEXT I @ RETURN
30      T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L)+128)
        @ NEXT L
40      RETURN
50 !
60      ASSIGN# 1 TO "CHARSET"
70      FOR I=1 TO 46
80      READ# 1 ; CHAR$(I)
90      NEXT I @ ASSIGN# 1 TO * @ RETURN
100 !
110     DAT$(1),DAT$(2),DAT$(3),DAT$(4),
        DAT$(5),DAT$(6),DAT$(7),DAT$(8)=""
120     DAT$(9)=DSPFLAG$ @ DAT$(10)=FILE2$ @ DAT$(11)=DATADRIVE$
130     DAT$(12)=GRAPHDRIVE$ @ DAT$(13)=VAL$ (DRIVE) @ DAT$(14)=""
140     FOR I=15 TO 19
150     DAT$(I)=FILE$(I-14)&" <"&VAL$ (E2(I.14))&"> <"&
        VAL$(E3(I-14))&">"
160     NEXT I
170     DAT$(20)="" @ DAT$(21)=VAL$ (YMIN)&" , "&VAL$ (YMAX)
180     DAT$(22)=VAL$ (XMIN)&" , "&VAL$ (XMAX)
190     DAT$(23),DAT$(24),DAT$(25)=""
200     DAT$(26)=DSPCRT$ @ DAT$(27)="N/A" @ DAT$(28)=DSPXY$
210     DAT$(29)=SCALING$ @ DAT$(30)=PENSWITCH$ @ DAT$(31)=PLOTAXES$
220     DAT$(32)=PLOTLABEL$ @ DAT$(33)=VAL$ (XCLICK) @
        DAT$(34)=VAL$ (YCLICK)
230     DAT$(35)=ZPRINT$
240     RETURN
250 !
260     IF DSPCRT$="YES" THEN DSPCRT$="NO" ELSE DSPCRT$="YES"
270     GOTO menu
280     IF DSPFLAG$="YES" THEN DSPFLAG$="NO" ELSE DSPFLAG$="YES"
290     GOTO menu
300     IF DSPXY$="YES" THEN DSPXY$="NO" ELSE DSPXY$="YES"
310     GOTO menu
320     CLEAR @ DISP "Enter storage file name <10 characters> [TEST] :" @
        INPUT FILE2$
330     IF LEN (FILE2$)=0 THEN FILE2$="TEST"
340     GOTO menu
350     CLEAR @ DISP "Enter the minimum on X <-100,100> [0] :" @
        INPUT T$ @ IF LEN (T$)=0 THEN XMIN=0 ELSE XMIN=VAL (T$)
360     IF YMIN<-100 OR YMIN>100 THEN 350
370     DISP @ DISP @ DISP "Enter the maximum on X <-100,100> [0] :" @
        INPUT T$ @ IF LEN (T$)= 0 THEN XMAX=0 ELSE XMAX=VAL (T$)
380     IF XMAX<-100 OR XMAX>100 THEN 370 ELSE GOTO menu
390     CLEAR @ DISP "Enter the minimum on Y <.100,100> [0] :" @
        INPUT T$ @ IF LEN (T$)=0 THEN YMIN=0 ELSE YMIN=VAL (T$)
400     IF YMIN<-100 OR YMIN>100 THEN 390
```

```
410     DISP @ DISP @ DISP "Enter the maximum on Y <-100,100> [0] :" @
        INPUT T$ @ IF LEN (T$)= 0 THEN YMAX=0 ELSE YMAX=VAL (T$)
420     IF YMAX<-100 OR YMAX>100 THEN 410 ELSE GOTO menu
430     CLEAR @ DISP "Enter the drive number <0,1 or both-"data read
        only> [0] :" @ INPUT T$
440     IF LEN (T$)=0 THEN T$="0" @ GOTO 480
450     IF T$[1,1]="B" OR T$[1,1]="b" THEN FLAG=0 @ GOTO 470
460     IF VAL (T$)=0 OR VAL (T$)=1 THEN 470 ELSE 430
470     IF CRSR=5 AND (T$[1,1]="B" OR T$[1,1]="b") THEN 430
480     IF CRSR=4 THEN DATADRIVE$=T$[1,1] ELSE GRAPHDRIVE$=T$[1,1]
490     GOTO menu
500     CLEAR @ DISP "Enter the file name" @ INPUT T$
510     IF LEN (T$)=0 THEN FILE$(CRSR-1)="NULL" @ GOTO 540
520     FILE$(CR$R-1)=T$
530     J=CRSR-1 @ GOSUB fileinput
540     GOTO menu
550     CLEAR @ DISP "Drive number <0,1> [1]" @ INPUT T$
560     IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 580
570     DRIVE=VAL (T$) @ IF DRIVE=0 OR DRIVE=1 THEN 580 ELSE 550
580     CLEAR @ CAT ":D70"&VAL$ (DRIVE)
590     DISP "Press <END LINE> to continue :" @ INPUT T$
600     GOTO menu
610     CLEAR @ DISP "Enter the raw data filenames [10] :" @
        DISP "Press <END LINE> when the last name has been entered."
620     FOR J=1 TO TOTAL
630     INPUT FILE$(J)
640     N=J
650     IF LEN (FILE$(J))=0 THEN FILE$(J)="NULL" @ N=J-1 @ J=TOTAL
660     NEXT J
670     FOR J=1 TO N
680     GOSUB fileinput
690     NEXT J
700     GOTO menu
710     IF ZPRINT$="NO" THEN ZPRINT$="YES" @ PRINTER IS 705,90 ELSE
        ZPRINT$="NO" @ PRINTER IS 1
720     GOTO menu
730     IF PLOTAXES$="NO" THEN PLOTAXES$="YES" ELSE PLOTAXES$="NO"
740     GOTO menu
750     IF SCALING$="Man" THEN SCALING$="Auto" ELSE SCALING$="Man"
760     GOTO menu
770     IF PENSWITCH$="Man" THEN PENSWITCH$="Auto" ELSE PENSWITCH$="Man"
780     GOTO menu
790     IF PLOTLABEL$="NO" THEN PLOTLABEL$="YES" ELSE PLOTLABEL$="NO"
800     GOTO menu
810     CLEAR @
        DISP "Enter the x-axis labels as literal strings <10 max> :"
820     FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN XCLICK=I-1 @
        GOTO 840
830     XCLICK(I)=VAL (T$) @ NEXT I @ XCLICK=10
840     GOTO menu
```

```
850      CLEAR @
         DISP "Enter the y-axis labels as literal strings <10 max> :"
860      FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN YCLICK=I-1 @
         GOTO 880
870      YCLICK(I)=VAL (T$) @ NEXT I @ YCLICK=10
880      GOTO menu
920 !
930 fileinput:
940 !
950      IF DATADRIVE$="B" OR DATADRIVE$="b" THEN DRIVE$=VAL$ (0) ELSE
         DRIVE$=DATADRIVE$
960      ASSIGN# 1 TO FILE$(J)&":D70"&DRIVE$
970      READ# 1 ; E1(J),E2(J),E3(J),E4(J),T1(J),A,I_RANGE(J)
980      READ# 1 ; I_TYPE$(J),A,A,EXTDATA$(J),N(J)
990      READ# 1 ; V_RANGE(J),ADVOLTAGE(J),A,A,A,A,A,A
1000     FOR I=1 TO N(J) @ READ# 1 ; X(I,J),Y(I,J) @ NEXT I
1010     IF DATADRIVE$="B" OR DATADRIVE$="b" THEN FLAG=0
1020     IF ERRN =67 OR ERRN =66 THEN 1040
1030     ASSIGN# 1 TO *
1040     RETURN
1050 !
1060 plotting:
1070 !
1080 !   Graphics routine
1090 !
1100     IF DSPCRT$="NO" AND DSPXY$="NO" THEN 2430
1110     CLEAR @ AWRITE 10,33,"Plotting"
1120     SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @ FACTOR=1
1130     FOR J=1 TO TOTAL
1140     IF FILE$(J)="NULL" THEN 1160
1150     IF I_TYPE$(J)="milli" THEN SETMILLI=1 ELSE SETMICRO=1
1160     NEXT J
1170     IF SETMILLI=1 AND SETMICRO=1 THEN PRODUCT=1
1180     MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
1190     FOR J=1 TO TOTAL
1200     IF FILE$(J)="NULL" THEN 1290
1210     IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE
         FACTOR=1
1220     LOW=1 @ HIGH=N(J)
1230     IF E2(J)>MAXX THEN MAXX=E2(J)
1240     IF E3(J)<MINX THEN MINX=E3(J)
1250     FOR I=LOW TO HIGH
1260     IF Y(I,J)*FACTOR<MINY THEN MINY=Y(I,J)*FACTOR
1270     IF Y(I,J)*FACTOR>MAXY THEN MINY=Y(I,J)*FACTOR
1280     NEXT I
1290     NEXT J
1300     IF DSPCRT$ <> "YES" THEN 1530
1310     GRAPHALL @ FRAME
1320     LOCATE 30,200,25,95
1330     XEXP=ABS ((MAXX-MINX)/20) @ YEXP=ABS ((MAXY-MINY)/20)
1340     SCALE MAXX+XEXP,MINX-XEXP,MINY-YEXP,MAXY+YEXP
```

```
1350     FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
1360     LAXES -((MAXX-MINX)/60),(MAXY-MINY)/4/5,0,0,10,5,3
1370     MOVE MINX,MINY
1380     LORG 4 @ X$=CHR$ (46)
1390     FOR J=1 TO TOTAL
1400     IF FILE$(J)="NULL" THEN 1470
1410     IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE
         FACTOR=1
1420     LOW=1 @ HIGH=N(J)
1430     FOR I=LOW TO HIGH
1440     MOVE X(I,J),Y(I,J)*FACTOR
1450     LABEL X$
1460     NEXT I
1470     NEXT J
1480     CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
1490     IF PRODUCT=1 THEN LABEL "microamps" ELSE LABEL I_TYPE$(1)&"amps"
1500     LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "volts (V)"
1510     IF DSPFLAG$="YES" THEN GSTORE FILE2$&":D70"&GRAPHDRIVE$
1520     INPUT T$ @ ALPHALL
1530     IF DSPXY$ <> "YES" THEN 2430
1540 !
1550 ! Mechanical plotting routine
1560 !
1570     GOSUB label_check
1580     XSCALE=8.5 @ YSCALE=7 @ A=MINX @ MINX=MAXX @ MAXX=A
1590     XSCALING=XSCALE/(MAXX-MINX)
1600     YSCALING=YSCALE/(MAXY-MINY)
1610     XCENTER=MAXX-(MAXX-MINX)/2
1620     YCENTER=MAXY-(MAXY-MINY)/2
1630     OUTPUT 723 ;"GP"
1640     TAKE KEYBOARD
1650     CLEAR @ DISP "Set zero positions now !" @
         DISP "Press <END LINE> to continue"
1660     OUTPUT 723 ;"OP 7 OT OP 12 50T OP 14 50T"
1670     KYY=NUM (KEY$ ) @ IF NOT KYY THEN 1660
1680     WAIT 1000
1690     IF PLOTAXES$="NO" THEN 2260
1700     X=MINX*XSCALING-XCENTER*XSCALING+XSCALE/2
1710     Y=MAXY*YSCALING-YCENTER*YSCALING+YSCALE/2
1720     IF PLOTLABEL$="YES" THEN 1830
1730     OUTPUT 723 :"OP 7 ";X;"T OP 12 50T OP 7 0T OP 14 50T"
1740     WAIT 2000
1750     OUTPUT 723 ;"OP 7 7.0T OP 11 1500 14 50T WA .2T OP 7 ":X;"T OP 12
         50T"
1760     OUTPUT 723 :"OP 7 0.0T OP 11 1500 14 50T"
1770     WAIT 3100
1780     OUTPUT 723 ;"OP 7 ";Y;"T OP 14 50T OP 7 ";0;"T OP 12 50T"
1790     WAIT 750
1800     OUTPUT 723 ;"OP 7 8.5T OP 11 1500 12 50T WA .2T OP 7 ";Y;"T OP 14
         50T"
1810     OUTPUT 723 :"OP 7 0.0T OP 11 1500 12 50T"
```

```
1820    WAIT 3100
1830    Y=INT (Y*10000)/10000 @ X=INT (X*10000)/10000
1840    WAIT 1000
1850    XPOS=XSCALE/6
1860    YPOS=YSCALE/5
1870    IF Y-YSCALE/60<0 THEN Y1=0 ELSE Y1=Y-YSCALE/60
1880    IF Y+YSCALE/60>YSCALE THEN Y2=YSCALE ELSE Y2=Y+YSCALE/60
1890    Y1=INT (Y1*10000)/10000 @ Y2=INT (Y2*10000)/10000
1900    LXSCALING=550
1910    FOR I=1 TO XCLICK
1920    IF SCALING$ <> "Man" THEN 1940
1930    X1=XCLICK(I)*XSCALING-XCENTER*XSCALING+4.25 @ GOTO 1960
1940    X1=INT (I*(XSCALE/6)*10000)/10000
1950    IF X1>XSCALE THEN 2050
1960    Y3=INT ((Y2-Y1)*10000)/10000
1970    OUTPUT 723 ;"OP 7 ";X1;"T OP 12 50T OP 7 ";Y1;"T OP 14 50T"
1980    WAIT 1500
1990    OUTPUT 723 ;"OP 11 500 7 ";Y1+Y3:" 14 50T"
2000    WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (XCLICK(I)) @
        GOTO 2020
2010    LA$=VAL$ (INT (((MAXX-MINX)/6*I+MINX+.0001)*1000)/1000)
2020    XIN=X1-8.5/LXSCALING*LEN (LA$)*7/2
2030    YIN=7.25 @ GOSUB xylabel
2040    NEXT I
2050    IF X-XSCALE/73<0 THEN X1=0 ELSE X1=X-XSCALE/73
2060    IF X+XSCALE/73>XSCALE THEN X2=XSCALE ELSE X2=X+XSCALE/73
2070    X1=INT (X1*10000)/10000 @ X2=INT (X2*10000)/10000
2080    FOR I=1 TO YCLICK
2090    IF SCALING$ <> "Man" THEN 2110
2100    Y1=YCLICK(I)*YSCALING-YCENTER*YSCALING+3.5 @ GOTO 2140
2110    Y1=INT (I*(YSCALE/5)*10000)/10000
2120    IF Y1>YSCALE THEN 2260
2130    IF Y1=Y THEN 2220
2140    X3=INT ((X2-X1)*10000)/10000
2150    OUTPUT 723 ;"OP 7 ";Y1;"T OP 14 50T OP 7 ";X1;"T OP 12 50T"
2160    WAIT 1000
2170    OUTPUT 723 ;"OP 11 500 7 ";X1+X3;" 12 50T"
2180    WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (YCLICK(I)) @ GOTO
        2200
2190    LA$=VAL$ (INT (((MAXY-MINY)/5*I+MINY+.000001)*10000)/10000)
2200    XIN=8.75
2210    YIN=Y1+.12 @ GOSUB xylabel
2220    NEXT I
2230    IF PENSWITCH$="Auto" THEN 2260
2240    CLEAR @ DISP "Change pen color ?  Press <END LINE> to continue."
2250    RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
2260    WAIT 1000
2270    FOR J=1 TO TOTAL
2280    IF FILE$(J)="NULL" THEN 2410
2290    IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE
        FACTOR=1
```

```
2300     LOW=1 @ HIGH=N(J)
2310     FOR I=LOW TO HIGH
2320     X=X(I,J)*XSCALING-XCENTER*XSCALING+4.25
2330     Y=Y(I,J)*FACTOR*YSCALING-YCENTER*YSCALING+3.5
2340     OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
2350     IF I=LOW THEN WAIT 500 ELSE WAIT 150
2360     OUTPUT 723 ;"OP 11 100T"
2370     NEXT I
2380     IF PENSWITCH$="Auto" THEN 2410
2390     CLEAR @ DISP "Change pen color ?  Press <END LINE> to continue."
2400     RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
2410     NEXT J
2420     GOSUB filelabel
2430     GOTO menu
2440 !
2450 beginning:
2460     CLEAR
2470     DIM Y(800,5),X(800,5),EXPMT(5),INTPOT(5),FINPOT(5),V_RANGE(5)
2480     DIM SCANS(5),DROPTYME(5),I_RANGE(5),I_TYPE$(5)[10],C(25)
2490     DIM INCPOT(5),PTYME1(5),EXTDATA$(5)[4],N(5),NP(25),ADVOLTAGE(5)
2500     DIM A$(36)[50],B$(36)[50],FILE$(5)[15],FILE2$[15],DAT$(36)[40]
2510     DIM T$[50],T1$[50],PERIOD$[50],
             DATADRIVE$[5],GRAPHDRIVE$[5],DRIVE$[5]
2520     DIM DSPFLAG$[3],DSPCRT$[3],DSPXY$[3],CHAR$(46)[35],LA$[80]
2530     DIM XCLICK(10),YCLICK(10)
2540     ON ERROR GOSUB 3210 @ AWRITE 0,0
2550     DSPFLAG$="NO" @ FILE2$="TEST" @ DATADRIVE$="B" @ GRAPHDRIVE$="0"
         @ DRIVE=1
2560     FLAG=1 @ TOTAL=5 @ SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @ YMIN=0 @
         YMAX=0
2570     FOR J=1 TO TOTAL @ FILE$(J)="NULL" @ E2(J),E3(J)=0 @ NEXT J
2580     DSPCRT$="YES" @ DSPXY$="NO" @ XMIN,XMAX=0 @ PLOTAXES$="YES"
2590     SCALING$="Auto" @ PENSWITCH$="Man" @ PLOTLABEL$="NO" @ XCLICK=6
2600     YCLICK=5 @ ZPRINT$="NO"
2610     TAKE KEYBOARD @ GOSUB 20 @ GOSUB 60
2620     A$(1)="Filer directory"
2630     A$(2)="Mass storage directory"
2640     A$(3)="Plotting directory"
2650     A$(4)="Start plotting"
2660     A$(5)="Chain Autost"
2670     A$(6)="End program"
2680     A$(7)="NULL"
2690     A$(8)="Exit to main menu"
2700     A$(9)="Store graph on disk"
2710     A$(10)="Graph storage file name"
2720     A$(11)="Numeric data drive number"
2730     A$(12)="Graphic data drive number"
2740     A$(13)="Catalog of disk"
2750     A$(15)="File <anodic limit> <cathodilimit>"
2760     A$(20)="Enter all files"
2770     A$(21)="Set min and max for y-axis only"
```

```
2780     A$(22)="Set min and max for x-axis only"
2790     A$(23)="NULL"
2800     A$(24)="NULL"
2810     A$(25)="Exit to main menu"
2820     A$(26)="Plot on CRT"
2830     A$(27)="Plot on printer"
2840     A$(28)="Plot on X-Y recorder"
2850     A$(29)="Manual or Automatic scaling"
2860     A$(30)="Manual or Automatic pen switching"
2870     A$(31)="Plot axes (including labels"
2880     A$(32)="Plot ticks and labels only"
2890     A$(33)="X-axis labels"
2900     A$(34)="Y-axis labels"
2910     A$(35)="Activate printer"
2920     PERIOD$=".............................................."
2930     FOR I=1 TO 13 @ T$=A$(I) @ GOSUB 30 @ B$(I)=T1$ @ NEXT I
2932     T$=A$(15) @ GOSUB 30 @ B$(15)=T1$ @ A$(14)=A$(8) @ B$(14)=B$(8)
2934     FOR I=16 TO 19 @ A$(I)=A$(15) @ B$(I)=B$(15) @ NEXT I
2936     FOR I=20 TO 35 @ T$=A$(I) @ GOSUB 30 @ B$(I)=T1$ @ NEXT I
2940     SCRN=3 @ A1=1 @ A2=6
2950 menu: TAKE KEYBOARD @ GOSUB 110 @ PAGEFLAG=0
2960     CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$ (64+I-A1+1)&CHR$
         (41)&PERIOD$[1,4]&A$(I)&PERIOD$[1,45-LEN (A$(I))]&" "&DAT$(I) @
         NEXT I
2970     AWRITE 1,8,B$(A1) @ CRSR=1
2980     AWRITE 20,2,"Change any parameters ?" @ AWRITE 21,2,"Press the
         indicated letters or use the the "." and "," keys for slewing :"
2990     AWRITE 22,2,"Press '4' to change any parameters or to start
         experiment :"
3000     TAKE KEYBOARD
3010     KYY=NUM (KEY$) @ IF NOT KYY THEN 3010
3020     IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @
         CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
3030     IF KYY<> 46 THEN 3060
3040     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
         CRSR=A2-A1+1
3050     AWRITE CRSR,8,B$(A1+CRSR-1)
3060     IF KYY<> 44 THEN 3090
3070     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @ IF CRSR>A2-A1+1 THEN
         CRSR=1
3080     AWRITE CRSR,8,B$(A1+CRSR-1)
3090     IF KYY<> 52 THEN 3000
3100     IF SCRN<> 3 THEN 3160
3110     IF CRSR=1 THEN SCRN=1 @ A1=14 @ A2=22 @ GOTO 2960
3120     IF CRSR=2 THEN SCRN=2 @ A1=8 @ A2=13 @ GOTO 2960
3130     IF CRSR=3 THEN SCRN=4 @ A1=25 @ A2=35 @ GOTO 2960
3140     IF CRSR=4 THEN 1060
3150     RELEASE KEYBOARD @ IF CRSR=5 THEN CHAIN "Autost" ELSE GOTO 3200
3160     PAGEFLAG=1 @ RELEASE KEYBOARD
3170     IF SCRN=1 THEN ON CRSR GOTO 3190,500,500,500,500,500,610,390,350
3180     IF SCRN=2 THEN ON CRSR GOTO 3190,280,320,430,430,550
```

```
          ELSE ON CRSR GOTO 3190,260,3000,300,750,770,730,790,810,850,710
3190      TAKE KEYBOARD @ SCRN=3 @ A1=1 @ A2=6 @ GOTO 2960
3200      CLEAR @ END
3210 ! Error trap subroutine
3220      IF ERRN =71 THEN 3330
3230      IF ERRN =66 OR ERRN =12 THEN 3330
3240      IF ERRN =11 THEN menu
3250      IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 3330
3260      IF FLAG=1 AND ERRN =67 AND (DATADRIVE$="B" OR DATADRIVE$="b")
          THEN FLAG=0 @ GOTO 960
3270      IF FLAG=1 AND ERRN =67 THEN CLEAR @
          DISP "Place correct disk in drive and press <END LINE> :" @
          RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
3280      IF ERRN =67 AND (DATADRIVE$="B" OR DATADRIVE$="b") THEN
          DRIVE$=VAL$ (ABS (VAL (DRIVE$ )-1)) @ FLAG=1 @ GOTO 960
3290      IF ERRN =130 THEN BEEP 300,1000 @ RELEASE KEYBOARD @
          DISP "Place disk in drive and then press <END LINE>" @ INPUT T$ @
          TAKE KEYBOARD
3300      IF ERRN =130 AND ERRL =390 THEN 960
3310      IF ERRN =130 AND ERRL =860 THEN 1510
3320      DISP ERRN,ERRL @ WAIT 5000
3330      RETURN
3340 xylabel:
3350 ! Beginning of labeling subroutine
3360 ! Range of characters is defined by LXSCALING and should be within
3370 ! the interval 100 to 600 inclusive, where the larger the number the
3380 ! smaller the character.
3390 ! Inputs LA$,LXSCALING
3400      LRATIO=230/190 ! X/Y
3410      LYSCALING=INT (LXSCALING/LRATIO*10000)/10000
3420      IF LXSCALING>400 THEN LSPACE=2 ELSE LSPACE=1
3430      LX=-((5+LSPACE)*8.5/LXSCALING)+XIN
3440      OUTPUT 723 ;"OP 7 ";XIN;"T OP 12 50T OP 7 ";YIN;"T OP 14 50T"
3450      WAIT 500
3460      FOR LI=1 TO LEN (LA$)
3470      LT=NUM (LA$[LI,LI])
3480      IF LT=32 THEN LT=47
3490      LY=YIN
3500      LPOINT=0
3510      LX=LX+(LSPACE+5)*8.5/LXSCALING
3520      FOR LJ=1 TO 7
3530      LY=INT ((LY-7/LYSCALING)*10000)/10000
3540      LX1=LX
3550      FOR LK=1 TO 5
3560      LPOINT=LPOINT+1
3570      LX2=INT ((LX1+LK*8.5/LXSCALING)*10000)/10000
3580      IF CHAR$(LT-44)[LPOINT,LPOINT] <> "1" THEN 3630
3590      OUTPUT 723 ;"OP 7 ";LX2;"T OP 12 50T OP 7 ";LY;"T OP 14 50T"
3600      WAIT 200
3610      OUTPUT 723 ;"OP 11 100T"
3620      WAIT 200
```

```
3630     NEXT LK
3640     NEXT LJ
3650     NEXT LI
3660     RETURN
3670  filelabel:
3680     !
3690     CLEAR @ DISP "Set zero positions now!" @
         DISP "Press <END LINE> to continue"
3700     OUTPUT 723 :"OP 7 OT OP 12 50 14 50T"
3710     KYY=NUM (KEY$ ) @ IF NOT KYY THEN 3700
3720     LXSCALING=550
3730     LA$="FILES" @ XIN=0 @ YIN=0 @ GOSUB xylabel
3740     LA$="-----" @ XIN=0 @ YIN=-.14 @ GOSUB xylabel
3750     X=1
3760     FOR I=1 TO TOTAL
3770     IF FILE$(I)="NULL" THEN 3860
3780     X=X+1
3790     LA$=UPC$ (FILE$(I))
3800     FOR J=1 TO LEN (FILE$(I))
3810     T$=FILE$(I)[J,J]
3820     IF T$="·" THEN LA$[J,J]="."
3830     NEXT J
3840     XIN=0 @ YIN=0-X*.1875
3850     GOSUB xylabel
3860     NEXT I
3870     RETURN
3880  !
3890  label_error:
3900     DISP @ DISP "Assigned labels for plotting out of data range"
3910     DISP "Re-enter values via menu" @
         DISP "Press <END LINE> to continue."
3920     RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD @ GOTO menu
3930  !
3940  label_check:
3950     IF SCALING$="Auto" THEN RETURN
3960     FOR I=1 TO XCLICK @
         IF XCLICK(I)<MINX OR XCLICK(I)>MAXX THEN label_error
3970     NEXT I
3980     FOR I=1 TO YCLICK @
         IF YCLICK(I)<MINY OR YCLICK(I)>MAXY THEN label_error
3990     NEXT I
4000     RETURN
```

7. Triple-Step

```
10       GOTO beginning
20       OUTPUT 723 ;"OP 13 ";ROT(ROT)+INTEGRATE;"T" @ RETURN
30       OUTPUT 723 ;"OP 13 ";INTEGRATE;"T" @ RETURN
40       OFF TIMER# 1 @ IF J=INJECT THEN 640 ELSE J=J+1 @ BEEP 10,1000 @
         OUTPUT 723 ;"OP 13 ";1+INTEGRATE;"T" @ OI=1 @
         ON TIMER# 2,T21 GOTO 50 @ ON RET GOTO 550,560
50       OFF TIMER# 2 @ OI=0 @ BEEP 100,200 @ OUTPUT 723 ;"OP 13
         ";INTEGRATE;"T" @ ON TIMER# 3,T 22 GOTO 60 @ ON RET GOTO 550,560
60       OFF TIMER# 3 @ GOTO 40
70       OFF TIMER# 1 @ IF J=INJECT THEN 640 ELSE J=J+1 @ BEEP 10,1000 @
         OUTPUT 723 ;"OP 13 ";1+INTEGRATE;"T" @ OI=1 @ ON TIMER# 2,T21
         GOTO 80 @ ON RET GOTO 625,620,630
80       OFF TIMER# 2 @ OI=0 @ BEEP 100,200 @ OUTPUT 723 ;"OP 13
         ";INTEGRATE;"T" @ ON TIMER# 3,T22 GOTO 90 @
         ON RET GOTO  625,620,630
90       OFF TIMER# 3 @ GOTO 70
100      OFF TIMER# 1 @ OFF TIMER# 2 @ OFF TIMER# 3 @ GOTO menu
110      OFF TIMER# 1 @ OFF TIMER# 2 @ OFF TIMER# 3 @ GOTO 640
120      ON TO GOSUB 130,140,150,160,170,180 @ RETURN
130      E6=E1 @ RETURN
140      T7=T1 @ RETURN
150      T12=T3 @ RETURN
160      E12=E2 @ RETURN
170      E15=E3 @ RETURN
180      T25=T2 @ RETURN
190 !
200 experiment3: TAKE KEYBOARD @ CLEAR @ DISP "Working"
210      SCANS=1 @ COUNTER=0 @ E6=E1 @ E12=E2 @ E15=E3 @ T25=T2
220      T7=T1 @ T12=T3 @ IF IMAX>N THEN imaxerror
230 experiment2: T9=T7-18 @ OI=0 @ CLEAR 723 @ WAIT 4000 @
         OUTPUT 723 ;"GP"
240      INTEGRATE=8 @ OUTPUT 723 ;"CC 2,3,4,13T" @ GOSUB 20
250      OUTPUT 723 ;"SF 2,3,1,.005,12,4,3,1,.005,12T"
260      N1=8+ROT(ROT) @ N2=32768+ROT(ROT) @ N3=16384+32768+ROT(ROT)
270      IF FIAFLAG$="YES" THEN 470
280      OUTPUT 723 ;"MI 2 ";N+T6;"T"
290      OUTPUT 723 ;"WF 3.0 ";N+T6;"T WF 11.2 OT"
300      IF UPD$="Active" THEN 390
310      FOR I=1 TO T6
320      OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1;"T OP 7 ";E6;" 12
         ";T27;"T OP 12 ";T9;" 13 ";N2;"T"
330      OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3;"T OP 11 .02T OP 7 ";E12;"
         12 ";T25;"T"
340      NEXT I @ I=0
350      OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1;"T OP 7 ";E6;" 12
         ";T27;"T OP 12 ";T9;" 13 ";N2;"T"
360      OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3;"T OP 11 .02T OP 7 ";E12;"
         12 ";T25;"T"
```

```
370     E6=E6+INCPOT @ T9=T9+T5 @ T12=T12+T11 @ E12=E12+E11 @ E15=E15+E14
        @ T25=T25+T24 @ DISP A+C*I @ I=I+1 @ IF I<N THEN 350
380     GOSUB 120 @ GOTO 640
390     FOR I=1 TO T6
400     DISP "Waveform not applicable for batch work" @ WAIT 5000 @ GOTO
        menu
410 !
420     NEXT I @ I=0
430 !
440 !
450     E6=E6+INCPOT @ T9=T9+T5 @ T12=T12+T11 @ E12=E12+E11 @ E15=E15+E14
        @ T25=T25+T24 @ DISP A+C*I @ I=I+1 @ IF I<N THEN 430
460     GOSUB 120 @ GOTO 640
470     OUTPUT 723 ;"MI 2 ";4096;"T"
480     OUTPUT 723 ;WF 3.0 ";4096;"T WF 11.2 OT"
490     T=(T12+T9+T2+18)/1000
500     IF UPD$="Active" THEN 580
510     T6=0
540     I,J=0 @ ON TIMER# 1,T20 GOTO 40
550     N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13
        ";N1+OI;"T OP 7 ";E6; " 12 ";T27;"T OP 12 ";T9;" 13 ";N2+OI;"T"
560     OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3+OI;"T OP 11 .02T OP 7
        ";E12;" 12 ";T25;"T" @ DISP E6,I @ RET=2 @ I=I+1 @ GOTO 550
570     GOTO 640
580     T6=0
590     EI=(E12-E6)/20 @ EO=E6+E1 @ TO=T25/20
610     I,J=0 @ ON TIMER# 1,T20 GOTO 70
620     N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13
        ";N1+OI;"T OP 7 ";E6;" 12 1T OP 13 ";N2+OI;"T"
625     FOR K=1 TO 20 @ OUTPUT 723 ;"OP 7 ";EO;" 12 ";TO;"T" @ EO=EO+EI @
        NEXT K @ EO=E6+EI @ RET=3
630     OUTPUT 723 ;"OP 7 ";E6;" 12 ";T9;"T OP 14 .03 13 ";N3+OI;" 12 20T
        OP 11 .02T" @ DISP E6,I @ RET=2 @ I=I+1 @ GOTO 620
640     DISP "Waiting ";(30000-T8*1000)/1000;" seconds.",,N
650     WAIT 30000-T8*1000 @ DISP "Continuing"
660 !
670 ! Input data from memory cards
680     IF SKIPFLAG$="YES" THEN PLOTFIG$="NO" @ GOTO 970
690 !
700     SEND 7 ; UNL MLA TALK 23 SCG 5
710     FOR I=1 TO T6 @ ENTER 7 USING "#,K" ; JUNK @ NEXT I
720     FOR I=1 TO N
730     ENTER 7 USING "#,K" ; TEMP(I)
740     NEXT I
750 !
760     DISP ,,,TEMP(IMAX)
770     IF SCANS=1 THEN 790
780     FOR I=1 TO N @ Y(I)=Y(I)+TEMP(I) @ NEXT I @ GOTO 800
790     FOR I=1 TO N @ Y(I)=TEMP(I) @ NEXT I
800     SCANS=SCANS+1 @ IF SCANS<TOTALSCANS+1 THEN GOTO experiment2
810     COUNTER=COUNTER+1
```

```
820 !
830      IF COULOMB$="q" THEN 890
840      FOR I=1 TO N
850      Y(I)=Y(I)/TOTALSCANS
860      Y(I)=-(Y(I)/10*ADVOLTAGE*I_RANGE/V_RANGE)
870      NEXT I
880      GOTO 940
890      FOR I=1 TO N
900      Y(I)=Y(I)/TOTALSCANS
910      Y(I)=-(1000000*2*.000001*Y(I)/ADVOLTAGE*I_RANGE/(V_RANGE*100))
920      NEXT I
930 !
940      SCANFLAG=1 @ GOSUB datastore @ SCANFLAG=0
950 !
960      PRINT "I(E1)= ";Y(IMAX);"
970      PRINT "E(det)= ";E6,"E(ads)= ";E15,"E(a)= ";E12
980      PRINT "T(det)= ";T9+18,"T(ads)= ";T12,"T(a)= ";T25
990      PRINT
1000 !
1010     IF FIAFLAG$ <> "YES" THEN 1070
1020     IF E1=E5 THEN 1070
1030     E6=E6+INCPOT @ IF SGN (INCPOT)=1 AND E6>E5 THEN E6=E1 @ GOTO 1070
1040     IF SGN (INCPOT)=-1 AND E6<E5 THEN E6=E1 @ GOTO 1070
1050     SCANS=1 @ GOTO experiment2
1060 !
1070     IF T1=T4 THEN 1120
1080     T7=T7+T5 @ IF SGN (T5)=1 AND T7>T4 THEN T7=T1 @ GOTO 1120
1090     IF SGN (T5)=-1 AND T7<T4 THEN T7=T1 @ GOTO 1120
1100     SCANS=1 @ GOTO experiment2
1110 !
1120     IF T10=T3 THEN 1170
1130     T12=T12+T11 @ IF SGN (T11)=1 AND T12>T10 THEN T12=T3 @ GOTO 1170
1140     IF SGN (T11)=-1 AND T12<T10 THEN T12=T3 @ GOTO 1170
1150     SCANS=1 @ GOTO experiment2
1160 !
1170     IF E2=E10 THEN 1220
1180     E12=E12+E11 @ IF SGN (E11)=1 AND E12>E10 THEN E12=E2 @ GOTO 1220
1190     IF SGN (E11)=-1 AND E12<E10 THEN E12=E2 @ GOTO 1220
1200     SCANS=1 @ GOTO experiment2
1210 !
1220     IF E3=E13 THEN 1270
1230     E15=E15+E14 @ IF SGN (E14)=1 AND E15>E13 THEN E15=E3 @ GOTO 1270
1240     IF SGN (E14)=-1 AND E15<E13 THEN E15=E3 @ GOTO 1270
1250     SCANS=1 @ GOTO experiment2
1260 !
1270     IF T2=T23 THEN 1320
1280     T25=T25+T24 @ IF SGN (T24)=1 AND T25>T23 THEN 1320
1290     IF SGN (T24)=-1 AND T25<T23 THEN 1320
1300     SCANS=1 @ GOTO experiment2
1310 !
1320     IF ROTMIN=0 THEN 1360
```

```
1330     ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN @ GOSUB 20 @ GOTO 1360
1340     GOSUB 20 @ SCANS=1 @ GOTO experiment2
1350 !
1360     IF PLOTFIG$="NO" THEN menu
1370 !
1380 plotter: !  Graphics routine
1390 !
1400     LOW=1 @ HIGH=N
1410     MINX=0 @ MAXX=0 @ MINY=YMIN @ MAXY=YMAX
1420     IF X(N)>X(1) THEN MAXX=X(N) @ MINX=X(1) ELSE MAXX=X(1) @
         MINX=X(N)
1430     FOR I=LOW TO HIGH
1440     IF Y(I)<MINY THEN MINY=Y(I)
1450     IF Y(I)>MAXY THEN MAXY=Y(I)
1460     NEXT I
1470     GRAPHALL @ FRAME
1480     LOCATE 30,200,25,95
1490     SCALE MAXX,MINX,MINY,MAXY
1500     FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
1510     LAXES -((MAXX-MINX)/50),(MAXY-MINY)/4/5,0,0,10,5,3
1520     MOVE MINX,MINY
1530     LORG 4 @ X$=CHR$ (46)
1540     FOR I=LOW TO HIGH
1550     MOVE X(I),Y(I)
1560     LABEL X$
1570     NEXT I
1580     CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
1590     LABEL I_TYPE$&"amps"
1600     LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "volts (V)"
1610     GOTO 1790
1620 !
1630 ! Store data on disk
1640 !
1650     FD$=":D70"&VAL$ (FIGUREDRIVE)
1660     IF FIGSTORE$="YES" THEN GSTORE FIGUREFILE$&FD$ @ GOTO 1680 ELSE
1680
1670     GSTORE FIGUREFILE$&FD$
1680 datastore: IF DATASTORE$="YES" THEN 1690 ELSE 1780
1690     DD$=VAL$ (COUNTER)&":D70"&VAL$ (DATADRIVE)
1700     PURGE DATAFILE$&DD$
1710     CREATE DATAFILE$&DD$,20+N*2,10
1720     ASSIGN# 1 TO DATAFILE$&DD$
1730     PRINT# 1 ; E6,E5,E1,0,T1,T2,I_RANGE
1740     PRINT# 1 ; I_TYPE$[1,5],T3,0,"00"
1750     PRINT# 1 ; N,0,E2,0,0,V_RANGE,ADVOLTAGE,TOTALSCANS,0
1760     FOR I=1 TO N @ PRINT# 1 ; X(I),Y(I) @ NEXT I
1770     ASSIGN# 1 TO *
1780     IF SCANFLAG=1 THEN RETURN
1790     WAIT 1000 @ RELEASE KEYBOARD @ INPUT T$ @ ALPHALL @ GOTO menu
1800 !
1810 ! inputs
```

```
1820 !
1830     CLEAR @ DISP "Enter the beginning detection potential <-10,+10>
         [-1.0] :"
1840     INPUT T$ @ IF LEN (T$)=0 THEN E1=-1 @ GOTO 1860 ELSE E1=VAL (T$)
         @ GOTO 1860
1850     GOTO 1830
1860     IF E1<-10 OR E1>10 THEN 1830
1870     IF E1=E5 THEN INCPOT=0
1880     GOTO menu
1890 !
1900     CLEAR @ DISP "Enter the beginning anodic cleaning potential
         <-10,+10> [0.8] :"
1910     INPUT T$ @ IF LEN (T$)=0 THEN E2=.8 @ GOTO 1930 ELSE E2=VAL (T$)
         @ GOTO 1930
1920     GOTO 1900
1930     IF E2<-10 OR E2>10 THEN 1900
1940     IF E2=E10 THEN E11=0
1950     GOTO menu
1960 !
1970 !
1980     CLEAR @ DISP "Enter the beginning detection time <20,600000 msec>
         [50] :" @ INPUT T$
1990     IF LEN (T$)=0 THEN T1=50 @ GOTO 2010 ELSE T1=VAL (T$) @ GOTO 2010
2000     GOTO 1980
2010     IF T1<20 OR T1>600000 THEN 1980
2020     IF T1=T4 THEN T5=0
2030     GOTO menu
2040 !
2050     CLEAR @ DISP "Enter the beginning anodic cleaning time <0,600000
         msec> [200] :"
2060     INPUT T$ @ IF LEN (T$)=0 THEN T2=200 @ GOTO 2080 ELSE T2=VAL (T$)
         @ GOTO 2080
2070     GOTO 2050
2080     IF T2<0 OR T2>600000 THEN 2050
2090     IF T2=0 THEN T2=.001
2100     IF T2=T23 THEN T24=0
2110     GOTO menu
2120 !
2130 !
2140     CLEAR @ DISP "Enter the data file name <7 characters> [PADTEST] "
2150     INPUT T$ @ IF LEN (T$)=0 THEN DATAFILE$="PADTEST" ELSE
         DATAFILE$=T$
2160     IF LEN (T$)<8 OR DATAFILE$="PADTEST" THEN 2210
2170     DISP @ DISP @ DISP "File name is longer than 7 characters."
2180     DISP "Do you wish to change it?  <Y,N> [N] :" @ INPUT T$
2190     IF LEN (T$)=0 THEN menu
2200     IF T$[1,1]="Y" OR T$[1,1]="y" THEN 2140
2210     GOTO menu
2220 !
2230     CLEAR @ DISP "Enter the figure file name <10 characters>
         [TEST_PAD] :"
```

```
2240    INPUT T$ @ IF LEN (T$)=0 THEN FIGUREFILE$="TEST_PAD" ELSE
        FIGUREFILE$=T$
2250    IF LEN (T$)<11 OR FIGUREFILE$="TEST_PAD" THEN 2300
2260    DISP @ DISP @ DISP "File name ";T$;" is Longer than 10
        characters." 2270 DISP "Do you wish to change it?  <Y,N> [N] :" @
        INPUT T$
2280    IF LEN (T$)=0 THEN menu
2290    IF LEN (T$)<> 0 AND (T$[1,1]="Y" OR T$[1,1]="Y") THEN 2230
2300    GOTO menu
2310 !
2320    IF DATADRIVE=0 THEN DATADRIVE=1 ELSE DATADRIVE=0
2330    GOTO menu
2340 !
2350    IF FIGUREDRIVE=0 THEN FIGUREDRIVE=1 ELSE FIGUREDRIVE=0
2360    GOTO menu
2370 !
2380    IF COULOMB$="q" THEN COULOMB$="i" ELSE COULOMB$="q"
2390    GOTO menu
2400 !
2410    IF DATASTORE$="YES" THEN DATASTORE$="NO" ELSE DATASTORE$="YES"
2420    GOTO menu
2430 !
2440    IF FIGSTORE$="YES" THEN FIGSTORE$="NO" ELSE FIGSTORE$="YES"
2450    GOTO menu
2460 !
2470    IF UPD$="Active" THEN UPD$="Not active" ELSE UPD$="Active"
2480    GOTO menu
2490 !
2500    CLEAR @ DISP "Enter the drive number <0 1> [1] :" @ INPUT T$
2510    IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 2530 ELSE DRIVE=VAL (T5) @
        GOTO 2530
2520    GOTO 2500
2530    IF DRIVE=0 OR DRIVE=1 THEN 2540 ELSE 2500
2540    CAT ":D70"&VAL$ (DRIVE)
2550    DISP "Press <END LINE> to continue." @ INPUT T$
2560    GOTO menu
2570 !
2580    IF PLOTFIG$="YES" THEN PLOTFIG$="NO" ELSE PLOTFIG$="YES"
2590    GOTO menu
2600 !
2610    CLEAR @ DISP "Enter the beginning cathodic cleaning potential
        <-10,+10> [-1.0] :"
2620    INPUT T$ @ IF LEN (T$)=0 THEN E3=-1 @ GOTO 2640 ELSE E3=VAL (T$)
        @ GOTO 2640
2630    GOTO 2610
2640    IF E3<-10 OR E3>10 THEN 2610
2650    IF E3=E13 THEN E14=0
2660    GOTO menu
2670 !
2680    CLEAR @ DISP "Enter the beginning adsorption time <0,600000 msec>
        [500] :"
```

```
2690    INPUT T$ @ IF LEN (T$)=0 THEN T3=500 @ GOTO 2710 ELSE T3=VAL (T$)
        @ GOTO 2710
2700    GOTO 2680
2710    IF T3<0 OR T3>600000 THEN 2680
2720    IF T3=0 THEN T3=.001
2730    IF T3=T10 THEN T11=0
2740    GOTO menu
2750 !
2760    CLEAR @ DISP "Enter the minimum on Y <-50,max Y> [0] :" @
        INPUT T$
2770    IF LEN (T$)=0 THEN YMIN=0 @ GOTO 2790 ELSE YMIN=VAL (T$) @
        GOTO 2790
2780    GOTO 2760
2790    IF YMIN<-50 OR YMIN>50 THEN 2760
2800    DISP @ DISP @ DISP @ DISP "Enter the maximum on Y <min Y, 50> [0]
        :" 2810 INPUT T$ @ IF LEN (T$)=0 THEN YMAX=0 @ GOTO 2830 ELSE
        YMAX=VAL (T$) @ GOTO 2830
2820    GOTO 2800
2830    IF YMAX<YMIN OR YMAX>50 THEN 2800
2840    GOTO menu
2850    CLEAR @ DISP "Enter the current range <0.02, 10> [5] :" @
        INPUT T$
2860    IF LEN (T$)=0 THEN I_RANGE=5 @ GOTO 2880 ELSE I_RANGE=VAL (T$) @
        GOTO 2880
2870    GOTO 2850
2880    IF I_RANGE<.02 OR I_RANGE>10 THEN 2850
2890    DISP @ DISP
2900    DISP "Enter the scale <milliamps (m,M), microamps (u,U)> [M] :" @
        INPUT T$
2910    IF LEN (T$)=0 THEN I_TYPE$="milli" @ GOTO 2940 ELSE I_TYPE$=T$
2920    IF T$[1,1]="M" OR T$[1,1]="m" THEN I_TYPE$="milli" @ GOTO 2940
2930    IF T$[1,1]="U" OR T$[1,1]="u" THEN I_TYPE$="micro" @ GOTO 2940
        ELSE 2900
2940    DISP @ DISP @ DISP I_RANGE;" ";I_TYPE$;"amps, per what voltage
        range <0,5000> [10] :" @ INPUT T$
2950    IF LEN (T$)=0 THEN V_RANGE=10 @ GOTO 2970 ELSE V_RANGE=VAL (T$) @
        GOTO 2970
2960    GOTO 2940
2970    IF V_RANGE<0 OR V_RANGE>5000 THEN 2940
2980    GOTO menu
2990    CLEAR @ DISP "Total number of cleaning pulses <1,--> [5] :"
3000    INPUT T$ @ IF LEN (T$)=0 THEN T6=5 @ GOTO 3020 ELSE T6=VAL (T$) @
        GOTO 3020
3010    GOTO 2990
3020    IF T6<1 THEN 2990
3030    GOTO menu
3040    CLEAR @ DISP "Enter the ending detection potential <-10,+10>
        [0.60] :"
3050    INPUT T$ @ IF LEN (T$)=0 THEN E5=.6 @ GOTO 3070 ELSE E5=VAL (T$)
        @ GOTO 3070
3060    GOTO 3040
```

```
3070    IF E5<-10 OR E5>10 THEN 3040
3080    IF E5=E1 THEN INCPOT=0
3090    GOTO menu
3100    CLEAR @ DISP "Enter the potential increment, E-d <-2, 2
        [.005 min]> [0.05] :"
3110    INPUT T$ @ IF LEN (T$)=0 THEN INCPOT=.05 @
        GOTO 3190 ELSE INCPOT=VAL (T$) @ GOTO 3130
3120    GOTO 3100
3130    IF INCPOT>ABS (E5-E1) THEN 3100
3140    IF INCPOT>-.005 AND INCPOT<0 THEN 3100
3150    IF INCPOT<.005 AND INCPOT>0 THEN 3100
3160    IF INCPOT<-2 OR INCPOT>2 THEN 3100
3170    IF INT(INCPOT*1000)/.005 <> INCPOT*1000/.005 THEN 3100
3180    IF E1=E5 THEN INCPOT=0
3190    GOTO menu
3200    CLEAR @ DISP "Enter the A/D voltage range <1, 10> [10] :" @
        INPUT T$ 3210 IF LEN (T$)=0 THEN ADVOLTAGE=10 @ GOTO 3240 ELSE
        ADVOLTAGE=VAL (T$) @ GOTO 3230
3220    GOTO 3200
3230    IF ADVOLTAGE=10 OR ADVOLTAGE=1 THEN 3240 ELSE 3200
3240    GOTO menu
3250    CLEAR @
        DISP "Enter the number of signal averaged scans <1, --> [1] :"
3260    INPUT T$ @ IF LEN (T$)=0 THEN TOTALSCANS=1 @ GOTO 3280 ELSE
        TOTALSCANS=VAL (T$) @ GOTO 3280
3270    GOTO 3250
3280    TOTALSCANS=INT (TOTALSCANS)
3290    IF TOTALSCANS<1 THEN 3250
3300    GOTO menu
3310    CLEAR @ DISP "Enter the ending detection time <20,600000 msec>
        [1000] :" @ INPUT T$
3320    IF LEN (T$)=0 THEN T4=1000 @ GOTO 3340 ELSE T4=VAL (T$) @
        GOTO 3340
3330    GOTO 3310
3340    IF T4<T1 OR T4>600000 THEN 3310
3350    IF T4=T1 THEN T5=0
3360    GOTO menu
3370    CLEAR @ DISP "Enter the detection time increment <-600000,600000
        msec> [50] :" @ INPUT T$
3380    IF LEN (T$)=0 THEN T5=50 @ GOTO 3400 ELSE T5=VAL (T$) @ GOTO 3400
3390    GOTO 3370
3400    IF T5<-600000 OR T5>600000 THEN 3370
3410    T5=INT (T5*1000)/1000
3420    IF T1=T4 THEN T5=0
3430    GOTO menu
3440    CLEAR @ DISP "Enter the waiting reduction time <0,28 sec> [0] :"
        @ INPUT T$
3450    IF LEN (T$)=0 THEN T8=0 @ GOTO 3470 ELSE T8=VAL (T$) @ GOTO 3470
3460    GOTO 3440
3470    IF T8<0 OR T8>28 THEN 3440
3480    GOTO menu
```

```
3490    CLEAR @ DISP "Enter the number corresponding to the potential to
        be monitored <1,N> [1] :" @ INPUT T$ @ GOTO 3520
3500 imaxerror: CLEAR @ DISP "The monitoring potential number is to
        large" @ DISP "Press < END LINE> to continue."
3510    RELEASE KEYBOARD @ INPUT T$ @ GOTO 3490
3520    IF LEN (T$)=0 THEN IMAX=1 @ GOTO 3540 ELSE IMAX=VAL (T$) @
        GOTO 3540
3530    GOTO 3490
3540    IF IMAX<1 OR IMAX<> INT (IMAX) THEN 3490
3550    GOTO menu
3560    CLEAR @ DISP "Enter the final reduction/adsorption time
        <0,600000> [500] :"
3570    INPUT T$ @ IF LEN (T$)=0 THEN T10=500 @
        GOTO 3590 ELSE T10=VAL (T$) @ GOTO 3590
3580    GOTO 3560
3590    IF T10<0 OR T10>600000 THEN 3560
3600    IF T10=0 THEN T10=.001
3610    IF T10=T3 THEN T11=0
3620    GOTO menu
3630    CLEAR @ DISP "Enter the reduction/adsorption time increment
        <-600000,600000> [0] :"
3640    INPUT T$ @ IF LEN (T$)=0 THEN T11=0 @ GOTO 3660 ELSE T11=VAL (T$)
        @ GOTO 3660
3650    GOTO 3630
3660    IF T11<-600000 OR T11>600000 THEN 3630
3670    T11=INT (T11*1000)/1000
3680    IF T3=T10 THEN T11=0
3690    GOTO menu
3700    IF FIAFLAG$="NO" THEN FIAFLAG$="YES" ELSE FIAFLAG$="NO"
3710    GOTO menu
3720    IF ZPRINT$="NO" THEN ZPRINT$="YES" @ PRINTER IS 705,90 ELSE
        ZPRINT$="NO" @ PRINTER IS 1
3730    GOTO menu
3740    CLEAR @ DISP "Enter the delay time before any injections <0.5,
        99999999> [300,000] :"
3750    INPUT T$ @ IF LEN (T$)=0 THEN T20=300000 @
        GOTO 3770 ELSE T20=VAL (T$) @ GOTO 3770
3760    GOTO 3740
3770    IF T20<.5 OR T20>99999999 THEN 3740
3780    GOTO menu
3790    CLEAR @ DISP "Enter the single injection time <0.5, 99999999>
        [30,000] :"
3800    INPUT T$ @ IF LEN (T$)=0 THEN T21=30000 @
        GOTO 3820 ELSE T21=VAL  (T$) @ GOTO 3820
3810    GOTO 3790
3820    IF T21<.5 OR T21>99999999 THEN 3790
3830    GOTO menu
3840    CLEAR @ DISP "Enter the time between individual injections <0.5,
        99999999> [60,000] :"
3850    INPUT T$ @ IF LEN (T$)=0 THEN T22=60000 @ GOTO 3870 ELSE T22=VAL
        (T$) @ GOTO 3870
```

```
3860    GOTO 3840
3870    IF T22<.5 OR T22>99999999 THEN 3840
3880    GOTO menu
3890    CLEAR @
        DISP "Enter the number of like injections <1,10000> [5] :"
3900    INPUT T$ @ IF LEN (T$)=0 THEN INJECT=5 @
        GOTO 3920 ELSE INJECT=IP (VAL (T$)) @ GOTO 3920
3910    GOTO 3890
3920    IF INJECT<1 OR INJECT>10000 THEN 3890
3930    GOTO menu
3940    IF SKIPFLAG$="NO" THEN SKIPFLAG$="YES" ELSE SKIPFLAG$="NO"
3950    GOTO menu
3960    CLEAR @ DISP "Enter the ending anodic cleaning potential <-10,10>
        [.8] :"
3970    INPUT T$ @ IF LEN (T$)=0 THEN E10=.8 @
        GOTO 3990 ELSE E10=VAL (T$) @ GOTO 3990
3980    GOTO 3960
3990    IF E10<-10 OR E10>10 THEN 3960
4000    IF E10=E2 THEN E11=0
4010    GOTO menu
4020    CLEAR @ DISP "Enter then anodic cleaning potential increment
        <-2,2 [.005 min] [0.05] :"
4030    INPUT T$ @ IF LEN (T$)=0 THEN E11=.05 @
        GOTO 4110 ELSE E11=VAL (T$) @ GOTO 4050
4040    GOTO 4020
4050    IF E11>ABS (E10-E2) THEN 4020
4060    IF E11>-.005 AND E11<0 THEN 4020
4070    IF E11<.005 AND E11>0 THEN 4020
4080    IF E11<-2 OR E11>2 THEN 4020
4090    IF INT (E11*1000)/.005<> E11*1000/.005 THEN 4020
4100    IF E2=E10 THEN E11=0
4110    GOTO menu
4120    CLEAR @ DISP "Enter the ending cathodic cleaing potential
        <-10,10> [-1] :"
4130    INPUT T$ @ IF LEN (T$)=0 THEN E13=-1 @
        GOTO 4150 ELSE E13=VAL (T$) @ GOTO 4150
4140    GOTO 4120
4150    IF E13<-10 OR E13>10 THEN 4120
4160    IF E13=E3 THEN E14=0
4170    GOTO menu
4180    CLEAR @ DISP "Enter then cathodic cleaning potential increment
        <-2,2 [.005 min] [0.05] :"
4190    INPUT T$ @ IF LEN (T$)=0 THEN E14=.05 @
        GOTO 4270 ELSE E14=VAL  (T$) @ GOTO 4210
4200    GOTO 4180
4210    IF E14>ABS (E13-E3) THEN 4180
4220    IF E14>-.005 AND E14<0 THEN 4180
4230    IF E14<.005 AND E14>0 THEN 4180
4240    IF E14<-2 OR E14>2 THEN 4180
4250    IF INT (E14*1000)/.005<> E14*1000/.005 THEN 4180
4260    IF E3=E13 THEN E14=0
```

```
4270    GOTO menu
4280    CLEAR @ DISP "Enter the ending anodic cleaning time <0,600000
        msec> [200] :"
4290    INPUT T$ @ IF LEN (T$)=0 THEN T23=200 @
        GOTO 4310 ELSE T23=VAL (T$) @ GOTO 4310
4300    GOTO 4280
4310    IF T23<0 OR T23>600000 THEN 4280
4320    IF T23=0 THEN T23=.001
4330    IF T23=T2 THEN T24=0
4340    GOTO menu
4350    CLEAR @ DISP "Enter the Anodic cleaning time increment
        <-600000,600000 msec> [50] :" @ INPUT T$
4360    IF LEN (T$)=0 THEN T24=50 @ GOTO 4380 ELSE T24=VAL (T$) @ GOTO
        4380
4370    GOTO 4350
4380    IF T24<-600000 OR T24>600000 THEN 4350
4390    T24=INT(T24*1000)/1000
4400    IF T2=T23 THEN T24=0
4410    GOTO menu
4420    CLEAR @ AWRITE 1,0,"Rotation speed(s) -- e.g., 1,2,3... , 1-5, *
        for all"
4430    FOR I=1 TO 10 @ AWRITE I+7,12,VAL$ (I)&")"&PERIOD$[1,5-LEN (VAL$
        (I))]&ROT$(I)&ROT1$(I) @ NEXT I
4440    FOR I=1 TO 7 @ AWRITE I+7,30,VAL$
        (I+10)&")"&PERIOD$[1,3]&ROT$(I+10)&ROT1$(I+10) @ NEXT I
4450    AWRITE 20,2,"" @ LINPUT CODE$ @ IF LEN (CODE$)=0 THEN menu
4460    GOSUB decode @ IF error=1 THEN 4420
4470    FOR I=1 TO 17 @ ROT1$(I)="" @ IF CODE(I)<> 0 THEN ROT1$(I)="*"
4480    NEXT I @ J=1 @ FOR I=1 TO 17 @ IF ROT1$(I)="*" THEN
        ROT(J)=ROT2(I) @ J=J+1
4490    NEXT I @ ROTMAX=J-1 @ IF ROTMAX=0 THEN ROTMIN=0 @ ROT=0 ELSE
        ROTMIN=1 @ ROT=1
4500    GOTO 4420
4510    CLEAR @ DISP "Enter the delay time before charge measurement
        <.001, 99999999> [0.001] :"
4520    INPUT T$ @ IF LEN (T$)=0 THEN T27=.001 @
        GOTO 4540 ELSE T27=VAL (T$) @ GOTO 4540
4530    GOTO 4510
4540    IF T27<.001 OR T27>99999999 THEN 4510
4545    GOTO menu
4550 !
4551    CLEAR @ DISP "Enter the beginning integration potential <-10, 10>
        [-0.20] :"
4553    INPUT T$ @ IF LEN (T$)=0 THEN E30=-.2 @ GOTO 4557 ELSE E30=VAL
        (T$) @ GOTO 4557
4555    GOTO 4551
4557    IF E30<-10 OR E30>10 THEN 4551
4559    GOTO menu
4560 !
4570 beginning:
4571    CLEAR @ ON ERROR GOSUB 6030 @ AWRITE 0,0
```

```
4572    DISP "Alternate waveform selection (* indicates loaded upon
        execution)" @ DISP
4573    DISP "1) Zero-background, surface controlled (sulfurs), 3-step,
        FIA work only"
4574    DISP "2) *Zero-background, mt controlled (carbohydrates), 3-step,
        FIA work only"
4575    DISP "3) UPD stripping beginning at deposition potential, batch
        and FIA"
4576    DISP "4) Zero-background, surface controlled (sulfurs), 4-step,
        FIA work only"
4577    DISP "5) Continue with program"
4580    DISP @ DISP "Waveform <1,5> [1]" @ INPUT T @ IF T<1 OR T>5 THEN
        4572
4581    CLEAR @ DISP "Position cursor over get statement with cursor
        controls and press <END LINE>."
4582    DISP "Press RUN to restart program and select option 5 in the
        previous menu"
4583    IF T=1 THEN AWRITE 10,0,"GET "&CHR$ (34)&"WFM_1"&CHR$ (34) @
        AWRITE 11,0 @ DISP @ PAUSE
4584    IF T=2 THEN AWRITE 10,0,"GET "&CHR$ (34)&"WFM_2"&CHR$ (34) @
        AWRITE 11,0 @ DISP @ PAUSE
4585    IF T=3 THEN AWRITE 10,0,"GET "&CHR$ (34)&"WFM_3"&CHR$ (34) @
        AWRITE 11,0 @ DISP @ PAUSE
4586    IF T=4 THEN AWRITE 10,0,"GET "&CHR$ (34)&"WFM_4"&CHR$ (34) @
        AWRITE 11,0 @ DISP @ PAUSE
4589    CLEAR
4590    DIM Y(3000),X(3000),TEMP(3000)
4600    DIM
        A$(62)[50],B$(62)[50],DAT$(62)[25],DATAFILE$[20],FIGUREFILE$[20]
4610    DIM T$[50],T1$[50],PERIOD$[50],DATASTORE$[10],FIGSTORE$[10]
4620    DIM PLOTFIG$[10],I_TYPE$[5],FD$[15],DD$[15]
4630    DIM CODE(20),ROT(20),ROT2(20),ROT1$(20)[1],ROT$(20)[4]
4640    WFM=2
4650    FOR I=1 TO 10 @ ROT$(I)=VAL$ (I*500) @ ROT1$(I),ROT1$(I+10)="" @
        NEXT I
4660    ROT$(3)="1400" @ FOR I=10 TO 70 STEP 10 @
        ROT$(I/10+10)=VAL$ (I^2) @ NEXT I
4670    FOR I=1 TO 17 @ READ T @ ROT2(I)=T @ ROT(I)=0 @ NEXT I
4680    E1=-1 @ E5=.6 @ E2=.8 @ T1=100 @ T2=200 @ T4=100 @ T3=500 @ T5=0
        @ T6=5
4690    DATAFILE$="PADTEST" @ FIGUREFILE$="TEST_PAD" @ DATADRIVE=1 @ T8=0
4700    FIGUREDRIVE=1 @ DATASTORE$="YES" @ FIGSTORE$="NO" @ DRIVE=1 @
        E3=-1 4710 PLOTFIG$="YES" @ YMIN,YMAX=0 @ I_RANGE=5 @
        I_TYPE$="milli" @ INCPOT=.05
4720    SCANFLAG=0 @ ADVOLTAGE=10 @ TOTALSCANS=1 @ V_RANGE=10 @ IMAX=1
4730    T10=500 @ T11=0 @ FIAFLAG$="NO" @ ZPRINT$="NO" @ PRINTER IS 1 @
        E30=-.2
4740    T20=300000 @ T21=30000 @ T22=60000 @ INJECT=5 @ SKIPFLAG$="NO"
4750    E10=.8 @ E13=-1 @ T23=200 @
        E11,E14,T24,ROT,ROT(0),ROTMAX,ROTMIN=0
4760    COULOMB$="i" @ T27=.001 @ RINSE$="NO" @ INTEGRATE=8
```

```
4770    GOSUB 5750 @ TAKE KEYBOARD
4780    A$(1)="Experimental directory"
4790    A$(2)="Mass storage directory"
4800    A$(3)="Plotting directory"
4810    A$(4)="Begin experiment"
4820    A$(5)="Chain Autost"
4830    A$(6)="End program"
4840    A$(7)="Exit to main menu"
4850    A$(8)="Beginning detection potential, E1...i"
4860    A$(9)="Ending detection potential, E5...i"
4870    A$(10)="Potential increment, E-d...i"
4880    A$(11)="Beginning detection time (msec), T1...ii"
4890    A$(12)="Ending detection time (msec), T4...ii"
4900    A$(13)="Detection time increment (msec), T5...ii"
4910    A$(14)="Beginning adsorption time (msec), T3...iii"
4920    A$(15)="Ending Adsorption time (msec), T10...iii"
4930    A$(16)="Adsorption time increment (msec), T11...iii"
4940    A$(17)="Cleaning pulses, T6"
4950    A$(18)="Delay time before charge measurement, T27"
4960    A$(19)="Continuance of experimental directory"
4970    A$(19)="Activate alternate waveform"
4980    A$(20)="UPD beginning integration potential, E30"
4990    A$(21)="Continuance of experimental directory"
5000    A$(22)="Exit to previous experimental menu"
5010    A$(23)="Current range"
5020    A$(24)="A/D voltage range"
5030    A$(25)="Number of signal averaged decays"
5040    A$(26)="Waiting reduction time"
5050    A$(27)="Potential NUMBER of voltage monitoring"
5060    A$(28)="Hold detection potential constant"
5070    A$(29)="Delsy time before injections, T20"
5080    A$(30)="Injection time, T21"
5090    A$(31)="Delay time between injections, T22"
5100    A$(32)="Number of injections"
5110    A$(33)="Converting to current or charge"
5120    A$(34)="Continuance of experimental directory"
5130    A$(35)="Exit to main menu"
5140    A$(36)="Data file name"
5150    A$(37)="Figure file name"
5160    A$(38)="Data file drive number"
5170    A$(39)="Figure file drive number"
5180    A$(40)="Store data on disk"
5190    A$(41)="Store figure on disk"
5200    A$(42)="Catalog of disk"
5210    A$(43)="NULL"
5220    A$(44)="Exit to main menu"
5230    A$(45)="Plot raw data curve"
5240    A$(46)="Enter max and min on Y only"
5250    A$(47)="Activate printer"
5260    A$(48)="Conversion override"
5270    A$(49)="NULL"
```

```
5280     A$(50)="Exit to previous experimental menu"
5290     A$(51)="Beginning anodic potential, E2...iv"
5300     A$(52)="Ending anodic potential, E10...iv"
5310     A$(53)="Anodic potential increment, E11...iv"
5320     A$(54)="Beginning cathodic potential, E3...v"
5330     A$(55)="Ending cathodic potential, E13...v"
5340     A$(56)="Cathodic potential increment...v"
5350     A$(57)="Beginning cleaing time, T2...vi"
5360     A$(58)="Ending cleani"g time, T23...vi"
5370     A$(59)="Cleaning time increment, T24...vi"
5380     A$(60)="Rotation speeds...vii"
5390     A$(61)="Activate automatic rinse for FIA"
5400     PERIOD$="................................................."
5410     FOR I=1 TO 61 @ T$=A$(I) @ GOSUB 5770 @ B$(I)=T1$ @ NEXT I
5420     SCRN=1 @ A1=1 @ A2=6
5430 menu: TAKE KEYBOARD @ GOSUB 5790
5440     CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$ (64+I-A1+1)&CHR$
         (41)&PERIOD$[1,4]&A$(I)&PERIOD$[1,45-LEN (A$(I))]&" "&DAT$(I) @
         NEXT I
5450     AWRITE 1,8,B$(A1) @ CRSR=1
5460     AWRITE 20,2,"Change any parameters ?" @ AWRITE 21,2,"Press the
         indicated letters or use the the "." and "," keys for slewing :"
5470     AWRITE 22,2,"Press '4' to change any parameters or to start
         experiment :"
5480     AWRITE 23,2,"Lower case Roman numerals indicate precedence, vi
         being the lowest."
5490     TAKE KEYBOARD
5500     KYY=NUM (KEY$) @ IF NOT KYY THEN 5500
5510     IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @
         CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
5520     IF KYY<> 46 THEN 5550
5530     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
         CRSR=A2-A1+1
5540     AWRITE CRSR,8,B$(A1+CRSR-1)
5550     IF KYY<> 44 THEN 5580
5560     AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @ IF CRSR>A2-A1+1 THEN
         CRSR=1
5570     AWRITE CRSR,8,B$(A1+CRSR-1)
5580     IF KYY<> 52 THEN 5490
5590     IF SCRN<> 1 THEN 5650
5600     IF CRSR=1 THEN SCRN=2 @ A1=7 @ A2=21 @ GOTO 5440
5610     IF CRSR=2 THEN SCRN=3 @ A1=35 @ A2=42 @ GOTO 5440
5620     IF CRSR=3 THEN SCRN=4 @ A1=44 @ A2=48 @ GOTO 5440
5630     IF CRSR=5 THEN RELEASE KEYBOARD @ CHAIN "Autost"
5640     IF CRSR=4 THEN singlevariable ELSE RELEASE KEYBOARD @ GOTO 5740
5650     PAGEFLAG=1 @ RELEASE KEYBOARD
5660     IF SCRN=2 THEN ON CRSR GOTO
         5700,1830,3040,3100,1980,3310,3370,2680,3560,3630,2990,
         4510,2470,4551,5710
5670     IF SCRN=5 THEN ON CRSR GOTO
         5720,2850,3200,3250,3440,3490,3700,3740,3790,3840,3890,2380,5730
```

```
5680    IF SCRN=6 THEN ON CRSR GOTO
        5710,1900,3960,4020,2610,4120,4180,2050,4280,4350,4420,6690
5690    IF SCRN=3 THEN ON CRSR GOTO
        5700,2140,2230,2320,2350,2410,2440,2500 ELSE ON CRSR GOTO
        5700,2580,2760,3720,3940
5700    TAKE KEYBOARD @ SCRN=1 @ A1=1 @ A2=6 @ GOTO 5440
5710    TAKE KEYBOARD @ SCRN=5 @ A1=22 @ A2=34 @ GOTO 5440
5720    TAKE KEYBOARD @ SCRN=2 @ A1=7 @ A2=21 @ GOTO 5440
5730    TAKE KEYBOARD @ SCRN=6 @ A1=50 @ A2=61 @ GOTO 5440
5740    CLEAR @ END
5750    ON KEY# 1 GOTO 100 @ ON KEY# 2 GOTO 110 @ ON KEY# 3 GOSUB 30 @ ON
        KEY# 4 GOSUB 6120 @ FOR I=7 TO 14 @ ON KEY# I GOTO menu @ NEXT I
5760    ON KEY# 5 GOSUB 6390 @ ON KEY# 6 GOSUB 30 @ RETURN
5770    T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128)
        @ NEXT L
5780    RETURN
5790    DAT$(1),DAT$(2),DAT$(3),DAT$(4),DAT$(5),DAT$(6),DAT$(7)=""
5800    DAT$(8)=VAL$ (E1) @ DAT$(9)=VAL$ (E5) @ DAT$(10)=VAL$ (INCPOT)
5810    DAT$(11)=VAL$ (T1)
5820    DAT$(12)=VAL$ (T4) @ DAT$(13)=VAL$ (T5)
5830    DAT$(14)=VAL$ (T3) @ DAT$(15)=VAL$ (T10) @ DAT$(16)=VAL$ (T11)
5840    DAT$(17)=VAL$ (T6) @ DAT$(20),DAT$(21),DAT$(22)=""
5850    DAT$(18)=VAL$ (T27) @ DAT$(19)=UPD$ @ DAT$(20)=VAL$ (E30)
5860    DAT$(23)=VAL$ (I_RANGE)&" "&I_TYPE$[1,5]&"amps"&"/ "&
        VAL$ (V_RANGE)&" V"
5870    DAT$(24)=VAL$ (ADVOLTAGE) @ DAT$(25)=VAL$ (TOTALSCANS)
5880    DAT$(26)=VAL$ (T8) @ DAT$(27)=VAL$ (IMAX) @ DAT$(28)=FIAFLAG$
5890    DAT$(29)=VAL$ (T20) @ DAT$(30)=VAL$ (T21) @ DAT$(31)=VAL$ (T22)
5900    DAT$(32)=VAL$ (INJECT) @ DAT$(33)=COULOMB$ @ DAT$(34)=""
5910    DAT$(35)="" @ DAT$(36)=DATAFILE$ @ DAT$(37)=FIGUREFILE$
5920    DAT$(38)=VAL$ (DATADRIVE) @ DAT$(39)=VAL$ (FIGUREDRIVE)
5930    DAT$(40)=DATASTORE$ @ DAT$(41)=FIGSTORE$ @ DAT$(42)=VAL$ (DRIVE)
5940    DAT$(43),DAT$(44)="" @ DAT$(45)=PLOTFIG$
5950    DAT$(46)=VAL$ (YMIN)&", "&VAL$ (YMAX) @ DAT$(47)=ZPRINT$
5960    DAT$(48)=SKIPFLAG$ @ DAT$(49),DAT$(50)=""
5970    DAT$(51)=VAL$ (E2) @ DAT$(52)=VAL$ (E10) @ DAT$(53)=VAL$ (E11)
5980    DAT$(54)=VAL$ (E3) @ DAT$(55)=VAL$ (E13) @ DAT$(56)=VAL$ (E14)
5990    DAT$(57)=VAL$ (T2) @ DAT$(58)=VAL$ (T23) @ DAT$(59) (T24)
6000    DAT$(60)="" @ DAT$(61)=RINSE$
6010    RETURN
6020 !
6030 ! Error trap subroutine
6040    IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 6100
6050    IF ERRN =67 OR ERRN =66 THEN 6100
6060    IF ERRN =55 THEN OUTPUT 723 ;"CC 2,3,4T" @ I=0 @ GOTO 500
6070    IF ERRN =11 THEN menu
6080    IF ERRN =130 THEN BEEP 300,700 @ RELEASE KEYBOARD @
        DISP "Place disk in drive and then press <END LINE>" @ INPUT T$ @
        TAKE KEYBOARD @ GOTO menu
6090    DISP ERRN ,ERRL @ WAIT 2000
6100    RETURN
```

```
6110 !
6120 ! Display results on 'printer is' default
6130    PRINT CHR$ (12) @ FOR K=1 TO 60 @ PRINT CHR$ (64+K)&CHR$
        (41)&PERIOD$[1,4]&A$(K)&PERIOD$[1,45-LEN (A$(K))]&" "&DAT$(K) @
        NEXT K @ PRINT CHR$ (12) @ RETURN
6140    END
6150 !
6160 singlevariable: ! Single variable check
6170    CLEAR @ DISP "Calculating"
6180    SINGLEFLAG,T,N,A,B,C,T0=0
6190    IF E1<> E5 THEN T0=1 @ GOTO 6270
6200    IF T1<> T4 THEN T0=2 @ GOTO 6270
6210    IF T3<> T10 THEN T0=3 @ GOTO 6270
6220    IF E2<> E10 THEN T0=4 @ GOTO 6270
6230    IF E3<> E13 THEN T0=5 @ GOTO 6270
6240    IF T2<> T23 THEN T0=6 @ GOTO 6270
6250    IF ROTMIN<> ROTMAX THEN T0=7 @ GOTO 6270
6260    IF FIAFLAG$="YES" THEN N=1 @ GOTO experiment3 ELSE menu
6270    ON T0 GOSUB 6280,6310,6320,6290,6300,6330,6340 @
        N=ABS (INT ((B-A)/C))+1 @ GOTO 6350
6280    A=E1 @ B=E5 @ C=INCPOT @ RETURN
6290    A=E2 @ B=E10 @ C=E11 @ RETURN
6300    A=E3 @ B=E13 @ C=E14 @ RETURN
6310    A=T1 @ B=T4 @ C=T5 @ RETURN
6320    A=T3 @ B=T10 @ C=T11 @ RETURN
6330    A=T2 @ B=T23 @ C=T24 @ RETURN
6340    A=ROTMIN @ B=ROTMAX @ C=1 @ RETURN
6350    FOR I=0 TO N-1 @ X(I+1)=A+C*I @ NEXT I
6360    SINGLEFLAG=1
6370    GOTO experiment3
6380 !
6390    ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN
6400    GOSUB 20 @ N1=8+ROT(ROT) @ N2=32768+ROT(ROT) @
        N3=16384+32768+ROT(ROT) @ RETURN
6410 decode:
6420 !
6430    ON ERROR GOTO error3 @ error=0 @ FOR I=1 TO 20 @
        CODE(I)=0 @ NEXT I
6440    FOR I=1 TO LEN (CODE$) @ IF CODE$[1,1]=CHR$ (32) THEN
        CODE$=CODE$[2,LEN (CODE$)] @ GOTO 6440
6450    IF CODE$[1,1] <> "*" THEN 6470
6460    FOR I=1 TO 100 @ CODE(I)=1 @ NEXT I @ GOTO 6580
6470    T$="1"
6480    FOR I=0 TO 9 @ IF CODE$[1,1]=VAL$ (I) THEN T$="-1"
6490    NEXT I @ IF T$ <> VAL$ (-1) THEN CODE$=CODE$[2,LEN (CODE$)]
        ELSE 6510
6500    IF LEN (CODE$)=0 THEN error3 ELSE 6480
6510    T=VAL (CODE$) @ IF T<0 OR T>99 THEN error2 ELSE CODE(T)=1
6520    IF LEN (VAL$ (T))=LEN (CODE$) THEN 6580
6530    CODE$=CODE$[1+LEN (VAL$ (T)),LEN (CODE$)] @ IF LEN (CODE$)=0 THEN
        CODE(T)=1 @ GOTO 6580
```

```
6540     T$=CODE$[1,1] @ CODE$=CODE$[2,LEN (CODE$)] @ IF T$="," OR T$="-"
         THEN 6550 ELSE error1
6550     t1=VAL (CODE$) @ IF t1<0 OR t1>99 THEN T=t1 @ GOTO error2
6560     IF T$="," THEN CODE(t1)=1 @ GOTO 6510
6570     FOR I=T+1 TO t1 @ CODE(I)=1 @ NEXT I @ GOTO 6510
6580     ON ERROR GOSUB 6030 @ RETURN
6590 !
6600 error1: error=1
6610     DISP "Character ";T$;" not allowed." @ DISP @
         DISP "Press <END LINE> to continue." @ INPUT T$
6620 !
6630 error2: error=1
6640     DISP "The value ";T;" is to large." @ DISP @
         DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
6650 !
6660 error3: error=1
6670     DISP "String does not follow syntax." @ DISP @
         DISP "Press <END LINE> to continue." @  INPUT T$ @ RETURN
6680     DATA
         48,80,112,160,256,304,336,560,576,1040,16,32,64,128,256,512,1024
6690 ! Rinse settings
6700     E1,E5,E2,E10,E3,E13=0
6710     T1,T4,T3,T10,T2,T23=200
6720     T20=15000 @ T21=30000 @ T22=30000
6730     INJECT=100 @ FIAFLAG$="YES" @ T6=5 @ N=1
6740     GOTO experiment3
```

8. Waveforms

```
7000 ! ZERO-BACKGROUND INTEGRAL WAVEFORM (SULFUR CMPDS), WFM1 -. 3-STEP
7010     ! 400  DISP "Waveform not applicable for batch work" @ WAIT 5000
           @ GOTO menu
7020     ! 410 !
7030     ! 430 !
7040     ! 440 !
7045     ! 590 !
7050     ! 620 N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12
           ";T12;" 13 ";N1+OI;"T OP 7 ":E6;" 12 100T OP 13 ";N2+OI;"T OP 7
           ";E12;" 12 ";T25;"T"
7055     ! 625 !
7060     ! 630 OUTPUT 723 ;"OP 7 ";E6;" 12 ";T9;"T OP 14 .03 13 ";N3+OI;"
           12 20T OP 11 .02T" @ DISP E6,I @ RET=2 @ I=I+1 @ GOTO 620
7070     ! 4640 WFM=1
7080 !
7100 ! ZERO-BACKGROUND POTENTIAL STEP INTEGRAL WAVEFORM (CARBOHYDRATES),
       WFM2 -- 3-STEP
7102     ! 400 DISP "Waveform not applicable for batch work" @ WAIT 5000 @
           GOTO menu
7104     ! 410 !
7106     ! 430 !
7108     ! 440 !
7120     ! 590 EI=(E12-E6)/20 @ E0=E6+EI @ T0=T25/20
7140     ! 620 N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12
           ";T12;" 13 ";N1+OI;"T OP 7 ";E6;" 12 1T OP 13 ";N2+OI;"T"
7150     ! 625 FOR K=1 TO 20 @ OUTPUT 723 ;"OP 7 ";E0;" 12 ";T0;"T" @
           E0=E0+EI @ NEXT K @ E0=E6+EI @ RET=3
7160     ! 630 OUTPUT 723 ;"OP 7 ";E6;" 12 ";T9;"T OP 14 .03 13 ";N3+OI;"
           12 20T OP 11 .02T" @ DISP E6,I @ RET=2 @ I=I+1 @ GOTO 620
7190     ! 4640 WFM=2
7195 !
7200 ! UPD POTENTIAL INCLUSIVE (INTEGRATION FOR POTENTIAL SWEEP)
       WAVEFORM, WFM3
7210     ! 400 OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1;"T OP 7
           ";E30;"T OP 13 ";N2;"T OP 7 ";E6;" 12 ";T27;"@ OP 12 ";T9;"T"
7220     ! 410 OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3;"T OP 11 .02T OP 7
           ";E12;" 12 ";T25;"T"
7230     ! 430 OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1;"T OP 7
           ";E30;"T OP 13 ";N2;"T OP 7 ";E6;" 12 ";T27;"T OP 12 ";T9;"T"
7240     ! 440 OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3;"T OP 11 .02T OP 7
           ";E12;" 12 ";T25;"T"
7245     ! 590 !
7250     ! 620 N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12
           ";T12;" 13 ";N1+OI;"T OP 7 ";E30;"T OP 13 ";N2+OI;"T OP 7
           ";E6;" 12 ";T27;"T OP 12 ";T9;"T"
7255     ! 625 !
7260     ! 630 OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3+OI;"T OP 11 .02T OP 7
           ";E12;" 12 ";T25;"T" @ DISP E6,I @ RET=2 @ I=I+1 @ GOTO 620
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7270    ! 4640 WFM=3
7280 !
7300 ! ZERO-BACKGROUND INTEGRAL WAVEFORM (SULFUR CMPDS), WFM4 -- 4-STEP
7310    ! 400 DISP "Waveform not applicable for batch work" @ WAIT 5000 @
          GOTO menu
7320    ! 410 1
7330    ! 430 !
7340    ! 440 !
7345    ! 590 !
7350    ! 620 N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12
          ";T12;" 13 ";N1+OI;"T OP 7 ";E6;" 12 100T OP 13 ";N2+OI;"T OP 7
          ";E12;" 12 ";T25;"T"
7355    ! 625 !
7360    ! 630 OUTPUT 723 ;"OP 7 ";E6;" 12 ";T9;"T OP 14 .03 13 ";N3+OI;"
          12 20T OP 11 .02T OP 7 ";E30;" 12 "T30;"T" @ DISP E6,I @ RET=2
          @ I=I+1 @ GOTO 620
7370    ! 4640 WFM=4
7380    !
8000 END
```