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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

Glen Gary Neuburger
*Iowa State University*

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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)

Iowa State University

Ph.D. 1987

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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

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

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Major: Analytical Chemistry

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Iowa State University
Ames, Iowa
1987
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<td>A/D</td>
<td>Analog-to-digital</td>
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<td>A/DC</td>
<td>Analog-to-digital conversion</td>
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<td></td>
<td>Analog-to-digital converter</td>
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<tr>
<td>AI</td>
<td>Artificial Intelligence</td>
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<td>ASV</td>
<td>Anodic stripping voltammetry</td>
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<td>CHEMFET</td>
<td>Chemical field-effect transistor</td>
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<td>CPPP</td>
<td>Constant potential pulse polarography</td>
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<td>CPPV</td>
<td>Constant potential pulse voltammetry</td>
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<td>Digital-to-analog</td>
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<td>D/AC</td>
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<td></td>
<td>Digital-to-analog converter</td>
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<td>DME</td>
<td>Dropping mercury electrode</td>
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<td>DPASV</td>
<td>Differential pulse anodic stripping voltammetry</td>
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<td>Differential pulse polarography</td>
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<td>Differential pulse voltammetry</td>
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<tr>
<td>EC</td>
<td>Electrochemical</td>
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<td>EPROM</td>
<td>Erasable-programmable-read-only memory</td>
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<td>FT</td>
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<td>FT/NMR</td>
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<td>FT-UV-vis</td>
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<td>Abbreviation</td>
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<tr>
<td>HP</td>
<td>Hewlett Packard</td>
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<tr>
<td>I/O</td>
<td>Input and/or output</td>
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<tr>
<td>ISE</td>
<td>Ion-selective electrode</td>
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<td>ISFET</td>
<td>Ion-selective field-effect transistor</td>
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<td>k</td>
<td>multiples of 1024</td>
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<tr>
<td>LC</td>
<td>Liquid chromatography</td>
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<td>LC/EC</td>
<td>Liquid chromatography with electrochemical detection</td>
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<td>Mass spectrometry/mass spectrometry (used to denote parent-daughter structural elucidation)</td>
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<td>PAD</td>
<td>Pulsed amperometric detection</td>
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<td>Pulsed coulometric detection</td>
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<td>PCS</td>
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<td>Potential sweep pulsed coulometric detection</td>
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<td>RAM</td>
<td>Random access read/write memory</td>
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<td>RPA</td>
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<td>rpm</td>
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<tr>
<td>RRDE</td>
<td>Rotating ring-disk electrode</td>
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<td>S/H</td>
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<td>UPD</td>
<td>Underpotential deposition</td>
<td></td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
<td></td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet visible spectroscopy</td>
<td></td>
</tr>
</tbody>
</table>
### DEFINITION OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE</td>
<td>Potential step increment</td>
</tr>
<tr>
<td>τ</td>
<td>Drop lifetime, s</td>
</tr>
<tr>
<td>θ</td>
<td>Fractional surface coverage</td>
</tr>
<tr>
<td>φ</td>
<td>Scan rate, V min⁻¹</td>
</tr>
<tr>
<td>A</td>
<td>Area, cm²</td>
</tr>
<tr>
<td>a</td>
<td>Activity of analyte</td>
</tr>
<tr>
<td>a_{ox}</td>
<td>Activity of oxidized form of the analyte</td>
</tr>
<tr>
<td>a_{red}</td>
<td>Activity of reduced form of the analyte</td>
</tr>
<tr>
<td>c_b</td>
<td>Bulk concentration of analyte</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient, cm² s⁻¹</td>
</tr>
<tr>
<td>E_{2/3}</td>
<td>Half-wave potential</td>
</tr>
<tr>
<td>E_d</td>
<td>Detection potential (CPPP)</td>
</tr>
<tr>
<td>E_f</td>
<td>Final potential (polarography)</td>
</tr>
<tr>
<td>E_i</td>
<td>Initial potential (polarography)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday Constant, 96,487 eq mol⁻¹</td>
</tr>
<tr>
<td>i_{DC}</td>
<td>Constant potential (dc) polarographic current</td>
</tr>
<tr>
<td>i-E</td>
<td>Current-potential, in reference to Figures</td>
</tr>
<tr>
<td>i_{NP}</td>
<td>Normal pulse polarographic current</td>
</tr>
<tr>
<td>i_{RP}</td>
<td>Reverse pulse polarographic current</td>
</tr>
<tr>
<td>i-t</td>
<td>Current-time, in reference to transient flow profiles (CPPP)</td>
</tr>
<tr>
<td>n</td>
<td>Equivalent number of electrons</td>
</tr>
<tr>
<td>n_{ox}</td>
<td>Equivalent number of electrons in oxidation mechanism</td>
</tr>
<tr>
<td>n_{red}</td>
<td>Equivalent number of electrons in reduction mechanism</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant, 8.316 J mol(^{-1}) deg(^{-1})</td>
</tr>
<tr>
<td>T</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>(t_p)</td>
<td>Potential-pulse lifetime or period</td>
</tr>
<tr>
<td>(v_f)</td>
<td>Flow rate, mL min(^{-1})</td>
</tr>
<tr>
<td>(V_R)</td>
<td>Retention volume</td>
</tr>
<tr>
<td>(V_s)</td>
<td>Sample volume injected</td>
</tr>
</tbody>
</table>
**DEFINITION OF TERMS**

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>batch</strong></td>
<td>Refers to experiments performed in a cell of constant volume. Commonly used for experiments employing rotating ring-disk electrodes.</td>
</tr>
<tr>
<td><strong>detection limit</strong></td>
<td>The lowest measurable concentration for a specified signal-to-noise ratio.</td>
</tr>
<tr>
<td><strong>final potential</strong></td>
<td>Used in the description of two-step pulsed polarographic waveforms. Indicates that potential at which the current is measured.</td>
</tr>
<tr>
<td><strong>initial potential</strong></td>
<td>Used in the description of two-step pulsed polarographic waveforms. Indicates that potential at which the current is not measured.</td>
</tr>
<tr>
<td><strong>irreversible</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>kinetically-controlled</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>mass-transport controlled</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>potential</strong></td>
<td>Used solely as a synonym for &quot;voltage&quot;.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>reversible</td>
<td>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.</td>
</tr>
<tr>
<td>sensitivity</td>
<td>The rate of change of the measured signal with the variation of bulk analyte concentration.</td>
</tr>
<tr>
<td>surface-controlled</td>
<td>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.</td>
</tr>
<tr>
<td>underpotential deposition</td>
<td>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.</td>
</tr>
</tbody>
</table>
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 $\mu$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.
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.\textsuperscript{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. 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.
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, multi-wavelength 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. 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.

More recent advances are in the development of FT-UV-vis spectrometers. Groton has recently introduced 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 separa-
tions. Universal detection of most organic compounds may be
achieved by absorption monitoring at 185 nm. 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, includ­
ing direct liquid introduction, mechanical transfer, and
thermospray. 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 measure­
ments, 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 moni-
toring 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.  

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. 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 diffi-
culties 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,\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{21} These detectors are also gaining advantage with the use of photodiode arrays in conjunction with low volume detection cells.\textsuperscript{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 or circular dichroism. 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.

H. Conductivity Detection

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

I. Element Specific Detection

Several flame-based detectors have been introduced for use in LC. Of these, the most common are flame photometric, flame ionization and thermionic detection.
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,\textsuperscript{35-37} light scattering,\textsuperscript{38} indirect absorption based polarimetric measurements,\textsuperscript{39} photothermal deflection,\textsuperscript{40} photothermal refraction,\textsuperscript{41} multiphoton effects,\textsuperscript{42-45} the Raman Effect,\textsuperscript{46} andphoto-acoustic measurements.\textsuperscript{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-silicate coated electrode, sulfide and cyanide with a silver sulfide membrane electrode, and monovalent cations with a neutral ligand plastic membrane electrodes. Indirect detection methods have also been applied to potentiometric detection in LC; several anions have been detected with a chloride electrode, amino acids, transition and rare earth metal ions with a copper sensitive membrane electrode, and carboxylic acids with a pH electrode.

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. Potentiometric detection with chemically or electrochemically pretreated silver electrodes or copper electrodes 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, organic acids, alkaline earth metal ions, transition metal ions, inorganic anions (e.g., nitrite, nitrate and bromate, chlorate, iodate), oxidizing inorganic anions (e.g., CN⁻, Cl⁻, Br⁻, I⁻ and SCN⁻), reducing inorganic anions (e.g., ascorbic acid, hydrazine, and hydroxylamine), and several complexing organic ligands, such as, glycine, histidine, L-cysteine, EDTA, ethylenediamine, dopamine, and imidazole. 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 → Cu⁺, 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 electroinactive 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\textsuperscript{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\textsuperscript{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. Series and parallel dual electrodes have been used for the characterization of the chemical and electrochemical mechanisms of 6-methylpterin. Several advantages can be gained by monitoring current differences for both series and parallel configurations. 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 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. Microarray electrodes may afford a greater S/N than a single electrode of equal area. 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. 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.

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. Pulsed amperometric techniques have also been described for use with solid noble metal electrodes. 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.\textsuperscript{45-52} Chemical coating of electrodes also has been described\textsuperscript{53} for reducing surface fouling effects.

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

Several new electrochemical detectors have appeared. Biampereometric 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.\textsuperscript{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.\textsuperscript{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\textsuperscript{58} in conjunction with reverse phase HPLC.
III. PULSE POLAROGRAPHIC METHODS

Since their inception by J. Heyrovsky, 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.

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. 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, 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.\textsuperscript{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,\textsuperscript{15} and
Barker and Gardner,\textsuperscript{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 convention-
al 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.\textsuperscript{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 ($\Delta E$) 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 $\Delta E$ 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.\textsuperscript{19-21}

5. Constant pulse amplitude normal pulse polarography

This technique\textsuperscript{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.

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 polarography25 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 measured 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.\textsuperscript{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,\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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\textsuperscript{23,34} (dc distortion effects) or by capacitive charging currents\textsuperscript{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.\textsuperscript{35,36} Depletion effects may limit this effect with the normal pulse mode or with any such waveforms which have fixed initial potentials.

2. \textit{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.\textsuperscript{14,37}

3. \textit{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.\textsuperscript{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. 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. 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. 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.

**G. Square-Wave Polarography**

This technique may be described as the combination of a large-amplitude square-wave modulation with a staircase waveform 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. 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.
<table>
<thead>
<tr>
<th>Waveform Name</th>
<th>( -E )</th>
<th>( i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Staircase</td>
<td>![Staircase Diagram]</td>
<td>![Staircase Current Diagram]</td>
</tr>
<tr>
<td>Differential Staircase</td>
<td>![Differential Staircase Diagram]</td>
<td>![Differential Staircase Current Diagram]</td>
</tr>
<tr>
<td>Modified Normal Pulse</td>
<td>![Modified Normal Pulse Diagram]</td>
<td>![Modified Normal Pulse Current Diagram]</td>
</tr>
<tr>
<td>Successive-Drop (fixed-amplitude) Pseudoderivative Normal Pulse</td>
<td>![Successive-Drop Pseudoderivative Normal Pulse Diagram]</td>
<td>![Successive-Drop Pseudoderivative Normal Pulse Current Diagram]</td>
</tr>
</tbody>
</table>
Waveform Name

Variable Amplitude Pseudoderivative Normal Pulse

\[ \Delta i = i_{j+k} - i_j \]

Constant Pulse Amplitude Normal Pulse

\[ \Delta E_p, \Delta E_s \]

Subtractive Normal Pulse

\[ \Delta i = i_2 - i_1 \]

Differential Normal Pulse

\[ \Delta i = i_1 - i_2 \]

Alternate-Drop Normal Pulse

\[ \Delta i = i_2 - i_1 \]
Waveform Name

- **Optimized Normal Pulse**: $\Delta i = i_1 - i_2$

- **Reverse Pulse**: $\Delta E_P$

- **Constant Potential Pulse**: $\Delta E_P$

- **Constant-Current Normal Pulse**: $\Delta E_P$

- **Constant-Current Differential Pulse**: $\Delta t_P$
<table>
<thead>
<tr>
<th>Waveform Name</th>
<th>$\Delta i = i_2 - i_1$</th>
<th>$\Delta E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard Differential Pulse</strong></td>
<td>$\Delta i = i_2 - i_1$</td>
<td>$\Delta E_p$</td>
</tr>
<tr>
<td><strong>Modified Differential Pulse</strong></td>
<td>$\Delta i = i_2 - i_1$</td>
<td>$\Delta E_p$</td>
</tr>
<tr>
<td><strong>Differential Single-Pulse</strong></td>
<td>$\Delta i = i_1 - i_2$</td>
<td>$\Delta E_p$</td>
</tr>
<tr>
<td><strong>Differential Double-Pulse</strong></td>
<td>$\Delta i = i_1 - i_2$</td>
<td>$\Delta E_p$</td>
</tr>
<tr>
<td><strong>Alternate-Drop Differential Pulse</strong></td>
<td>$\Delta i = i_1 - i_2$</td>
<td>$\Delta E_p$</td>
</tr>
</tbody>
</table>
Waveform Name

Successive-Drop
Differential Double-Pulse

\[ \Delta i = i_2 - i_1 \]

Optimized
Differential Pulse

\[ \Delta i = i_1 - i_2 \]

Square-Wave

\[ \Delta i = i_1 - i_2 \]
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.\textsuperscript{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.
Herzfeld\textsuperscript{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 $\theta$, for $\theta < 1$. Later workers, such as Rogers and Stehney,\textsuperscript{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
A. Introduction to UPD Compilation

This section is included to help in the interpretation of the UPD summary; a compilation of the literature on under-potential 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 $\Delta E_p$ or $E_{r/d}$ 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 $\Delta E_p$ or $E_{\text{c}},d$, 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$_2$)$_5^{3+}$, Cr(OH$_2$)$_5^{2+}$, Cr(OH$_2$)$_5OSO$_3^+$, Cr(NH$_3$)$_5OH^{3+}$, Cr(en)$_3^{3+}$, Eu(OH$_2$)$_3^{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 informa-
tion 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

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>, (comma)</td>
<td>used as a separator between like elements in an attribute, e.g., r-oxid. CO, HCOOH, HCOH</td>
</tr>
<tr>
<td>; (semicolon)</td>
<td>used as a separator between dislike elements in the attribute definitions, e.g., LEED; 0.5 M HClO₄</td>
</tr>
<tr>
<td>* (asterisk)</td>
<td>used to denote the continuation of a substrate/adatom(s) pair</td>
</tr>
<tr>
<td>&quot; (tilde)</td>
<td>approximately-equal-to, denotes that the concentrations of the compounds stated are only approximate</td>
</tr>
<tr>
<td>...benz.</td>
<td>...benzene</td>
</tr>
<tr>
<td>...hydraz.</td>
<td>...hydrazine</td>
</tr>
<tr>
<td>...meth.</td>
<td>...methane</td>
</tr>
<tr>
<td>('number')</td>
<td>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.</td>
</tr>
<tr>
<td>('number')</td>
<td>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.</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>(compound)</td>
<td>denotes a specific example of a group of compounds listed for electrocatalytic study (cf. r-)</td>
</tr>
<tr>
<td>+e</td>
<td>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.</td>
</tr>
<tr>
<td>+s</td>
<td>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.</td>
</tr>
<tr>
<td>-I</td>
<td>denotes that iodide pretreatment of the substrate was used prior to the experiments</td>
</tr>
<tr>
<td>ΔEₚ ( , , )</td>
<td>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.</td>
</tr>
<tr>
<td>ΔEₚ=f(face)</td>
<td>denotes that the peak potential for the specific face has been determined but is probably summarized in graphical form.</td>
</tr>
<tr>
<td>A/B {adatom(s)}</td>
<td>codeposition of A and B on the listed substrate</td>
</tr>
<tr>
<td>A/B {substrate}</td>
<td>denotes that the substrate used was made from an alloy of A and B</td>
</tr>
<tr>
<td>A/m-B {substrate}</td>
<td>denotes the deposition of a monolayer or less of B onto A</td>
</tr>
<tr>
<td>A-B {substrate}</td>
<td>denotes that A is deposited electrochemically on B unless otherwise stated in the attributes section</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>A:B {substrate}</td>
<td>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.</td>
</tr>
<tr>
<td>a- (a,c-)</td>
<td>anion effects of supporting electrolyte(s); may also denote adsorption effects of neutrals, such as CO₂.</td>
</tr>
<tr>
<td>a-sup.</td>
<td>see a-</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>ads.</td>
<td>adsorption [of]</td>
</tr>
<tr>
<td>ads. kinetics</td>
<td>adsorption kinetics are discussed</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>anal.</td>
<td>analytical</td>
</tr>
<tr>
<td>as ...</td>
<td>denotes that the electrodeposited ion was of a different composition that the supporting electrolyte. For example, as PbF₂, denotes that the F⁻ anion is different from the supporting electrolyte anion.</td>
</tr>
<tr>
<td>B-carbide</td>
<td>Boron Carbide</td>
</tr>
<tr>
<td>benzoquin.</td>
<td>benzoquinone</td>
</tr>
<tr>
<td>benzotriaz.</td>
<td>benzotriazole</td>
</tr>
<tr>
<td>buff.</td>
<td>buffer [of]</td>
</tr>
<tr>
<td>BuPyCl</td>
<td>butyl pyridinium chloride</td>
</tr>
<tr>
<td>c- (a,c-)</td>
<td>cation adsorption effects are discussed</td>
</tr>
<tr>
<td>c-sup.</td>
<td>see c-</td>
</tr>
<tr>
<td>carb.</td>
<td>carbide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>catal.</td>
<td>catalytic or catalysts</td>
</tr>
<tr>
<td>cf.</td>
<td>see the listed reference</td>
</tr>
<tr>
<td>char.</td>
<td>characterization</td>
</tr>
<tr>
<td>codepos.</td>
<td>codeposition [of]</td>
</tr>
<tr>
<td>comp.</td>
<td>comparison [of], or compared [to]</td>
</tr>
<tr>
<td>d (depos.)</td>
<td>deposition</td>
</tr>
<tr>
<td>depos. (d)</td>
<td>deposition</td>
</tr>
<tr>
<td>disc.</td>
<td>discussion [of]</td>
</tr>
<tr>
<td>DS</td>
<td>Desorption Spectra</td>
</tr>
<tr>
<td>E&lt;sub&gt;k&lt;/sub&gt;,d ( , )</td>
<td>the characteristic half-wave deposition potential, this is directly followed with the information, (supporting electrolyte, pH of the solution)</td>
</tr>
<tr>
<td>e-</td>
<td>Concentration variation of either adsorbed anions or supporting electrolyte(s), or both</td>
</tr>
<tr>
<td>ED</td>
<td>Electron Diffraction</td>
</tr>
<tr>
<td>eff.</td>
<td>effect[s] [of]</td>
</tr>
<tr>
<td>Ellip.</td>
<td>Ellipsometry</td>
</tr>
<tr>
<td>EM</td>
<td>Electron Microprobe</td>
</tr>
<tr>
<td>en</td>
<td>ethylenediamine</td>
</tr>
<tr>
<td>EPE</td>
<td>Electronic PhotoEmission</td>
</tr>
<tr>
<td>Et&lt;sub&gt;4&lt;/sub&gt;NClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>ethylammonium perchlorate</td>
</tr>
<tr>
<td>evol.</td>
<td>evolution [of]</td>
</tr>
<tr>
<td>exam.</td>
<td>example, denotes that the UPD example is used for demonstration purposes in a theoretical discussion</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Fe-TsPc</td>
<td>iron tetrasulfonated phthalocyanines</td>
</tr>
<tr>
<td>FIM</td>
<td>Field Ion Microscope</td>
</tr>
<tr>
<td>gen. disc.</td>
<td>general discussion, applicable to UPD as a whole</td>
</tr>
<tr>
<td>gen. theory</td>
<td>general theory, applicable to UPD as a whole</td>
</tr>
<tr>
<td>graph.</td>
<td>graphite</td>
</tr>
<tr>
<td>HOAc</td>
<td>acetic acid</td>
</tr>
<tr>
<td>hydroquin.</td>
<td>hydroquinone</td>
</tr>
<tr>
<td>increas.</td>
<td>increase</td>
</tr>
<tr>
<td>mc</td>
<td>mica</td>
</tr>
<tr>
<td>mech.</td>
<td>mechanism [of]</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>mono.</td>
<td>monolayer [of]</td>
</tr>
<tr>
<td>monosacch.</td>
<td>monosaccharides, listed under catalytic effects of reactions (cf. r-)</td>
</tr>
<tr>
<td>mono. red. sep. bulk</td>
<td>denotes that submonolayer or monolayer deposition is separate from bulk deposition</td>
</tr>
<tr>
<td>Moss.</td>
<td>Mossbauer Effect</td>
</tr>
<tr>
<td>mult.</td>
<td>multiple</td>
</tr>
<tr>
<td>NA</td>
<td>adatom or attribute information not available at the time of compilation</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate anion</td>
</tr>
<tr>
<td>org.</td>
<td>original</td>
</tr>
<tr>
<td>oxid.</td>
<td>oxidation [of]</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>part.-part. inter.</td>
<td>particle-particle interactions, denotes that interactions between UPD atoms are discussed</td>
</tr>
<tr>
<td>pg:graph</td>
<td>pyrolytic graphite</td>
</tr>
<tr>
<td>phenyldinitrometh.</td>
<td>phenyldinitromethane</td>
</tr>
<tr>
<td>phenynitrometh.</td>
<td>phenynitromethane</td>
</tr>
<tr>
<td>photo. exam.</td>
<td>photographic examination in conjunction with radiotracer methods (RTM)</td>
</tr>
<tr>
<td>pot.</td>
<td>potential</td>
</tr>
<tr>
<td>PPC</td>
<td>propylene carbonate</td>
</tr>
<tr>
<td>Pt(S)-I</td>
<td>an abbreviation for Pt(S)[6(111)x(111)]-I, an I pretreated crystal face of Pt</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>r-</td>
<td>compound(s) following this symbol were studied for &quot;catalytic&quot; effects due to UPD</td>
</tr>
<tr>
<td>R (bold)</td>
<td>Review of UPD</td>
</tr>
<tr>
<td>react.</td>
<td>reactivity [of]</td>
</tr>
<tr>
<td>red.</td>
<td>reduction [of]</td>
</tr>
<tr>
<td>ref.</td>
<td>reference</td>
</tr>
<tr>
<td>reg.</td>
<td>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.</td>
</tr>
<tr>
<td>revers.</td>
<td>reversibility</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflected High Energy Electron Diffraction</td>
</tr>
<tr>
<td>RTM</td>
<td>RadioTracer Methods</td>
</tr>
<tr>
<td>rxns.</td>
<td>reactions [of]</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>sep.</td>
<td>separate [from]</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Scattering</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation, use of, to monitor UPD monolayer growth on substrate</td>
</tr>
<tr>
<td>solns.</td>
<td>solutions</td>
</tr>
<tr>
<td>SRS</td>
<td>Specular Reflectance Studies {Spectroscopy}, includes differential specular reflectance</td>
</tr>
<tr>
<td>strip.</td>
<td>stripping</td>
</tr>
<tr>
<td>substr.</td>
<td>substrate</td>
</tr>
<tr>
<td>surf.</td>
<td>surface</td>
</tr>
<tr>
<td>T {bold}</td>
<td>theoretical discussion of UPD</td>
</tr>
<tr>
<td>Temp.</td>
<td>Temperature [effects of]</td>
</tr>
<tr>
<td>thermo.</td>
<td>thermodynamics [discussion of]</td>
</tr>
<tr>
<td>trans. to Ar electrochem.</td>
<td>see UHV</td>
</tr>
<tr>
<td>UHV</td>
<td>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.</td>
</tr>
</tbody>
</table>
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.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Adatom(s)</th>
<th>Attributes</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Bi</td>
<td>1 M HNO$_3$</td>
<td>94, 95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HClO$_4$; KCl</td>
<td>268</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 M HClO$_4$; $\Delta E_p$=0.065</td>
<td>193, 268</td>
</tr>
<tr>
<td>Bi/Pb</td>
<td></td>
<td>HClO$_4$/KCl</td>
<td>267</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td>SERS; 0.1 M KCl; a-pyridine</td>
<td>342</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M HClO$_4$; a-Cl$^-$, HS$_2$O$_4^-$, thiourea</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T; 0.5 M Na$_2$SO$_4$</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>XRD; 0.5 M NaCl; $\Delta E_p$=0.19 (cf. 193)</td>
<td>279</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M Na$_2$SO$_4$ (3); $\Delta E_p$=0.16</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>1 M HClO$_4$; 0.5 M Na$_2$SO$_4$</td>
<td>274</td>
</tr>
<tr>
<td>Hg</td>
<td></td>
<td>surf. char.</td>
<td>148</td>
</tr>
<tr>
<td>Li</td>
<td></td>
<td>1 M LiClO$_4$ in ACN; $\Delta E_p$=0.96</td>
<td>193</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M LiClO$_4$ in PPC; $\Delta E_p$=1.00</td>
<td>193</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>SERS; 0.1 M KCl; a-Cl$^-$, pyridine</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SHG; 0.1 M NaOAc; surf. depos. monitoring</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 M NaClO$_4$ (3.5)</td>
<td>164</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SERS; 0.1 M KCl/0.05 M pyridine (5.5)</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 mM La(ClO$_4$)$_3$/3 mM HClO$_4$; r-Cr(NH$_3$)$_6^{3+}$ red.</td>
<td>207, 208</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 M NaClO$_4$/3 mM HClO$_4$; r-reds. of Cr(OH$_2$)$_6^{3+}$, Cr(OH$_2$)$_5F^{2+}$, Cr(OH$_2$)$_5$SO$_3^-$, Cr(NH$_3$)$_5OH^{2+}$, Cr(en)$_3^{3+}$, Eu(OH$_2$)$_6^{3+}$</td>
<td>207, 208</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 M LiClO$_4$ in MeOH; r-red. of dinitrobenzenes</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a-I$^-$</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 M HNO$_3$</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 M Na$_2$SO$_4$ (2); 0.5 M NaClO$_4$ (2); a-Cl$^-$, Br$^-$, I$^-$</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T; NaClO$_4$/HClO$_4$; H$_2$SO$_4$</td>
<td>211</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 M NaOH; 0.1 M Na$_2$SO$_4$ (4); 0.1 M Na$_2$CO$_3$</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T (2); 0.5 M KCl</td>
<td>264, 273</td>
</tr>
<tr>
<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Ag</td>
<td>Pb</td>
<td>Continued</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>( \text{HClO}_4; \text{KCl} )</td>
<td>268</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>( 0.5 \text{ M solns. of NH}_4\text{ClO}_4; \text{NaF; NH}_2\text{SO}_3\text{H; KI; KCl; KSCN; KBr} )</td>
<td>266</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>SHG</td>
<td>91</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>( \text{NaClO}_4/\text{HClO}_4 ) (5); catal. surf. area measurements</td>
<td>109</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>SERS</td>
<td>196</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>RTM; 0.16 M sodium tartrate; 0.3 M NaOH</td>
<td>218</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>1 M NaClO(_4) (3); ( \Delta E_p=0.16 )</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>0.5 M KCl; ( \Delta E_p=0.12 )</td>
<td>193</td>
</tr>
<tr>
<td>Pb/Bl</td>
<td></td>
<td>( \text{HClO}_4/\text{KCl} )</td>
<td>267</td>
</tr>
<tr>
<td>Pb/Tl</td>
<td></td>
<td>( 0.5 \text{ M NH}_4\text{ClO}_4; 0.5 \text{ M KCl} )</td>
<td>267</td>
</tr>
<tr>
<td>Po</td>
<td></td>
<td>Photo. exam.; surf. char.</td>
<td>80</td>
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<tr>
<td>Sn</td>
<td></td>
<td>1 M KCl/10 mM HCl</td>
<td>278</td>
</tr>
<tr>
<td>Tl</td>
<td></td>
<td>SERS; 0.1 M KCl; a-pyridine</td>
<td>342</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>SERS; 0.1 M KCl (8); a-benzotriaz.</td>
<td>178</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>T; SRS; 1 M ( \text{HClO}_4 )</td>
<td>308</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>SERS; 0.5 M Na(_2)SO(_4)/1 mM ( \text{HClO}_4 )</td>
<td>34</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>40 mM La(( \text{ClO}_4 ))(_3)/3 mM ( \text{HClO}_4 ); r-Cr(NH(_3))(_3)(^{3+}) red.</td>
<td>207, 208</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>0.5 M NaClO(_4)/3 mM ( \text{HClO}_4 ); r-reds. of Cr(( \text{OH}_2 ))(_6)(^{3+}), Cr(( \text{OH}_2 ))(_5)(^{2+}), Cr(( \text{OH}_2 ))(_5)(^{3+}), Cr(NH(_3))(_5)OH(_2)(^{3+}), Cr(en)(_3)(^{3+}), Eu(( \text{OH}_2 ))(_n)(^{3+})</td>
<td>207, 208</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>a-I(^-)</td>
<td>25</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>0.5 M Na(_2)SO(_4) (2); 0.5 M NaClO(_4) (2); a-Cl(^-), Br(^-), I(^-)</td>
<td>198</td>
</tr>
<tr>
<td>*</td>
<td></td>
<td>0.5 M KCl</td>
<td>265, 210</td>
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<td>*</td>
<td></td>
<td>NaClO(_4) in MeOH; a-Cl(^-)</td>
<td>271</td>
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<tr>
<td>*</td>
<td></td>
<td>RTM; 0.16 M sodium tartrate; 0.3 M NaOH</td>
<td>218</td>
</tr>
<tr>
<td>*</td>
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<td>1 M Na(_2)SO(_4) (3); ( \Delta E_p=0.275 )</td>
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<tr>
<td>Ag</td>
<td>Tl</td>
<td>* 0.5 M KCl; $\Delta E_p = 0.18$</td>
<td>268, 193</td>
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<td>Tl/Pb</td>
<td>0.5 M NH$_4$ClO$_4$; 0.5 M KCl</td>
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<tr>
<td>Zn</td>
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<td>SEM; XRD; 1 M KOH; $\Delta E_p = 0.15$</td>
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<td>Ag-glass</td>
<td>Pb</td>
<td>Au vapor depos.; LEED; RHEED;</td>
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<td>0.5 M NaClO$_4$ (2)</td>
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<td>Ag-mc</td>
<td>Pb</td>
<td>Au vapor depos.; LEED; RHEED;</td>
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<td>0.5 M NaClO$_4$ (2)</td>
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<td>Ag(100)</td>
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<td>0.5 M HClO$_4$; r$_O_2$ red.; +s</td>
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<tr>
<td></td>
<td>Cd</td>
<td>T; 0.5 M Na$_2$SO$_4$</td>
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<td>Pb</td>
<td>0.5 M NaCl (3); effects of SDS</td>
<td>27</td>
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<tr>
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<td>$\Delta E_p = 200-300$ mV</td>
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<td></td>
<td>* T; 0.5 M NaClO$_4$/5 mM HClO$_4$</td>
<td>44, 46</td>
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<td>* T; 0.5 M Na$_2$SO$_4$/5 mM HClO$_4$</td>
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<td>ads. kinetics</td>
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<td>* 0.5 M HClO$_4$; r$_O_2$ red.; a-Cl$^-$</td>
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<td>* 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</td>
<td>37</td>
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<td></td>
<td></td>
<td>* 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.</td>
<td>38</td>
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<td></td>
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<td>* 0.5 M NaOAc/0.1 M HOAc; 0.5 M Na$_2$SO$_4$/1 mM HClO$_4$; surf. char.</td>
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<td>* 0.1 M HClO$_4$; r-Fe-TsPc</td>
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<td>* 0.5 M HClO$_4$; r$_O_2$ red.; +s</td>
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<td>* 0.2 M LiClO$_4$ in MeOH; r-nitrobenz. oxid., nitrosobenz. oxid.</td>
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<td>* HClO$_4$; H$_2$SO$_4$; r-red. of quinone, H$^+$, persulfate</td>
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<td>* T; isotherm ads.</td>
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<td>Attributes</td>
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<td>* SEM; 0.5 M NaClO₄/1 mM HClO₄</td>
<td>298</td>
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<tr>
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<td></td>
<td>* 1 M HClO₄</td>
<td>98</td>
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<tr>
<td></td>
<td></td>
<td>* 0.5 M NaClO₄; 0.5 M Na₂SO₄ (2-4); r-red. of Fe³⁺, Ce⁴⁺, NO₃⁻; +s</td>
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<td>Tl</td>
<td>0.5 M NaCl (3); effects of SDS</td>
<td>27</td>
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<td>ΔEₚ = 200-300 mV</td>
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<td>* T; 0.5 M Na₂SO₄/5 mM HClO₄; ads. kinetics</td>
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<td></td>
<td>* 0.5 M HClO₄; r-O₂ red.; a-Cl⁻</td>
<td>350</td>
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<td>* 0.5 M NaOAc/0.1 M HOAc; 0.5 M Na₂SO₄/1 mM HClO₄; surf. char.</td>
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<td></td>
<td>* SRS; 0.5 M Na₂SO₄/1 mM HClO₄</td>
<td>34</td>
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<td>* HClO₄; H₂SO₄; r-red. of quinone, H⁺, persulfate</td>
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<td></td>
<td></td>
<td>* T; isotherm ads.</td>
<td>327</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M KCl</td>
<td>153, 210</td>
</tr>
<tr>
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<td></td>
<td>* T; 0.5 M KCl; 0.5 M NaClO₄/10 mM HClO₄</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>* HClO₄; KCl</td>
<td>268</td>
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<td>* SEM; 0.5 M Na₂SO₄/1 mM HClO₄</td>
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<td>* 0.5 M NaClO₄; 0.5 M Na₂SO₄ (2-4); r-red. of Fe³⁺, Ce⁴⁺, NO₃⁻; +s</td>
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<tr>
<td>Ag(110)</td>
<td>Bi</td>
<td>0.5 M HClO₄; r-O₂ red.; +s</td>
<td>176</td>
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<tr>
<td></td>
<td>Pb</td>
<td>T; 0.5 M Na₂SO₄/5 mM HClO₄; ads. kinetics</td>
<td>180</td>
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<tr>
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<td></td>
<td>* 0.5 M HClO₄; r-O₂ red.; a-Cl⁻</td>
<td>350</td>
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<tr>
<td></td>
<td></td>
<td>* T; 0.5 M NaClO₄/5 mM HClO₄</td>
<td>44</td>
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<td>* SRS; as PbO; 0.5 M NaOAc/0.1 M HOAc; 0.5 M HClO₄; 0.5 M NaClO₄ (5.4); mult. layer UPD; comp. w/ Tl depos.</td>
<td>38</td>
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<tr>
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<td>* 0.5 M HClO₄; r-O₂ red.; +s</td>
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<tr>
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<td>Ag(110)</td>
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</tr>
<tr>
<td></td>
<td>*</td>
<td>0.5 M NaOAc/0.1 M HOAc; 0.5 M Na_2SO_4/1 mM HClO_4; surf. char.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>HClO_4; H_2SO_4; r-red. of quinone, H^+, persulfate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>1 M HClO_4</td>
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<tr>
<td></td>
<td>*</td>
<td>0.5 M NaClO_4; 0.5 M Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s</td>
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<tr>
<td>Tl</td>
<td>T; 0.5 M Na_2SO_4/5 mM HClO_4; ads. kinetics</td>
<td></td>
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<tr>
<td></td>
<td>*</td>
<td>0.5 M HClO_4; r-O_2 red.; a-Cl^-</td>
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<td>*</td>
<td>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</td>
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<tr>
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<td>*</td>
<td>SRS; 0.5 M Na_2SO_4/1 mM HClO_4</td>
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<td>HClO_4; H_2SO_4; r-red. of quinone, H^+, persulfate</td>
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<tr>
<td></td>
<td>*</td>
<td>0.5 M KCl</td>
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<td>*</td>
<td>T; 0.5 M KCl; 0.5 M NaClO_4/10 mM HClO_4</td>
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<td>0.5 M NaClO_4; 0.5 M Na_2SO_4 (2-4); r-red. of Fe^{3+}, Ce^{4+}, NO_3^-; +s</td>
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<tr>
<td>Ag(111)</td>
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<td>0.5 M HClO_4; r-O_2 red.; +s</td>
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<tr>
<td></td>
<td>Cd</td>
<td>T; 0.5 M Na_2SO_4</td>
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<tr>
<td></td>
<td>Cd/Tl</td>
<td>1 mM HClO_4; r-nitrate red.; comment to ref. 345</td>
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<td>T; a-0.5 M solns. of ClO_4^-, OAc^-, C_6H_5O_3^-</td>
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<td>*</td>
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<td>T; Ellip.; 1 M NaClO_4 (3)</td>
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<td>Ag(111)</td>
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<td>T; SRS; 0.3 M NaOAc/0.01 M HOAc; 0.5 M NaClO₄/0.2 M NaOH/0.1 M citric acid; HClO₄; 2-D nucleation</td>
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<td>*</td>
<td>SRS; as PbO; 0.5 M NaOAc/0.1 M HOAc; 0.5 M HClO₄; 0.5 M NaClO₄ (5.4); mult. layer UPD; comp. w/ Tl depos.</td>
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<td>0.5 M NaOAc/0.1 M HOAc; 0.5 M Na₂SO₄/1 mM HClO₄; surf. char.</td>
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<td>*</td>
<td>0.5 M HClO₄; r-Ο₂ red.; +s</td>
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<tr>
<td>*</td>
<td>0.5 M NaClO₄</td>
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<td>0.2 M LiClO₄ in MeOH; r-nitrobenz. oxid., nitrosobenz. oxid.</td>
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<td>T; 0.5 M Na₂SO₄/1 mM HClO₄; 2-D growth study</td>
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<tr>
<td>*</td>
<td>SEM; 0.5 M NaClO₄/1 mM HClO₄</td>
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<td>1 M HClO₄</td>
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<td>*</td>
<td>0.5 M NaClO₄; 0.5 M Na₂SO₄ (2-4); r-red. of Fe³⁺, Ce⁴⁺, NO₃⁻; +s</td>
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<td>0.5 M HClO₄; r-Ο₂ red.; a-Cl⁻</td>
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<td>*</td>
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<td>** T; 0.5 M NaSO₄/1 mM HClO₄; 2-D growth</td>
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<td>Cd/Tl</td>
<td>Ag vapor depos.; K₂SO₄/HClO₄;</td>
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<td>Li</td>
<td>LiClO₄ in PPC</td>
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<td>* T; gen. theory; kinetics</td>
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<td>* T; 0.2 M HClO₄; thermo.</td>
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<td>* T; 0.2 M H₂SO₄</td>
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<td>* QCM; 0.2 M H₂SO₄; 0.2 M NaClO₄ in ACN</td>
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<td>* T; Ellip.; HClO₄; H₂SO₄</td>
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<td>* RTM; 1 M HClO₄; a-Cl⁻, HSO₄⁻</td>
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<td>* HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
<td>9</td>
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<td>* 1 M H₂SO₄; r-Fe²⁺ oxid.</td>
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<td>* r-oxid. of MeOH, HCHO, HCOOH</td>
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<td>* exam.; gen. disc.; 0.1 M HClO₄</td>
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<td>* T; NaClO₄/HClO₄; H₂SO₄</td>
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<td>* T (2); 1 M HClO₄</td>
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<td>* phosphate buff. (8)</td>
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<td>* RTM; HClO₄</td>
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<td>Eₓₜ,q(0.1 M KNO₃, pH 4)=0.8</td>
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<td>* 0.5 M H$_2$SO$_4$; a-Cl$^-$; $\Delta E_p=0.59$ (cf. 193)</td>
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<td>* SRS (1); 1 M HClO$_4$</td>
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<td>* r-O$_2$ red.</td>
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<td>* Ellip.</td>
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<td>* r-O$_2$ red., H$_2$ evol.</td>
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<td>* H$_2$SO$_4$; HNO$_3$</td>
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<td>* 1 M HCl</td>
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<td>* NaOAc; r-O$_2$ red.</td>
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<td>* RTM; comp. w/ Po depos.</td>
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<td>* HClO$_4$; H$_2$SO$_4$; r-O$_2$ red., H$_2$O$_2$ red.</td>
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<td>* 0.5 M Na$_2$SO$_4$ (3); $\Delta E_p = 0.505$</td>
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<td>* 1 M H$_2$SO$_4$; r-Ti$^{3+}$ oxid.</td>
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<td>T; NaClO$_4$/HClO$_4$; H$_2$SO$_4$</td>
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<td>* 0.1 M NaClO$_4$; effect of anions, H$^+$</td>
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<td>* H$_2$SO$_4$; a-thiourea</td>
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<td>* r-O$_2$ red.</td>
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<td>* 0.1 M KCl</td>
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<td>T; 0.2 M H$_2$SO$_4$</td>
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<td>Ni</td>
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<td>* 0.1 M Na$_2$SO$_4$</td>
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<td>* 0.1 M KSCN; 0.1 M KNO$_3$</td>
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<td>T; 0.2 M HClO₄; thermo.</td>
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<td>* T; as PbO; 1 M NaOH; r-O₂ red.</td>
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<td>* T; 0.5 M NaClO₄/1 mM HClO₄</td>
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<td>* XRD; ED; as PbF₂; 0.01 M HClO₄</td>
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<td>* Ellip.; 1 M HClO₄</td>
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<td>* SRS; 1 M HClO₄; cf. 6,280</td>
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<td>* 0.5 M KCl</td>
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<td>* 0.1 M Et₄NClO₄/10 mM HClO₄ in ACN; comp. w/ aqueous UPD</td>
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<td>* QCM; 0.2 M H₂SO₄; 0.2 M NaClO₄ in ACN</td>
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<td>* HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
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<td>* r-oxid. of MeOH, HCHO, HCOOH</td>
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<td>* 1 M HNO₃</td>
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<td>* SRS; 1 M NaClO₄; 0.5 M Na₂SO₄</td>
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<td>* 0.5 M Na₂SO₄ (2); 0.5 M NaClO₄ (2); a-Cl⁻, Br⁻, I⁻</td>
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<td>* T; NaClO₄/HClO₄; H₂SO₄</td>
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<td>* ~ 0.1 M Na₂CO₃</td>
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<td>* SRS; HClO₄</td>
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### Substrate Adatom(s) Attributes Reference(s)

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  NaOAc; r-O<sub>2</sub> red.  
  *  
  RTM; comp. w/ Po depos.  
  *  
  0.5 M KCl/0.1 mM HCl  
  *  
  1 M NaClO<sub>4</sub> (3); ∆E<sub>p</sub>=0.40  
  *  
  1 M NaClO<sub>4</sub>/0.2 M KCl (3); ∆E<sub>p</sub>=0.33  
  
**Pd**  
*  
  1 M H<sub>2</sub>SO<sub>4</sub>  
  *  
  r-oxid. of MeOH, HCHO, HCOOH  
  *  
  r-H<sub>2</sub> evol.  
  
**Po**  
*  
  1 M HNO<sub>3</sub>  
  *  
  e-H<sup>+</sup>  
  *  
  Photo. exam.; surf. char.  
  
**Pt**  
*  
  1 M H<sub>2</sub>SO<sub>4</sub>  
  *  
  r-oxid. of MeOH, HCHO, HCOOH  
  
**Rh**  
*  
  r-oxid. of MeOH, HCHO, HCOOH  
  
**Ru**  
*  
  RTM; as RuNOCl<sub>3</sub>; HCl  
  
**Sb**  
*  
  phosphate buff. (8)  
  *  
  ~ 0.1 M Na<sub>2</sub>CO<sub>3</sub>  
  *  
  1 M HCl  
  
**Sn**  
*  
  T; SRS; 1 M HClO<sub>4</sub>  
  *  
  phosphate buff. (8)  
  *  
  4 M HCl  
  *  
  NaOAc; r-O<sub>2</sub> red.  
  *  
  +e  
  
**Tl**  
*  
  T; SRS; 1 M HClO<sub>4</sub>  
  *  
  T; 0.5 M KCl/0.1 mM HCl; 0.2 M HClO<sub>4</sub>  
  *  
  0.1 M Et<sub>4</sub>NClO<sub>4</sub>/10 mM HClO<sub>4</sub> in ACN; comp. w/ aqueous UPD  
  *  
  1 M KF; r-Ru(NH<sub>3</sub>)<sup>2+</sup> oxid.  
  *  
  T; NaOH; HClO<sub>4</sub>; NaOH/HClO<sub>4</sub>; r-O<sub>2</sub> red.  
  *  
  HClO<sub>4</sub>; H<sub>2</sub>SO<sub>4</sub>; r-O<sub>2</sub> red., H<sub>2</sub>O<sub>2</sub> red.  
  *  
  r-oxid. of MeOH, HCHO, HCOOH  

15, 81, 330, 193, 121, 325, 39, 282, 80, 121, 325, 205, 224, 232, 272, 308, 224, 329, 59, 330, 15, 28, 308, 332, 191, 165, 2, 9, 39
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<td>* HCIO4; H2SO4; HNO3; HCl</td>
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<td>* SRS; 1 M NaClO4; 0.5 M Na2SO4</td>
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<td>* 0.5 M Na2SO4 (2); 0.5 M NaClO4 (2);</td>
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<td>* T; NaClO4/HClO4; H2SO4</td>
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<td>* 0.5 M KCl</td>
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<td>* ~ 0.1 M Na2SO4</td>
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<td>* HCIO4; KCl; ΔEp(0.5 M KCl)=0.46 (cf. 193)</td>
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<td>* NaOAc; r-O&lt;sub&gt;2&lt;/sub&gt; red.</td>
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<td>* 0.5 M Na2SO4; a-Br&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>* 0.5 M KCl/0.1 mM HCl</td>
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<td>* 0.5 M Na2SO4 (3); ΔEp=0.685</td>
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<tr>
<td>Au(100)</td>
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<td>0.5 M HClO4; r-O&lt;sub&gt;2&lt;/sub&gt; red.; +s</td>
<td>176</td>
</tr>
<tr>
<td></td>
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<td>* DS; 1 M HClO4</td>
<td>286</td>
</tr>
<tr>
<td>Cu</td>
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<td>286</td>
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<tr>
<td></td>
<td></td>
<td>* 1 M HClO4</td>
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</tr>
<tr>
<td></td>
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<td>* RHEED; as CuSO4; 1 M HClO4</td>
<td>29</td>
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<tr>
<td>Pb</td>
<td>T; Ca(ClO4)下/10 mM HClO4</td>
<td>142</td>
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<td></td>
<td>* 1 mM PbF&lt;sub&gt;2&lt;/sub&gt;/10 mM HClO4; +s</td>
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<tr>
<td>Substrate</td>
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<td>Au(100)</td>
<td>Pb</td>
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<tr>
<td></td>
<td>* T; 0.5 M NaClO$_4$/1 mM HClO$_4$</td>
<td>101,102</td>
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</tr>
<tr>
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<td>* as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p$=f(face); +s</td>
<td>138</td>
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<tr>
<td></td>
<td>* SRS; 1 M HClO$_4$; cf. 6,280</td>
<td>7</td>
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<td>* 0.5 M HClO$_4$; r-O$_2$ red.; +s</td>
<td>176</td>
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<td></td>
<td>* DS; 1 M HClO$_4$</td>
<td>286</td>
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</tr>
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<td></td>
<td>* as PbF$_2$; 0.01 M HClO$_4$; ++ vicinal faces</td>
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<tr>
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<td>* AES; LEED</td>
<td>128,129</td>
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<td>DS; 1 M HClO$_4$</td>
<td>286</td>
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<td>Tl</td>
<td>DS; 1 M HClO$_4$</td>
<td>286</td>
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<tr>
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<td>176</td>
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<tr>
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<td>* DS; 1 M HClO$_4$</td>
<td>286</td>
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<td>Cu</td>
<td>DS; 1 M HClO$_4$</td>
<td>286</td>
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</tr>
<tr>
<td></td>
<td>* 1 M HClO$_4$</td>
<td>98</td>
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<tr>
<td>Pb</td>
<td>T; Ca(ClO$_4$)$_2$/10 mM HClO$_4$</td>
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<tr>
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<td>* as 1 mM PbF$_2$; 10 mM HClO$_4$; +s</td>
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<td>* T; 0.5 M NaClO$_4$/1 mM HClO$_4$</td>
<td>101,102</td>
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<td>* as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p$=f(face); +s</td>
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<td>* SRS; 1 M HClO$_4$; see refs. 6,280</td>
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<td></td>
<td>* 0.5 M HClO$_4$; r-O$_2$ red.; +s</td>
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<td>* DS; 1 M HClO$_4$</td>
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<td>* AES; LEED</td>
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<td>286</td>
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<td>Tl</td>
<td>DS; 1 M HClO$_4$</td>
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<td>0.5 M HClO$_4$; r-O$_2$ red.; +s</td>
<td>176</td>
</tr>
<tr>
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<td>* DS; 1 M HClO$_4$</td>
<td>286</td>
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<td>AES; LEED; RHEED; 0.1 M HClO$_4$</td>
<td>237</td>
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<td>* DS; 1 M HClO$_4$</td>
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<td>* 1 M HClO$_4$</td>
<td>98</td>
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<tr>
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<td>* RHEED; as CuSO$_4$; 1 M HClO$_4$</td>
<td>29</td>
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<tr>
<td>Pb</td>
<td>T; Ca(ClO$_4$)$_2$/10 mM HClO$_4$</td>
<td>142</td>
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</tr>
<tr>
<td></td>
<td>* as 1 mM PbF$_2$; 10 mM HClO$_4$; $\Delta E_p$=0.28; +s</td>
<td>141</td>
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<td>Substrate</td>
<td>Adatom(s)</td>
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<tr>
<td>Au(111)</td>
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<td>* T; 0.5 M NaClO$_4$/1 mM HClO$_4$</td>
<td>101,102</td>
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<tr>
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<td>* as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
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<td>* SRS; 1 M HClO$_4$; see refs. 6,280</td>
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</tr>
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<td>* 0.5 M HClO$_4$; r-O$_2$ red.; +s</td>
<td>176</td>
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<tr>
<td></td>
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<td>* DS; 1 M HClO$_4$</td>
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<td>* AES; LEED</td>
<td>128,129</td>
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<td>DS; 1 M HClO$_4$</td>
<td>286</td>
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<td>DS; 1 M HClO$_4$</td>
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<td>* as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(211)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
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<td>Au(221)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
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<tr>
<td>Au(310)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(311)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(320)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(331)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(332)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(410)</td>
<td>Pb</td>
<td>AES; LEED</td>
<td>128,129</td>
</tr>
<tr>
<td>Au(511)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(533)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(551)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
<tr>
<td>Au(554)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
<td>138</td>
</tr>
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<td>Au(755)</td>
<td>Pb</td>
<td>as PbF$_2$; 0.01 M HClO$_4$; $\Delta E_p=f$ (face); +s</td>
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<td>Au/m-Ag</td>
<td>Pb</td>
<td>0.5 M NaClO$_4$ (2)</td>
<td>301</td>
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<tr>
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<td>Tl 0.5 M NaClO$_4$ (2)</td>
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<tr>
<td>Au/m-Cu</td>
<td>Pb</td>
<td>0.5 M NaClO$_4$ (2)</td>
<td>301</td>
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<tr>
<td>Au/Pt</td>
<td>Pb</td>
<td>1 M NaOH; r-ethylene glycol oxid.</td>
<td>31</td>
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<tr>
<td>B/carb</td>
<td>Tl</td>
<td>HClO$_4$; H$_2$SO$_4$; HNO$_3$; HCl</td>
<td>166</td>
</tr>
<tr>
<td>Bi</td>
<td>Cd</td>
<td>0.5 M NH$_4$ClO$_4$/0.5 M HClO$_4$; HClO$_4$; KCl</td>
<td>268</td>
</tr>
<tr>
<td>Li</td>
<td>LiClO$_4$ in PPC</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>1 M HNO$_3$</td>
<td>82</td>
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</tr>
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<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
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</tr>
<tr>
<td>Bi</td>
<td>Pb</td>
<td>* T; NaClO$_4$/HCIO$_4$; H$_2$SO$_4$</td>
<td>211</td>
</tr>
<tr>
<td>Sn</td>
<td>C:glassy</td>
<td>0.5 M NH$_4$ClO$_4$/0.5 M HCIO$_4$; HCIO$_4$; KCl</td>
<td>268</td>
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<tr>
<td>C:glassy</td>
<td>Ag</td>
<td>1 M KNO$_3$ (3)</td>
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<td>Cu/Hg</td>
<td>0.1 M KNO$_3$/10 mM HNO$_3$</td>
<td>179</td>
</tr>
<tr>
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<td>H/Hg</td>
<td>0.1 M KNO$_3$/10 mM HNO$_3$</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>1 M KNO$_3$ (3)</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>Hg/Cu</td>
<td>0.1 M KNO$_3$/10 mM HNO$_3$</td>
<td>179</td>
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<tr>
<td></td>
<td>Hg/H</td>
<td>0.1 M KNO$_3$/10 mM HNO$_3$</td>
<td>179</td>
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<tr>
<td></td>
<td>K</td>
<td>XRD; LiCl/KCl melt</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>Li</td>
<td>XRD; LiCl/KCl melt</td>
<td>167</td>
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<tr>
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<td>Pb</td>
<td>0.5 M HCIO$_4$; r-0$_2$ red., H$_2$O$_2$ red.</td>
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<td>Pt</td>
<td>r-H$_2$ evol.</td>
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<tr>
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<td>Ru</td>
<td>r-H$_2$ evol.</td>
<td>119</td>
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<tr>
<td>C:graph.</td>
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<td>as AgNO$_3$; Na$_2$SO$_4$; NaClO$_4$; HCl; LiClO$_4$/ACN</td>
<td>233</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HCl</td>
<td>53</td>
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<tr>
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<td>* 0.2 M KNO$_3$</td>
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<td>* RTM; +e</td>
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</tr>
<tr>
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<td>HNO$_3$</td>
<td></td>
<td>53</td>
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<tr>
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<td>Cd</td>
<td>as CdSO$_4$; Na$_2$SO$_4$; NaClO$_4$; HCl; LiClO$_4$ in ACN</td>
<td>233</td>
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<td>Cu</td>
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<td>233</td>
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<td>* EM; XRF; 0.1 M KCIO$_4$/0.1 M HCIO$_4$</td>
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<td>K</td>
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<td>XRD; LiCl/KCl melt</td>
<td>167</td>
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<td>Pb</td>
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<td>as Pb(NO$_3$)$_2$; Na$_2$SO$_4$; NaClO$_4$; HCl; LiClO$_4$ in ACN</td>
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<td>Attributes</td>
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<td>C: graph.</td>
<td>Pb</td>
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<td>* HNO₃</td>
<td>53</td>
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<td>XRD; LiCl/KCl melt</td>
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<td>Li</td>
<td>XRD; LiCl/KCl melt</td>
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<td>Zn</td>
<td>RTM; +e</td>
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<td>Cd</td>
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<td>Bi</td>
<td>RTM; 0.25 M tartrate; a-0.1 M Cl⁻</td>
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<td></td>
<td>Cd</td>
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<td>T; SRS; 1 M HClO₄</td>
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<td>* RTM; 1 M HClO₄/24 mM H₂SO₄; a-HSO₄⁻</td>
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<td>* 1 M Na₂SO₄; ΔEp=0.225</td>
<td>193</td>
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<td>Li</td>
<td>1 M LiClO₄ in PPC; ΔEp=1.05</td>
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<td>Pb</td>
<td>Ellip.; 1 M NaClO₄ (3); surf. char.; presence of rhodamine-B dye</td>
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<td>* 0.5 M HClO₄; r-O₂ red.</td>
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<td></td>
<td></td>
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<td>* 1 M HNO₃</td>
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<td>* HClO₄; KCl; ΔEp(0.5 M KCl)=0.13 (cf. 193)</td>
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<td></td>
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<td></td>
<td>* RTM; comp. w/ Po depos.</td>
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<tr>
<td></td>
<td>Pb/Tl</td>
<td>0.5 M KCl</td>
<td>267</td>
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<td>Ru</td>
<td>RTM; as RuNOCl₃; HCl</td>
<td>205</td>
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<td>Tl</td>
<td>0.5 M HClO₄; r-O₂ red.</td>
<td>186</td>
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<td>* HClO₄; KCl; ΔEp(0.5 M KCl)=0.13 (cf. 193)</td>
<td>268</td>
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<td>* 1 M Na₂SO₄; ΔEp=0.335</td>
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<td>Tl/Pb</td>
<td>0.5 M KCl</td>
<td>267</td>
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<tr>
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<td>Zn</td>
<td>RTM; +e</td>
<td>126</td>
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<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
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<tr>
<td>Cu(100) Pb</td>
<td>as Pb(OAc)$_2$; 0.5 M NaClO$_4$/1 mM HClO$_4$; comp. w/ Ag(100,110,111)-Pb</td>
<td>36</td>
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<td>Cu(110) Pb</td>
<td>as Pb(OAc)$_2$; 0.5 M NaClO$_4$/1 mM HClO$_4$; comp. w/ Ag(100,110,111)-Pb</td>
<td>36</td>
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<td>Cu(111) Cu/Cd</td>
<td>T; Na$_2$SO$_4$; +e</td>
<td>63</td>
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<td>* T; 0.19 M Na$_2$SO$_4$/0.45 M (NH$_4$)$_2$SO$_4$/en</td>
<td>64</td>
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<td>Cd</td>
<td>T; Na$_2$SO$_4$; +e</td>
<td>63</td>
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<td>* T; 0.19 M Na$_2$SO$_4$/0.45 M (NH$_4$)$_2$SO$_4$/en</td>
<td>64</td>
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<td></td>
<td>Pb</td>
<td>T; Ellip.; 1 M NaClO$_4$ (3)</td>
<td>236</td>
</tr>
<tr>
<td></td>
<td>* as Pb(OAc)$_2$; 0.5 M NaClO$_4$/1 mM HClO$_4$; comp. w/ Ag(100,110,111)-Pb</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* e-OAc$^-$, en, H$^+$</td>
<td>65</td>
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</tr>
<tr>
<td>Cu/m-Ag Pb</td>
<td>0.5 M NaClO$_4$ (2)</td>
<td>301</td>
<td></td>
</tr>
<tr>
<td>Fe Mn</td>
<td>5 mM H$_2$SO$_4$</td>
<td>24</td>
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</tr>
<tr>
<td>Pb</td>
<td>0.5 M HClO$_4$; 0.4 M NaCl (3); a-Cl$^-$</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>5 mM H$_2$SO$_4$</td>
<td>24</td>
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<tr>
<td>Tl</td>
<td>0.5 M Na$_2$SO$_4$; a-Cl$^-$</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.5 M (NH$_4$)$_2$SO$_4$/10 mM H$_2$SO$_4$</td>
<td>242</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* 5 mM H$_2$SO$_4$</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Hg Nl</td>
<td>NA</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>r-H$_2$ evol.</td>
<td>119</td>
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</tr>
<tr>
<td>Ru</td>
<td>r-H$_2$ evol.</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* 1 M HCl; r-H$_2$ evol.</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>Ir Ag</td>
<td>1 M H$_2$SO$_4$</td>
<td>204</td>
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<tr>
<td>Cu</td>
<td>0.1 M NaClO$_4$; effect of anions, H$^+$</td>
<td>96</td>
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<tr>
<td>H</td>
<td>H$_2$SO$_4$</td>
<td>54</td>
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<tr>
<td>Pb</td>
<td>T; 1 M HClO$_4$; r-formic acid oxid.</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Mg Li</td>
<td>1 M LiClO$_4$ in PPC</td>
<td>241</td>
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</tr>
<tr>
<td>Mo Po</td>
<td>0.3 M HNO$_3$</td>
<td>80</td>
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</tr>
<tr>
<td>Ni Fe</td>
<td>0.5 M (NH$_4$)$_2$SO$_4$/10 mM H$_2$SO$_4$</td>
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<tr>
<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
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</tr>
<tr>
<td>Ni</td>
<td>Pb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>1 M HNO₃</td>
<td>82</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>0.5 M (NH₄)₂SO₄/10 mM H₂SO₄</td>
<td>242</td>
</tr>
<tr>
<td>Pb</td>
<td>Cd</td>
<td>5 M H₂SO₄; r-O₂ red.</td>
<td>76</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>RTM; 0.5 M H₂SO₄</td>
<td>136</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>RTM; +e</td>
<td>127</td>
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<tr>
<td>Pd</td>
<td>Ag</td>
<td>0.5 M H₂SO₄; r-formic acid oxid.</td>
<td>200</td>
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<tr>
<td></td>
<td></td>
<td>ΔEₚ(Ag on Pd or Pd-Pt)=0.4</td>
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<td></td>
<td>T; 1 M HClO₄; r-formic acid oxid.</td>
<td>14</td>
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<tr>
<td></td>
<td></td>
<td>comp. w/ depos. on Pt &amp; Rh</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>exam.; gen. disc.; 0.1 M HClO₄</td>
<td>67,68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RTM; 0.1 M NaClO₄</td>
<td>258</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eₚ(k, d(0.1 M KNO₃, pH 4))=0.5</td>
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</tr>
<tr>
<td>Au</td>
<td></td>
<td>0.5 M H₂SO₄; r-MeOH oxid.</td>
<td>339</td>
</tr>
<tr>
<td>Bi</td>
<td></td>
<td>T; SRS; 1 M HClO₄</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T; 1 M HClO₄; r-formic acid oxid.</td>
<td>14</td>
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<tr>
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<td></td>
<td>comp. w/ depos. on Pt &amp; Rh</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1 M HClO₄</td>
<td>228</td>
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<tr>
<td></td>
<td></td>
<td>XRD; 1 M HClO₄</td>
<td>230</td>
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<tr>
<td>Cd</td>
<td></td>
<td>T; 1 M HClO₄; r-formic acid oxid.</td>
<td>14</td>
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<tr>
<td></td>
<td></td>
<td>comp. w/ depos. on Pt &amp; Rh</td>
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<tr>
<td></td>
<td></td>
<td>1 M HClO₄</td>
<td>228</td>
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<tr>
<td>Cu</td>
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<td>T; 1 M HClO₄; r-formic acid oxid.</td>
<td>14</td>
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<td>comp. w/ depos. on Pt &amp; Rh</td>
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<td>0.1 M NaClO₄; effect of anions, H⁺</td>
<td>96</td>
</tr>
<tr>
<td>Pb</td>
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<td>T; 1 M HClO₄; r-formic acid oxid.</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>comp. w/ depos. on Pt &amp; Rh</td>
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<tr>
<td></td>
<td></td>
<td>1 M HClO₄</td>
<td>228</td>
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<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
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</tr>
<tr>
<td>Pd</td>
<td>Tl</td>
<td>T; 1 M HClO₄; r-formic acid oxid. comp. w/ depos. on Pt &amp; Rh</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 1 M HClO₄</td>
<td>228</td>
</tr>
<tr>
<td>Pd-Pt</td>
<td>Ag</td>
<td>0.5 M H₂SO₄; r-formic acid oxid. ΔEₚ(Ag on Pd or Pd-Pt)=0.4</td>
<td>200</td>
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<tr>
<td>Pt</td>
<td>Al</td>
<td>AlCl₃/BuPyCl</td>
<td>257</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>T, 0.5 M HClO₄</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 1 M HClO₄; a-Cl⁻, HSO₄⁻</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M HClO₄; 0.5 M H₂SO₄; 0.1 M NaOH; r-hydrazine oxid.</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* T; SRS; 1 M HClO₄</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* T (2); 1 M HClO₄</td>
<td>26,262</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* T (1,2); 0.2 M H₂SO₄</td>
<td>296,320,326</td>
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<tr>
<td></td>
<td></td>
<td>* T; 0.2 M H₂SO₄</td>
<td>317,318</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* XPS; 0.1 M H₂SO₄</td>
<td>143</td>
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<tr>
<td></td>
<td></td>
<td>* AES; XPS; 0.1 M H₂SO₄</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.1 M HClO₄</td>
<td>40,307</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 2 M HClO₄; r-formic acid oxid.</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HNO₃/KNO₃; HNO₃/H₃BO₃; H₂SO₄/Na₂SO₄; NaF; KCl</td>
<td>43</td>
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<tr>
<td></td>
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<td>exam.; gen. disc.; 0.1 M HClO₄</td>
<td>67,68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂SO₄; HClO₄</td>
<td>70</td>
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<tr>
<td></td>
<td></td>
<td>RTM; 1 M NaOH; e⁻H⁺</td>
<td>122</td>
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<tr>
<td></td>
<td></td>
<td>SRS; 1 M HClO₄</td>
<td>222</td>
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<tr>
<td></td>
<td></td>
<td>0.1 M HNO₃; 0.1 M KCl; 0.1 M KNO₃</td>
<td>239</td>
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<tr>
<td></td>
<td></td>
<td>KNO₃; HOAc/NaOAc; HClO₄; +e</td>
<td>244</td>
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<tr>
<td></td>
<td></td>
<td>RTM; 0.1 M KNO₃ (4); 1 M HClO₄/0.1 M NaClO₄; 1 M NaOH/0.1 M NaCN; 0.1 M NH₃; 0.1 M NaCN; Eₓ,d(0.1 M KNO₃, pH 4)=0.6</td>
<td>258</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* r-H₂ evol.</td>
<td>114</td>
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<td>Attributes</td>
<td>Reference(s)</td>
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</tr>
<tr>
<td>Pt</td>
<td>Ag</td>
<td>Continued</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>1 M H₂SO₄; eff. on H ads.</td>
<td>302</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>r-HCHO</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>0.2 M H₂SO₄; r-O₂ red.</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>LiCl-KCl melt</td>
<td>154</td>
<td></td>
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<tr>
<td>*</td>
<td>r-O₂ red., H₂ evol. (1)</td>
<td>225, 254</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>1 M H₂SO₄</td>
<td>325</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>0.5 M H₂SO₄; ΔE_p=0.43⁵</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>1 M LiClO₄ in ACN; ΔE_p=0.44⁵</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>Ag/Cu</td>
<td>RTM; 1 M NaOH; e-H⁺</td>
<td>122</td>
<td></td>
</tr>
<tr>
<td>Ag/Pd</td>
<td>RTM; 1 M NaOH; e-H⁺</td>
<td>122</td>
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<tr>
<td>Ag/Pt</td>
<td>RTM; 1 M NaOH; e-H⁺</td>
<td>122</td>
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<tr>
<td>Au</td>
<td>H₂SO₄; HClO₄</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>0.2 M H₂SO₄</td>
<td>324, 71</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>0.5 M H₂SO₄; r-MeOH oxid.</td>
<td>339</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>0.5 M HClO₄; increas. revers. of r-hydroquin./p-benzoquin., pyrocatechol/o-benzoquin.</td>
<td>185</td>
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<tr>
<td>*</td>
<td>0.5 M HClO₄; 0.5 M H₂SO₄; 0.1 M NaOH; r-hydrazine oxid.</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>T; SRS; 1 M HClO₄</td>
<td>308</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>0.1 M HClO₄</td>
<td>307, 71</td>
<td></td>
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<tr>
<td>*</td>
<td>0.5 M HClO₄; r-bezofuroxan/o-benzoquin. dioxime</td>
<td>188</td>
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<tr>
<td>*</td>
<td>0.5 M NaOH; r-NH₃ red., hydroxyamine oxid.</td>
<td>187</td>
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<tr>
<td>*</td>
<td>0.5 M HClO₄; r-phenyldinitrometh. red., phenylnitrometh. red.</td>
<td>189</td>
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<td>*</td>
<td>0.5 M HClO₄; r-O₂ red.</td>
<td>186</td>
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</tr>
<tr>
<td>*</td>
<td>0.5 M HClO₄; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl⁻</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>*</td>
<td>1 M NaOH; r-ethylene glycol oxid.</td>
<td>177</td>
<td></td>
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<tr>
<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
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</tr>
<tr>
<td>Pt</td>
<td>Bi</td>
<td>Continued</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M HClO₄; r-ethylene glycol oxid.</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 1 M HClO₄; r-formic acid oxid.</td>
<td>10</td>
</tr>
<tr>
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<td></td>
<td>* 2 M HClO₄; r-formic acid oxid.</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
<td>9</td>
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<tr>
<td></td>
<td></td>
<td>* 0.1 M HCl; ΔEₚ=0.56 (cf. 193)</td>
<td>52</td>
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<tr>
<td></td>
<td></td>
<td>* 1 M HNO₃</td>
<td>82</td>
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<tr>
<td></td>
<td></td>
<td>* 0.5 M HClO₄; 0.2 M NaOH; r-oxid. of</td>
<td>347</td>
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<tr>
<td></td>
<td></td>
<td>monosacch.; 3rd body effect; a-Cl⁻</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Temp.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* RTM; 0.25 M tartrate; a-0.1 M Cl⁻</td>
<td>260</td>
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<tr>
<td></td>
<td></td>
<td>* RTM; comp. w/ Po depos.</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* r-HCHO</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO₄</td>
<td>229</td>
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<tr>
<td></td>
<td></td>
<td>* XRD; 1 M HClO₄</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* NA</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.12 M HClO₄; ΔEₚ=0.49</td>
<td>72, 193</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td>0.5 M HClO₄; 0.5 M H₂SO₄; 0.1 M NaOH; r-hydrazine oxid.</td>
<td>181</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M HClO₄; 0.2 M NaOH; r-oxid. of</td>
<td>184</td>
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<tr>
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<td></td>
<td>aliphatic alcohols (MeOH); a-Cl⁻</td>
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<tr>
<td></td>
<td></td>
<td>* 1 M NaOH; r-ethylene glycol oxid.</td>
<td>177</td>
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<tr>
<td></td>
<td></td>
<td>* 0.5 M HClO₄; r-ethylene glycol oxid.</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 1 M HClO₄; r-formic acid oxid.</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 2 M HClO₄; r-formic acid oxid.</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* H₂SO₄</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M KOH</td>
<td>120</td>
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<tr>
<td></td>
<td></td>
<td>* RTM; 1 M HClO₄; a-Cl⁻, HSO₄⁻</td>
<td>155</td>
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<tr>
<td></td>
<td></td>
<td>* 50 mM H₂SO₄</td>
<td>214</td>
</tr>
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<td></td>
<td></td>
<td>* 0.5 M H₂SO₄</td>
<td>348</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO₄</td>
<td>229</td>
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<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
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</tr>
<tr>
<td>Pt</td>
<td>Cd/Tl</td>
<td>0.1 M HCl</td>
<td>49</td>
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<td>CdO₄ or I⁻ salts; mono. red. sep. bulk</td>
<td>110</td>
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<td>Cs</td>
<td>FIM; 0.5 M H₂SO₄</td>
<td>103</td>
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<tr>
<td>Cu</td>
<td>0.5 M HClO₄; 0.5 M H₂SO₄; 0.1 M NaOH; r-hydrazine oxid.</td>
<td>181</td>
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<tr>
<td></td>
<td>T; SRS; 1 M HClO₄</td>
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<tr>
<td></td>
<td>XPS; 0.1 M H₂SO₄</td>
<td>143</td>
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<tr>
<td></td>
<td>AES; XPS; 0.1 M H₂SO₄</td>
<td>144</td>
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<td>0.1 M HClO₄</td>
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<td>0.5 M HCl</td>
<td>69, 71, 238</td>
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<td></td>
<td>HCl; ΔEₚ(0.1 M HCl)=0.245 (cf. 193)</td>
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<td>0.5 M HClO₄; r-O₂ red.</td>
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<td>0.5 M HClO₄; 0.2 M NaOH; r-oxid. of alliphatic alcohols (MeOH); a-Cl⁻</td>
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<tr>
<td></td>
<td>1 M NaOH; r-ethylene glycol oxid.</td>
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<td>0.5 M HClO₄; r-ethylene glycol oxid.</td>
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<td>2 M HClO₄; r-formic acid oxid.</td>
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<td>HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
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<td>T; 1 M H₂SO₄</td>
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<td>T; 0.5 M H₂SO₄; surf. char.</td>
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<td>T; RTM; 1 M HClO₄; a-HSO₄⁻</td>
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<td>SRS (1); 0.5 M H₂SO₄</td>
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<td>0.5 M H₂SO₄; r-ethylene red.</td>
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<td>0.1 M HNO₃; 0.1 M KCl; 0.1 M KNO₃</td>
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<td>KNO₃; HOAc/NaOAc; HClO₄; +e</td>
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<td>0.5 M H₂SO₄</td>
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<td>0.2 M H₂SO₄</td>
<td>315-319, 324</td>
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<td>0.1 M NaClO₄; effect of anions, H⁺</td>
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<td>Pt</td>
<td>Cu</td>
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<td>* 0.1 M NaClO₄; mech. of depos.</td>
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<td>* SRS; 1 M HClO₄</td>
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<td>* 1 M H₂SO₄; eff. on H ads.</td>
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<td>* r-HCHO</td>
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<td>* 0.2 M H₂SO₄; r-O₂ red.</td>
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<td>* SRS</td>
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<td>* 96% H₃PO₄</td>
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<td>* HCl; H₂SO₄</td>
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<td>* 0.5 M H₂SO₄; ΔE_p=0.41</td>
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<tr>
<td>Cu/Ag</td>
<td>RTM; 1 M NaOH; e-H⁺</td>
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<td>Cs</td>
<td>2 mM Cs⁺ in PPC; ΔE_p=1.7</td>
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<td>Fe/Ni</td>
<td>10 mM H₂SO₄</td>
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<td>* 0.5 M H₂SO₄; r-oxid. of CO, MeOH, HCHO</td>
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<td>HCOOH</td>
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<td>* T; 1 M H₂SO₄</td>
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<td>* SRS; 1 M HClO₄</td>
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<td>* 1 M HClO₄</td>
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<td>* XRD; 1 M HClO₄</td>
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<tr>
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<td>K</td>
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<td>ClO₄⁻ or I⁻ salts; mono. red. sep. bulk</td>
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<td>*</td>
<td>20 mM K⁺ in PPC; ΔEₚ~1.3</td>
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<td>20 mM Li⁺ in PPC; ΔEₚ~1.30</td>
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<td>10 mM Na⁺ in PPC; ΔEₚ~1.1</td>
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<td>Ni</td>
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<td>0.1 M KSCN; 0.1 M KNO₃</td>
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<td>10 mM H₂SO₄</td>
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<td>0.5 M HClO₄; increas. revers. of r-hydroquin./p-benzoquin., pyrocatechol/o-benzoquin.</td>
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<td>*</td>
<td>0.5 M HClO₄; 0.5 M H₂SO₄; 0.1 M NaOH; r-hydrazine oxid.</td>
<td>181</td>
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<tr>
<td></td>
<td>*</td>
<td>T; SRS; 1 M HClO₄</td>
<td>308</td>
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<td>*</td>
<td>T; 1 M HClO₄; r-formic acid oxid.</td>
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<td>1 M HClO₄; r-formic acid oxid.</td>
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<td>2 M HClO₄; r-formic acid oxid.</td>
<td>11</td>
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<td>*</td>
<td>0.5 M HClO₄; r-benzofuroxan/o-benzoquin. dioxime</td>
<td>188</td>
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<tr>
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<td>*</td>
<td>1 M HClO₄; r-formic acid oxid.; comp. w/ other Pt catal.</td>
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<tr>
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<td>*</td>
<td>as Pb(ClO₄)₂; 1 M KF; r-Ru(NH₃)₂₊⁺ oxid.</td>
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<td>*</td>
<td>0.5 M NaOH; r-NH₃ red., hydroxylamine oxid.</td>
<td>187</td>
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<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
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<tr>
<td>Pt</td>
<td>Pb</td>
<td>* 0.5 M HClO₄; r-phenyldinitrometh. red., phenylnitrometh. red.</td>
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<td></td>
<td>* 0.5 M HClO₄; r-O₂ red.</td>
<td>186</td>
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<td>* 0.5 M HClO₄; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl⁻</td>
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<td>* 1 M NaOH; r-ethylene glycol oxid.</td>
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<td></td>
<td>* 0.5 M HClO₄; r-ethylene glycol oxid.</td>
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<td>* HClO₄; H₂SO₄; r-O₂ red., H₂O₂ red.</td>
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<td>* HNO₃</td>
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<td>* H₂SO₄ (1); HClO₄</td>
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<td>* T; NaClO₄/HClO₄; H₂SO₄</td>
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<td>* 0.1 M HNO₃; 0.1 M KCl; 0.1 M KNO₃</td>
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<td>* KNO₃; HOAc/NaOAc; HClO₄; +e</td>
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<td>* 0.5 M KCl; 0.5 M NaCl; ΔEₚ(0.5 M NaCl)=0.65 (cf. 193)</td>
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<td>* 0.5 M HClO₄; 0.2 M NaOH; r-oxid. of monosacch.; 3rd body effect; a-Cl⁻; Temp.</td>
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<td>* SRS; r-HCOOH oxid.</td>
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<td>* RTM; comp. w/ Po depos.</td>
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<td>* r-HCHO</td>
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<td>* 0.2 M H₂SO₄</td>
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<td>RTM; 1 M NaOH; e-H⁺</td>
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<td>* 0.5 M H₂SO₄; r-MeOH oxid.</td>
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<td>177</td>
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<td>* 0.5 M H₂SO₄; r-CO oxid.</td>
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<td>* 0.5 M H₂SO₄; r-MeOH oxid.</td>
<td>340</td>
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<td>* RTM; as RuNOCl₃; HCl</td>
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<td>* 0.5 M H₂SO₄; r-MeOH oxid.</td>
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<td>* RTM; 0.5 M H₂SO₄</td>
<td>136</td>
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<td>Se</td>
<td>0.5 M H₂SO₄; r-ethylene red.</td>
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<td>Sn</td>
<td>Moss.; acidic solns.</td>
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<td>* 0.5 M H₂SO₄</td>
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<td>* 0.5 M H₂SO₄; r-oxid. of CO, MeOH, HCHO</td>
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<td>HCOOH</td>
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<td>* r-MeOH oxid.</td>
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<td>* H₂SO₄; a-CO₂</td>
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<td>* 0.5 M H₂SO₄; r-MeOH oxid.</td>
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<td>* 0.1 M H⁺; ΔEₚ=0.53</td>
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<td>RTM; H₂SO₄; search of formal pot.</td>
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<td>0.5 M HClO₄; increas. revers. of r-hydroquin./p-benzoquin., pyrocatechol/o-benzoquin.</td>
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<td>* 0.5 M HClO₄; 0.5 M H₂SO₄; 0.1 M NaOH; r-hydrazine oxid.</td>
<td>181</td>
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<td></td>
<td>* 0.5 M HClO₄; r-benzofuroxan/o-benzoquin. dioxime</td>
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<td>* 1 M KF; r-Ru(NH₃)₂⁺ oxid.</td>
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<td>* 0.5 M NaOH; r-NH₃ red., hydroxyamine oxid.</td>
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<td>* 0.5 M HClO₄; r-phenyldinitrometh. red., phenylnitrometh. red.</td>
<td>189</td>
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<tr>
<td></td>
<td>* 0.5 M HClO₄; r-O₂ red.</td>
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<td>Attributes</td>
<td>Reference(s)</td>
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<td>Tl</td>
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<td>* 0.5 M HClO$_4$; 0.2 M NaOH; r-oxid. of aliphatic alcohols (MeOH); a-Cl$^-$</td>
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<td>* 1 M NaOH; r-ethylene glycol oxid.</td>
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<td>* 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ in ACN; r-oxid. of hydraz., methylhydraz., 1,1-dimethylhydraz.</td>
<td>168</td>
</tr>
<tr>
<td></td>
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<td>* 0.5 M HClO$_4$; r-ethylene glycol oxid.</td>
<td>183</td>
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<tr>
<td></td>
<td></td>
<td>* 1 M HClO$_4$; r-formic acid oxid.</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 2 M HClO$_4$; r-formic acid oxid.</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO$_4$; H$_2$SO$_4$; r-O$_2$ red., H$_2$O$_2$ red.</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* RTM; 0.1 M HCl</td>
<td>48</td>
</tr>
<tr>
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<td></td>
<td>* 0.1 M HCl</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO$_4$; H$_2$SO$_4$; HNO$_3$; HCl</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 50 mM H$_2$SO$_4$</td>
<td>214</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* RTM; 0.05 M H$_2$SO$_4$</td>
<td>215</td>
</tr>
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<td></td>
<td>* 0.5 M HClO$_4$; 0.2 M NaOH; r-oxid. of monosacch.; 3rd body effect; a-Cl$^-$; Temp.</td>
<td>347</td>
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<tr>
<td></td>
<td></td>
<td>* 0.5 M H$_2$SO$_4$</td>
<td>348</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* r-HCHO</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO$_4$</td>
<td>229</td>
</tr>
<tr>
<td>Tl/Cu</td>
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<td>0.1 M HCl</td>
<td>49</td>
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<td>Zn</td>
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<td>0.5 M H$_2$SO$_4$</td>
<td>348</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* RTM; +e</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HClO$_4$</td>
<td>229</td>
</tr>
<tr>
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<td>Ag</td>
<td>AES; 1 M H$_2$SO$_4$; $\Delta E_p=f($face$)$; +s</td>
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</tr>
<tr>
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<td>Cu</td>
<td>AES; LEED; 0.3 M HF; UHV single cryst. trans. to Ar electrochem.</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M H$_2$SO$_4$; for ver. of third strip. peak for H UPD</td>
<td>291</td>
</tr>
<tr>
<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
</tr>
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<td>-----------</td>
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<tr>
<td>Pt(100)</td>
<td>Cu</td>
<td>Continued</td>
<td></td>
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<tr>
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<td></td>
<td>* 0.5 M H₂SO₄; 0.01 M HClO₄; surf. char.</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; 1 M HCl; 0.1 M HClO₄; ΔEₚ(Cu,100,H₂SO₄)=0.0; comp. w/ 311 and poly.</td>
<td>288</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>0.5 M H₂SO₄; for ver. of third strip. peak by Cu codepos.</td>
<td>291</td>
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<td></td>
<td>* 0.5 M H₂SO₄; 0.01 M HClO₄; surf. char.</td>
<td>290</td>
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<tr>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; 1 M HCl; 0.1 M HClO₄; comp. w/ 311 and poly.</td>
<td>288</td>
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<tr>
<td></td>
<td></td>
<td>* 4 M H₂SO₄; Temp.</td>
<td>344</td>
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<tr>
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<td>AES; 1 M H₂SO₄; ΔEₚ= f(face); +s</td>
<td>100</td>
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<td>Cu</td>
<td>AES; LEED; 0.3 M HF; UHV single cryst. trans. to Ar electrochem.</td>
<td>22</td>
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<td></td>
<td>* 0.5 M H₂SO₄; for ver. of third strip. peak for H UPD</td>
<td>291</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; 0.1 M HClO₄; 0.1 M NaOH; 0.1 M NaHCO₃ (8.5); a,c-sup.; ΔEₚ(Cu,110,H₂SO₄)=0.27</td>
<td>289</td>
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<td>291</td>
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<tr>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; 0.1 M HClO₄; 0.1 M NaOH; 0.1 M NaHCO₃ (8.5); a,c-sup.;</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 4 M H₂SO₄; T</td>
<td>344</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>Ag</td>
<td>AES; 1 M H₂SO₄; ΔEₚ= f(face); +s</td>
<td>100</td>
</tr>
<tr>
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<td>Cu</td>
<td>AES; LEED; 0.3 M HF; UHV single cryst. trans. to Ar electrochem.</td>
<td>22</td>
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<td>* -I; AES; LEED; 1 M NaClO₄; surf. char.</td>
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<td>Attributes</td>
<td>Reference(s)</td>
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<td>--------------</td>
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<tr>
<td>Pt(111)</td>
<td>Cu</td>
<td>Continued</td>
<td>* 0.5 M H₂SO₄; for ver. of third strip. peak for H UPD</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; 0.01 M HClO₄; surf. char.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; 0.1 M HClO₄; 0.1 M NaOH; 0.1 M NaHCO₃ (8.5); a,c-sup.; AEₚ(Cu,111,H₂SO₄)=0.0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>* 0.5 M H₂SO₄; for ver. of third strip. peak by Cu codepos.</td>
</tr>
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<td>0.5 M H₂SO₄; for ver. of third strip. peak by Cu codepos.</td>
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<td></td>
<td></td>
<td>0.5 M H₂SO₄; 0.01 M HClO₄; surf. char.</td>
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<td></td>
<td>0.5 M H₂SO₄; 0.1 M HClO₄; 0.1 M NaOH; 0.1 M NaHCO₃ (8.5); a,c-sup.;</td>
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<td>4 M H₂SO₄; Temp.</td>
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<td></td>
<td>0.5 M H₂SO₄; for ver. of third strip. peak by Cu codepos.</td>
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<td></td>
<td>0.5 M H₂SO₄; for ver. of third strip. peak by Cu codepos.</td>
<td>291</td>
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<td>Pt(S)-I</td>
<td>Ag</td>
<td>AES; LEED; 1 M HClO₄; 3 UPD reg.</td>
<td>297</td>
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<td>Pt/Au</td>
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<td>1 M NaOH; r-ethylene glycol oxid.</td>
<td>31</td>
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<td>1 M HClO₄; r-formic acid oxid.; comp. w/ other Pt catal.</td>
<td>74</td>
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<tr>
<td>Pt/Hg</td>
<td>Bi</td>
<td>anal. use</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* HNO₃; HClO₄</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>anal. use</td>
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<tr>
<td></td>
<td></td>
<td>Co</td>
<td>anal. use</td>
</tr>
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<td>Substrate</td>
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<td>Attributes</td>
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</tr>
<tr>
<td>Pt/Hg</td>
<td>Cu</td>
<td>anal. use</td>
<td>93</td>
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<td>93</td>
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<td>*</td>
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<td>152</td>
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<td></td>
<td>Sn</td>
<td>anal. use</td>
<td>93</td>
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<tr>
<td></td>
<td>Tl</td>
<td>anal. use</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>*</td>
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<td>152</td>
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<td>Zn</td>
<td></td>
<td>152</td>
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<td>Rh</td>
<td>Ag</td>
<td>RTM; 0.1 M NaClO₄; $E_{\text{red}}(0.1 \text{ M KNO₃, PH } 4)=-0.1$</td>
<td>258</td>
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<td>1 M HClO₄; r-formic acid oxid.; comp. w/ rxns. at Pt</td>
<td>97</td>
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<tr>
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<td>Cd</td>
<td>1 M HClO₄; r-formic acid oxid.; comp. w/ rxns. at Pt</td>
<td>97</td>
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<tr>
<td></td>
<td>Cu</td>
<td>1 M H₂SO₄</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>0.1 M NaClO₄; effect of anions, H⁺</td>
<td>96</td>
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<td>H</td>
<td>H₂SO₄</td>
<td>54</td>
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<td>Pb</td>
<td>T; 1 M HClO₄; r-formic acid oxid.</td>
<td>13</td>
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<tr>
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<td>*</td>
<td>1 M HClO₄; r-formic acid oxid.; comp. w/ rxns. at Pt</td>
<td>97</td>
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<td>Ru</td>
<td>RTM; as RuNOCl₃; HCl</td>
<td>205</td>
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<tr>
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<td>Tl</td>
<td>1 M HClO₄; r-formic acid oxid.; comp. w/ rxns. at Pt</td>
<td>97</td>
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<td>NA</td>
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<td></td>
<td>Ru-Pt</td>
<td>Cu</td>
<td>0.5 M H₂SO₄; surf. char. by Cu depos.</td>
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<td></td>
<td>Sb</td>
<td>Li</td>
<td>LiClO₄ in PPC</td>
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<td>Sn</td>
<td>Cd</td>
<td>0.5 M NH₄ClO₄/0.5 M HClO₄; HClO₄; KCl</td>
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<tr>
<td></td>
<td></td>
<td>Hg</td>
<td>+e</td>
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<tr>
<td></td>
<td></td>
<td>Tl</td>
<td>0.5 M NH₄ClO₄/0.5 M HClO₄; HClO₄; KCl</td>
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<td></td>
<td></td>
<td>Zn</td>
<td>RTM; +e</td>
</tr>
<tr>
<td>Substrate</td>
<td>Adatom(s)</td>
<td>Attributes</td>
<td>Reference(s)</td>
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<tr>
<td>Ta</td>
<td>Ag</td>
<td>RTM; 0.1 M NaClO₄; $E_{\frac{1}{2},d}(0.1 \text{ M KNO}_3, \text{ pH } 4)=-0.45$</td>
<td>258</td>
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<tr>
<td>Bi</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>82</td>
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<tr>
<td>Po</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
</tr>
<tr>
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<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
</tr>
<tr>
<td>Po</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
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<tr>
<td>Po</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
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<tr>
<td>Po</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
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<td>W</td>
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<td>258</td>
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<td>257</td>
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<tr>
<td>Po</td>
<td></td>
<td>RTM; comp. w/ Po depos.</td>
<td>81</td>
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<tr>
<td>ZnO</td>
<td>Zn</td>
<td>SRS; 1 M KCl</td>
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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
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.
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

FROM I/E CONVERTER

DWG. 8255-0-SD
(SH.2)

Q211
2N4221

22.1K
1%

2N1K
1%

CR210

GATE SIG. III
R273(Q228)
(SH 2)

TO DIFFERENTIAL S/H INPUT

TO OPER.
MODE SWITCH S6D

+15V

TO DIFFERENTIAL S/H AMP.

-15V

NOTE 4

Q212A
Q1212A

R213
495Ω
1%

R215
294K
1%

R218
100Ω
1%

R219
402Ω
15K
1%

R217
470Ω
Q216B

S

C.201
 spéc.
10208

R212
470Ω
Q212B

R212
Q212

TO DIFFERENTIAL S/H AMP.

GATE SIG. III
R273(Q228)
(SH 2)

DIFF. PULSE

PULSE

SAMPLED DC.
D.C.

OPERATING MODE

SH.2

Q212A
Q1212A
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.
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.
Figure V-6. Schematic diagram of the rear panel of the PAR 174A potentiostat showing external connections for computer control.
- I/E Output
- 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.
Figure V-8. Schematic diagram of the hardware modifications for the Dionex UEM potentiostat allowing for additional offset compensation
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 $254 \times 16.67 + 16.67$ 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., $> 7 \times 16.67 + 16.67$ 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

<table>
<thead>
<tr>
<th>Integration number</th>
<th>Line 10-2&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Line 10-6</th>
<th>Line 10-8&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>L</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>L</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>3</td>
<td>L</td>
<td>H</td>
<td>H</td>
</tr>
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<td>4</td>
<td>L</td>
<td>L</td>
<td>L</td>
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<td>H</td>
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<td>H</td>
<td>L</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>9</td>
<td>L</td>
<td>L</td>
<td>H</td>
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<td>L</td>
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<tr>
<td>15</td>
<td>L</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>16&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>L</td>
</tr>
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<td>L</td>
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</tr>
<tr>
<td>20</td>
<td>H</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>etc.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Most significant bit.  
<sup>b</sup>Least significant bit.  
<sup>c</sup>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
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.
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 and 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.
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.
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

<table>
<thead>
<tr>
<th>Function</th>
<th>Type of &quot;experiment&quot; performed</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/AC Potential Switch for disconnecting the D/AC output from the interface (e.g., the electrochemical cell).</td>
<td>[A] Polarographic experiments</td>
</tr>
<tr>
<td></td>
<td>[B] Experiments employing the S/H circuit of the PAR 174A</td>
</tr>
<tr>
<td></td>
<td>[C] Experiments for direct current measurement, the S/H circuits of the PAR 174A are not used</td>
</tr>
<tr>
<td></td>
<td>[D] Digital plotting on X-Y recorder</td>
</tr>
<tr>
<td></td>
<td>[E] Alternate potentiostat inputs for electrochemical experiments</td>
</tr>
<tr>
<td></td>
<td>[F] Same as [E]</td>
</tr>
<tr>
<td><strong>Table V-2. Continued</strong></td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Cell</strong></td>
<td>Selection of the electrochemical cell used, C, R, W denote the counter, reference and working electrode connections, respectively.</td>
</tr>
<tr>
<td><strong>Time Constant</strong></td>
<td>The time constant of the analog integrator used for PCD experiments.</td>
</tr>
<tr>
<td><strong>X-out, Y-out</strong></td>
<td>External switching of signal outputs to recording devices.</td>
</tr>
<tr>
<td><strong>Amplification</strong></td>
<td>Selection of the magnitude of amplification to be employed for each of the two stages.</td>
</tr>
<tr>
<td><strong>Potential Input</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>Offset</strong></td>
<td>Offset circuitry may be used for any of the electrochemical experiments. In the X1 position the offset is 0.15 V turn⁻¹.</td>
</tr>
<tr>
<td><strong>S/H</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>Integrate</strong></td>
<td>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.</td>
</tr>
</tbody>
</table>
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.
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.
<table>
<thead>
<tr>
<th>Index</th>
<th>R_i(Ω)</th>
<th>Index</th>
<th>R_i(Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 K</td>
<td>13</td>
<td>10 K</td>
</tr>
<tr>
<td>2</td>
<td>15 K</td>
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<td>34.8 K</td>
<td>16</td>
<td>34.8 K</td>
</tr>
<tr>
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<td>49.9 K</td>
<td>17</td>
<td>49.9 K</td>
</tr>
<tr>
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<td>69.8 K</td>
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</tr>
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<td>8</td>
<td>100 K</td>
<td>20</td>
<td>100 K</td>
</tr>
<tr>
<td>9</td>
<td>150 K</td>
<td>21</td>
<td>150 K</td>
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<td>348 K</td>
</tr>
<tr>
<td>12</td>
<td>499 K</td>
<td>24</td>
<td>499 K</td>
</tr>
</tbody>
</table>

Resistances (±1%)
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.
Figure V-15. Diagram of the card edge connector for the analog integration circuitry of Fig. V-14. The allowable time constants $\tau$ for the analog integrator are also shown.
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.
Figure V-17. Schematic diagram and card edge connector for sample-and-hold circuitry for digital plotting with an X-Y recorder.
DG 300

LM741

\[ +15 \]

\[ -15 \]

\[ 8.2 \mu F \text{ mylar} \]

\[ \frac{13}{6} \]

\[ 9 \]

\[ 4 \]

\[ 7 \]

\[ -15 \]

\[ +15 \]

Power Supply

Inputs

[Power Supply Inputs]

D/A board, slot 7

Timer boards, slots 12 and 14

Output to X-Y recorder

[Output to X-Y recorder]
(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 rpm%, 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.
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

<table>
<thead>
<tr>
<th>Stage</th>
<th>$R_i (\Omega)$</th>
<th>$E_i (V)$</th>
<th>$w_i (rpm)$</th>
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<td>1</td>
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<td>100</td>
</tr>
<tr>
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<table>
<thead>
<tr>
<th>Stage</th>
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<td>512</td>
</tr>
<tr>
<td>7</td>
<td>1024</td>
</tr>
</tbody>
</table>

### Edge Connector

- [Power Supply Inputs]
  - $+15$ 1
  - $+15$ 2
  - $+5$ 3
  - $\frac{1}{2}$ 4
  - NC 5
  - NC 6
  - NC 7
  - $E_R$ 8
  - $D_1$ 9
  - $D_2$ 10
  - $D_3$ 11
  - $D_4$ 12
  - $D_5$ 13
  - $D_6$ 14
  - $D_7$ 15
  - NC 16
  - NC 17
  - NC 18
  - NC 19
  - NC 20
  - NC 21
  - NC 22

- [to rotator control]
  - Digital Input Lines
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 cm²), 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 cm²) 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 too 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 $1.5 \times 10^{-2}$ 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.\cite{1,2} Oxygen is reduced to $\text{H}_2\text{O}_2$ ($n=2$) with $E_\frac{1}{2} = \text{ca. 0.0 V vs. SCE}$ and $\text{H}_2\text{O}_2$ is reduced to $\text{H}_2\text{O}$ ($n=4$ for $\text{O}_2 + \text{H}_2\text{O}$) with $E_\frac{1}{2} = \text{ca. -1.2 V}$. 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. Various approaches have been described for elimination of dissolved oxygen in flow systems including placement of the entire apparatus in a drybox purged with inert gas. 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 \( \Delta E \). The ratio of the limiting currents for NP and DC polarography at a dropping mercury electrode (DME) is given by

\[
\frac{i_{NP}}{i_{DC}} = [\frac{3\pi}{7t_p}]^{1/2}
\]

where \( \tau \) is the drop lifetime, \( t_p \) is the pulse period and \( \tau = t_i + t_p \). The value of \( i_{DC} \) is given by

\[
i_{DC} = nFAC b [\frac{7D}{3\pi \tau}]^{1/2}
\]
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., \( E_i << E_{j^s} \) and \( \Delta E \) 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 \( E_d >> E_{j^s} \), 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 \( E_d << E_{j^s} \) is equal to \( i_{DC} \) (Eqn. 2). The limiting anodic current \( (i_{RP}) \) for \( E_d >> E_{j^s} \) is related to \( i_{DC} \) by

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

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

\[
- \frac{i_{RP}}{i_{DC}} = \frac{n_{\text{red}}}{n_{\text{ox}}} \left[ \frac{3\tau}{7t_p} \right]^{\frac{1}{2}} - 1 \tag{4}
\]
and in the limit for $\tau/t_p \rightarrow \infty$, Eqn. 4 becomes identical to Eqn. 1 for $n_{\text{red}} = n_{\text{ox}}$. If the product of the reaction at $E_i$ undergoes an irreversible homogeneous conversion to an electro-inactive product, $i_{R_p}$ is less than predicted by Eqn. 3\textsuperscript{9} and the deviation can be applied for kinetic studies of following chemical reactions coupled to the electron-transfer processes.\textsuperscript{12}

Maitoza and Johnson\textsuperscript{13} recognized that when RPP is used, dissolved oxygen is not detected for $E_d \gg \text{ca. 0.0 V vs. SCE}$, because of the irreversibility of oxygen at mercury. They demonstrated the amperometric form of RPP (i.e., constant $\Delta E$) 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\textsuperscript{14} recently applied this technique for the ion chromatographic determination of $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, $\text{Ni}^{2+}$, $\text{Pb}^{2+}$, $\text{Cd}^{2+}$ and $\text{Fe}^{2+}$ using a low capacity cation-exchange column with a tartrate buffer (pH 3.5-4.5) containing $\text{Mg}^{2+}$ as the mobile phase. Representative detection limits for 100 $\mu$L samples were 1.3 ng $\text{Zn}^{+2}$ and 6.4 ng $\text{Cu}^{+2}$. The detection limits were lowered 100-fold using a 10-mL sample with on-line preconcentration on a high-capacity precolumn.

Christie et al.\textsuperscript{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 = \frac{\Delta E}{\tau}

B. CPPP

scan rate = \frac{\Delta E}{\tau}
(DPP). In CPPP, $E_1$ is scanned with current sampling at a constant detection potential, $E_d$, and the current measured at $E_d$ is plotted vs. $E_1$. The i-E response curve obtained for a reducible analyte with $E_d << E^*_d$, 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 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.

Hara and Nomura noted for CPPP in agreement with Maitoza and Johnson 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 ($\Delta E$ 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., Middleton, 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 0.1M KNO₃/0.01M HNO₃ 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 0.5mM Pb(II) and Cd(II) in 0.1M KNO₃/0.01M HNO₃ with and without oxygen present. The reductions of Pb(II) and Cd(II) to their corresponding metal amalgams are reversible with Eₕ values of ca. -0.4 V and -0.6 V, respectively. As observed by Maitoza and Johnson¹³, 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 0.5 mM Pb(II) + 0.5 mM Cd(II) in 0.1 M KNO₃/0.01 M HNO₃

Conditions: ΔE = 5 mV, τ = 1.0 s.

Curves:

[A] NPP, air sat'd, Eᵢ = 0.2 V;
[B] NPP, Ar sat'd, Eᵢ = 0.2 V;
[C] RPF, air sat'd, Eᵢ = -1.3 V;
[D] RPF, Ar sat'd, Eᵢ = -1.3 V;
[E] CPPP, air sat'd, Eᵢ = 0.2 V;
[F] CPPP, Ar sat'd, Eᵢ = 0.2 V.
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 ($\tau$ 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 $\mu M$ 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 0.1M KNO₃. 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).

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^- \quad (0.0 \ V > E_1 > -1.2 \ V) \ [5]$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad (-1.2 \ V > E_1) \ [6]$$

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

The detection of $OH^-$ produced by the cathodic reaction at $E_1$ is observed also in RPP and was applied by Brestovisky et al.\textsuperscript{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 KNO₃/0.01 M HNO₃

Conditions: \( \Delta E = 5 \text{ mV}, \tau = 1.0 \text{ s} \).

Concentrations:

[A] Blank;

[B] 5.0 \( \text{M} \) Pb(II), 5.0 \( \mu \text{M} \) Cd(II);

[C] 10.0 \( \mu \text{M} \) Pb(II), 10.0 \( \mu \text{M} \) Cd(II);

[D] 15.0 \( \mu \text{M} \) Pb(II), 15.0 \( \mu \text{M} \) Cd(II);

[E] 20.0 \( \mu \text{M} \) Pb(II), 20.0 \( \mu \text{M} \) Cd(II).
Figure VI-4. Current-potential curves for unbuffered 0.1 M KNO₃

Conditions: \( \Delta E = 5 \text{ mV}, \tau = 1.0 \text{ s}, \)
\[ \text{natural pH} = 4.8. \]

Curves:

[A] NPP, air sat\'d, \( E_i = 0.2 \text{ V}; \)
[B] NPP, Ar sat\'d, \( E_i = 0.2 \text{ V}; \)
[C] RPP, air sat\'d, \( E_i = -1.5 \text{ V}; \)
[D] RPP, Ar sat\'d, \( E_i = -1.5 \text{ V}; \)
[E] CPP, air sat\'d, \( E_d = 0.2 \text{ V}; \)
[F] CPPP, Ar sat\'d, \( E_d = 0.2 \text{ V}. \)
response to OH\textsuperscript{-}, 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\textsuperscript{-} by reverse CPPP in Fig. VI-5 (curves A-E). The electrode reaction for $E >> ca. -0.1$ V is

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

For $E_1 >> ca. -0.1$ V, the anodic current corresponds to $i_{DC}$ for I\textsuperscript{-}. When $E_1 << ca. -0.1$ V, the anodic current equals that of $i_{NP}$ for I\textsuperscript{-}. 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\textsubscript{2}I\textsubscript{2}. Shown for comparison in Fig. VI-5 (curves F-J) are polarographic curves for I\textsuperscript{-} obtained by RPP ($E_1 = 0.2$ 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:

- $\Delta E = 5$ mV, $\tau = 1.0$ s.
- CPPP (A-E), $E_d = 0.2$ V.
- RPP (F-J), $E_1 = 0.2$ V.

Concentrations $I^-$ (mM):

- (A,F) blank;
- (B,G) 0.20;
- (C,H) 0.40;
- (D,I) 0.60;
- (E,J) 0.80.
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 mM 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 \( \Delta E = 10 \) mV and \( \tau = 1.0 \) 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 \( \tau \). 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 M KNO₃/0.01 M HNO₃, \( \nu_f = 0.50 \text{ mL min}^{-1} \).

**Sample:** 2.0 mM Pb(II) + 2.0 mM Cd(II) in 0.1 M KNO₃/0.01 M HNO₃; \( V_s = 2.0 \text{ mL} \).

**Detection:** \( E_i = -1.0 \text{ V}, E_d = 0.2 \text{ V}, \tau = 1.0 \text{ s} \).
Figure VI-7. Flow-injection polarographic analyses

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

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

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 $1.34 \times 10^{-2}$ M.
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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G. References


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 \( \pi \)-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.\textsuperscript{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.\textsuperscript{8,9} In the commercialized version, a Au detector has been recommended over a Pt detector.\textsuperscript{10,11} General comparisons of electrode materials for amperometric detection in LC have appeared;\textsuperscript{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\textsuperscript{3} is based on a detection potential corresponding to the surface-controlled anodic oxidation of adsorbed carbohydrate in a potential region where dissolved O\textsubscript{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\textsubscript{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 cm²; 900 rev min⁻¹) using a three-step potential waveform

Waveform: \( E_1 = \) varied (200 ms); \( E_2 = 0.60 \text{ V} \) (200 ms); \( E_3 = -1.0 \text{ V} \) (600 ms).

Curves:

[A] air sat'd 0.20 M NaOH;
[B] \( \text{N}_2 \) sat'd 0.20 M NaOH;
[C] air sat'd 2.0 mM glucose and 0.20 M NaOH;
[D] \( \text{N}_2 \) sat'd 2.0 mM glucose and 0.20 M NaOH.
tion; however, since the chromatographic systems commonly used in ion chromatography are constructed with O₂-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 O₂ 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 O₂ interference.

Carbohydrates can be detected anodically at Au electrodes in a potential region where O₂ 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: \[ E_1 = \text{varied (200 ms)}; \]
\[ E_2 = 1.0 \text{ V (200 ms)}; \]
\[ E_3 = -1.0 \text{ V (600 ms)}. \]

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.
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

$E = -1.3 \, V$

$10 \, \mu A$

B) Pt
PAD

$E_1 = -0.36 \, V$

$E_1 = -0.73 \, V$

$2 \, \mu A$

$10 \, min$

$(-2.6)$

$(5.4)$
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, 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.
C. References

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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 n mole 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. An excess amount of fructose or xylulose may be a sign of an inherited metabolic defect, such as essential fructosuria or essential pentosuria.
respectively.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{9} Refractive index detection suffers in that sensitivities are often unsatisfactory. Photometric detection following post-column derivatizations has been used\textsuperscript{13} but the added complication motivates the
search for more reliable and universal methods. The use of optical activity detection has been recently presented, but the scarcity of such instrumentation prohibits its use in modestly equipped laboratories. Flame ionization detectors 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. 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 for the detection of alcohols, amino acids, aminoglycosides and many inorganic and organic sulfur compounds. The three-step potential waveform has also been applied for PAD at gold electrodes. 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, 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 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.
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 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 $E > \text{ca.} -0.2 \text{ V}$, but ceases with the concurrent formation of surface oxide for $E > 0.6 \text{ V}$. At $E > 0.9 \text{ V}$, 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 ($\Delta E$): 10 mV
- Scan Rate ($\phi$): 2.4 V min$^{-1}$
- Rotation rate: 1600 rev min$^{-1}$

Curves: [a] Ar sat'd residual  
[b] air sat'd residual.
Figure VIII-3. Current-potential curves obtained with a staircase waveform applied to a Au RDE in 1.0 mM glucose/0.20 M NaOH

Pulse amplitude (ΔE): 10 mV

Scan Rate (ϕ): 2.4 V min⁻¹

Solution: 1.0 mM glucose, Ar sat’d

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 (\( \Delta E \)): 10 mV
Scan Rate (\( \phi \)): 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
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 ($\Delta E$): 10 mV

Scan Rate ($\phi$): 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
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 mM glucose in 0.20 M NaOH.

Carrier stream: 0.20 M NaOH at 0.5 mL min⁻¹

Curves: Variation of detection potential (E₁):

\[ E_2 = 0.70 \, \text{V}, \]
\[ t_1 = 250 \, \text{ms}, \]
\[ t_2 = 200 \, \text{ms}. \]
$E_1$ (V vs. Ag/AgCl)

$i_p(\mu A)$

$i_{bkd}(\mu A)$
Figure VIII-7. Optimization of two-step potential waveform by FI-PAD: variation of anodic cleaning potential

Samples injected: 50 μL of 1.0 mM glucose in 0.20 M NaOH.

Carrier stream: 0.20 M NaOH at 0.5 mL min⁻¹

Curves: Variation of anodic cleaning potential (E₂):

\[ E_1 = 0.15 \text{ V}, \]
\[ t_1 = 250 \text{ ms}, \]
\[ t_2 = 200 \text{ ms}. \]
$E_2$ (V vs. Ag/AgCl)

- $i_p$ ($\mu$A)
- $i_{bkd}$ ($\mu$A)
Figure VIII-8. Optimization of two-step potential waveform by FI-PAD:
variation of detection time

Samples injected: 50 µL of 1.0 mM glucose in 0.20 M NaOH.

Carrier stream: 0.20 M NaOH at 0.5 mL min⁻¹

Curves: Variation of detection time (t₁):

\[ E₁ = 0.15 \text{ V}, \]
\[ E₂ = 0.75 \text{ V}, \]
\[ t₂ = 200 \text{ ms}. \]
Figure VIII-9. Optimization of two-step potential waveform by FI-PAD: variation of anodic cleaning time

Samples injected: 50 μL of 1.0 mM glucose in 0.20 M NaOH.

Carrier stream: 0.20 M NaOH at 0.5 mL min⁻¹

Curves: Variation of anodic cleaning time ($t_2$):

E₁ = 0.15 V,
E₂ = 0.75 V,
$t_1$ = 350 ms.
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. 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-\(\mu\)L of 1.0 mM 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 ($i_p - c$ and $1/i_p - 1/c$) 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 (●)
Figure VIII-11. Multiple flow injection peaks with pulsed amperometric detection utilizing a Princeton Applied Research Model 174A potentiostat for glucose and sucrose

Waveform: \[ \begin{align*}
E_1 &= 0.15 \text{ V} \quad (t_1 = 300 \text{ ms}) \\
E_2 &= 0.75 \text{ V} \quad (t_2 = 200 \text{ ms})
\end{align*} \]

Samples injected: 50 µL of 1.0 mM carbohydrate in 0.20 M NaOH.

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

Peaks: [A] glucose [B] sucrose
A) Glucose

B) Sucrose

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 this method will find increasing application for carbohydrate detection in liquid chromatographic and flow injection systems.

F. References


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 $\mu$M ($S/N = 2$) for glucose which is a significant improvement from the value 35 $\mu$M for FI-PAD. The absolute detection limits for glucose and sucrose are ca. 50 pmoles and 125 pmoles, respectively, in 50 $\mu$L 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\textsuperscript{1-8}, amines and amino acids\textsuperscript{9-10} and, recently, sulfur compounds.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{4,10,11} However, the use of such "reciprocal plots" is not now being recommended.\textsuperscript{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.\textsuperscript{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.\textsuperscript{14–17} Cleaning of carbon electrode surfaces resulting from potential pulsed also is known,\textsuperscript{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.\textsuperscript{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.\textsuperscript{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

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

where \( i_{\text{ox}}(t) \), \( i_{\text{dl}}(t) \), \( i_{\text{ads}}(t) \) and \( i_{\text{mt}}(t) \) 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 \( \tau_j \), the total amperometric response is given by

\[ i_{\text{tot}}(t) = i_{\text{ox}}(t) + i_{\text{dl}}(t) + i_{\text{ads}}(t) + i_{\text{mt}}(t) + \sum_j A_j \sin(2\pi t/\tau_j) \]  \[ \text{[2]} \]

Integration of Eqn. 2 over a time period \( t_1 = t'' - t' \) yields,

\[ q_{\text{tot}}(t_1) = \int_{t'}^{t''} i_{\text{tot}}(t) \, dt \]

\[ = q_{\text{ox}}(t_1) + q_{\text{dl}}(t_1) + q_{\text{ads}}(t_1) + q_{\text{mt}}(t_1) + \sum_j \int_{t'}^{t''} A_j \sin(2\pi t/\tau_j) \]  \[ \text{[3]} \]

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 $180^\circ$ out of phase with the noise in $i_{tot}(t)$. The contribution of the ac noise in $i_{tot}(t)$ to noise in $q_{tot}(t)$ is at a minimum for $t_i$ equal to integral multiples ($k$) of $\tau_j$ ($k=t_i/\tau_j$). Since the predominant source of ac noise in electroanalytical measurements is correlated with the 60-Hz line frequency, $\tau_j$ is equal to 16.7 ms. Hence, the coulometric response is characterized by a S/N which increases with increasing values of $t_i = k \times 16.7$ ms ($k = \text{integer}$) 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:

$$\frac{(S/N)_{PCD}}{(S/N)_{PAD}} = \frac{t_i^P_{PCD}}{t_i^P_{PAD}} = \frac{t_i^P_{PCD}}{16.7} = k \quad [5]$$

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 fouling 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 $E_i$ (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.
t_1), integration is performed for a period t_1 (digital control I in Fig. IX-1) by an analog integrator. The integral is sampled for 16.7 ms (digital control 0) during the last 18 ms of period t_1 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_0x and i_d1; hence, t_1 = t_d + t_1. 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_1 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 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. The flow-through detector for FIA studies (Dionex Corporation, Sunnyvale, CA) was of the thin-layer design containing a Au indicating (0.02 cm²), 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 cm², 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$_2$SO$_4$. 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. $t_1$ obtained with the FI system (Fig. IX-2) is linear for $t_1 = 100-1000$ ms. The linearity of $q_p$ vs. $t_1$ is characteristic of a steady-state, mass-transport limited response at the RDE for $t_1 > 100$ ms. The background noise level does not change with a change in $t_1$. 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 mM 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 $c^b < 0.1$ mM. 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 mM ferrocyanide in 0.18 M H₂SO₄

Waveform:  
E₁ = 0.90 V (t₁ varied; t_d = 1 μs)  
E₂ = 1.70 V (t₂ = 200 ms)  
E₃ = 0.40 V (t₃ = 200 ms)

Conditions:  
0.50 mL min⁻¹ flow rate  
50 μL sample injected

Curves:  
(•) Peak charge response  
(▲) Peak-to-peak background noise
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:
- $E_1 = 0.175 \text{ V} \ (t_1 = 250 \text{ ms})$
- $E_2 = 0.75 \text{ V} \ (t_2 = 100 \text{ ms})$
- $E_3 = -1.00 \text{ V} \ (t_3 = 100 \text{ ms})$

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

Curves:
- (•) Normalized peak current response of glucose ($N = 5.32 \times 10^{-2} \text{ mM } \mu A^{-1}$)
- (▲) Normalized peak current response of sucrose ($N = 5.00 \times 10^{-2} \text{ mM } \mu A^{-1}$)
fouling during the detection process by adsorbed detection product. The detection limits in this case (50-μL samples) were ca. 0.035 mM for glucose and 0.050 mM 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 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 \( E_1 = 0.175V \) (\( t_1 = 500 \text{ ms}, t_d = 1 \mu\text{s}, t_1 = 500 \text{ ms} \)), \( E_2 = 0.75V \) (\( t_2 = 200 \text{ ms} \)), and \( E_3 = -1.0V \) (\( t_3 = 200 \text{ ms} \)). The plots are linear over the concentration range of 5-50 μM 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 mM glucose in 0.20 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 M NaOH;
- [B] N$_2$ sat'd 0.20 M NaOH;
- [C] Air sat'd 1.0 mM glucose/0.20 M NaOH;
- [D] N$_2$ sat'd 1.0 mM glucose/0.20 M NaOH.
Figure IX-5. Normalized calibration plots by FI-PCD for glucose and sucrose in 0.20 M NaOH

Waveform:
- $E_1 = 0.175 \text{ V } (t_i = 500 \text{ ms}; t_d = 1 \mu\text{s})$
- $E_2 = 0.75 \text{ V } (t_2 = 200 \text{ ms})$
- $E_3 = -1.00 \text{ V } (t_3 = 200 \text{ ms})$

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

Curves:
- (●) Normalized peak charge response for glucose ($N = 6.19 \times 10^4 \mu\text{M} \mu\text{coul}^{-1}$)
- (▲) Normalized peak charge response for sucrose ($N = 9.42 \times 10^4 \mu\text{M} \mu\text{coul}^{-1}$)
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 mM and 0.05 mM, respectively. Detection limits for glucose and sucrose by PCD were found to be 1.0 \(\mu M\) and 2.5 \(\mu M\), 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 \(\mu M\) 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 μM glucose

PCD waveform:  
\[ \begin{align*} 
E_1 &= 0.175 \text{ V} \ (t_1 = 500 \text{ ms}; \ t_d = 1 \mu\text{s}) \\
E_2 &= 0.75 \text{ V} \ (t_2 = 200 \text{ ms}) \\
E_3 &= -1.00 \text{ V} \ (t_3 = 200 \text{ ms}) 
\end{align*} \]

PAD waveform:  
\[ \begin{align*} 
E_1 &= 0.175 \text{ V} \ (t_1 = 250 \text{ ms}) \\
E_2 &= 0.75 \text{ V} \ (t_2 = 100 \text{ ms}) \\
E_3 &= -1.00 \text{ V} \ (t_3 = 100 \text{ ms}) 
\end{align*} \]

Conditions:  
0.50 mL min\(^{-1}\) flow rate  
50 μL sample injected
This work was supported by the National Science Foundation through Contract CHE-8312032.

H. References


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 Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Analytical Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
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1987
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Background and sensitivity variation for PS-PCD of 100 µM glucose in 0.20 M NaOH with sudden ionic and pH changes of the carrier in FIA.

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Nitrate salts were used for all metal ion solutions unless otherwise noted.

Table XI-1.

Detection limits of metals obtained with FI-PCD at a Au electrode with the waveform $E_1 = 0.90 \text{ V} (t_1 = 167 \text{ ms}, \quad t_d = 4 \text{ ms}, \quad t_1 = 200 \text{ ms})$, $E_2 = -0.30 \text{ V} (t_2 = 800 \text{ ms})$.

Nitrate salts were used for all metal ion solutions unless otherwise noted.

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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 (n) of the solution, and large changes in n 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., Δμ = 0.5M, would overwhelm the detection of small analyte concentrations.

The methods of pulsed amperometric detection\textsuperscript{1-13} (PAD) and, more recently, pulsed coulometric detection\textsuperscript{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.\textsuperscript{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.\textsuperscript{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\textsuperscript{14} at constant detection potentials. Upon stepping from the adsorption-reset potential (E\textsubscript{3}) to the initial detection potential (E\textsubscript{1}), the analog integrator is activated (digital control I) after a time delay t\textsubscript{d} (digital control D). The electrode potential is then scanned to the value E\textsubscript{2} (E\textsubscript{2} > E\textsubscript{1}) during the period t\textsubscript{2}. Subsequently, the potential is stepped back to E\textsubscript{1} for a time period t\textsubscript{1} during which the oxide formed for the scan to E\textsubscript{2} is cathodically stripped. The integrator is active for the entire sequence of changing the applied potential from E\textsubscript{1} to E\textsubscript{2} and back to E\textsubscript{1}. At the end of the detection cycle (t\textsubscript{det} = t\textsubscript{d} + t\textsubscript{2} + t\textsubscript{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\textsubscript{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\textsubscript{3} and, for a sufficiently long period t\textsubscript{3}, the concentration of analyte in the diffusion layer can become reestablished to the bulk analytical concentration, i.e., C\textsuperscript{S} = C\textsuperscript{b} for t\textsubscript{3} >> 0.

The rate of potential sweep from E\textsubscript{1} to E\textsubscript{2} (period t\textsubscript{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.
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 and PCD 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, $E_2 - E_1 = 1 V$, and $\Delta E = 50 \text{ mV}$.

The FI system used in carbohydrate studies was of all-steel construction to allow for elimination of dissolved O₂ by purging the mobile phase in the storage container with dispersed N₂, 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\(^1\) 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$_4$NO$_3$.

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
"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 $\Delta E$ 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 M NH$_4$NO$_3$ 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$_4$NO$_3$
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.
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 mM thiourea in 0.25 M NH₄NO₃ at a Au RDE (0.005 cm²; 900 rev min⁻¹)

Curves:
[A] Staircase; N₂ sat'd 0.25 M NH₄NO₃;
[B] Staircase; N₂ sat'd 0.1 mM thiourea/0.25 M NH₄NO₃;
[C] Integrated staircase; N₂ sat'd 0.25 M NH₄NO₃;
[D] Integrated staircase; N₂ sat'd 0.1 mM thiourea/0.25 M NH₄NO₃;
Figure X-5. Peak current response for 100 μM thiourea in 0.25 M NH₄NO₃ by PAD showing post-peak dips.

PAD Waveform:

- $E_1 = 1.0 \text{ V } (t_1 = 400 \text{ ms})$
- $E_2 = 1.2 \text{ V } (t_2 = 300 \text{ ms})$
- $E_3 = -0.6 \text{ V } (t_3 = 500 \text{ ms})$

Conditions:

- 0.50 mL min⁻¹ flow rate
- 100 μL sample injected
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 \( \mu \)M 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
Figure X-6B. Staircase voltammograms for 0.20 mM thiourea in 0.25 M NH$_4$NO$_3$
obtain at a Au RDE (0.005 cm$^2$; 1600 rev min$^{-1}$)

Conditions: scan rate = 4.8 V/min

Supporting Electrolyte: 0.25 M NH$_4$NO$_3$

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
were made in 0.25 M NH₄NO₃ 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 $E_{\text{peak}}$ 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., $E_1 > \text{ca. 0.3 V}$. This potential dependent behavior implies that waveform 1B would give a much lower signal response for $E_2 > \text{ca. 0.3 V}$ with $E_1 \approx 0$ 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 \(\mu\text{M}\) thiourea in 0.25 M NH\(_4\)NO\(_3\)

**PS-PCD waveform (1B):**
- \(E_1 = -0.4 \text{ V (}t_1 = 400 \text{ ms)}\)
- \(E_2 = 1.2 \text{ V (}t_2 = 400 \text{ ms)}\)
- \(E_3 = -0.6 \text{ V (}t_3 = 500 \text{ ms)}\)

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

**Conditions:**
- 0.50 mL min\(^{-1}\) flow rate
- 100 \(\mu\text{L}\) sample injected

**pH-step:** 5.1 to 3.8, point of step marked by arrow
Figure X-8. PAD voltammograms for 2.0 mM glucose in 0.20 M NaOH obtained at a Au RDE (0.005 cm$^2$; 900 rev min$^{-1}$)

Waveform:
- $E_1 =$ varied ($t_1 =$ 200 ms)
- $E_2 = 1.0 \text{ V} (t_2 =$ 200 ms)
- $E_3 = -1.00 \text{ V} (t_3 =$ 600 ms)

Curves:
- [A] Air sat'd 0.20 M NaOH;
- [B] N$_2$ sat'd, 0.20 M NaOH;
- [C]-[F] N$_2$ sat'd, 2.0 mM glucose/0.20 M NaOH; rotation speeds 400, 900, 1600, 2500 rpm min$^{-1}$, respectively.
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 $E_4 \approx -0.15$ 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 $> \text{ca.} -0.1$ 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 mM glucose in 0.20 M NaOH at a Au RDE (0.005 cm²; 900 rev min⁻¹)

Curves:

[A] Staircase; N₂ sat'd 0.20 M NaOH;
[B] Staircase; N₂ sat'd 1.0 mM glucose/0.20 M NaOH;
[C] Integrated staircase; N₂ sat'd 0.20 M NaOH;
[D] Integrated staircase; N₂ sat'd 1.0 mM glucose/0.20 M NaOH (shown as 1/4 full scale).
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. 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, respectfully, the detection of 1.0 mM glucose in 0.20, 0.50 and 1.0 M 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 μM glucose in 0.20 M NaOH with sudden ionic and pH changes of the carrier in FIA

Waveform (1A):
- $E_1 = -0.20 \text{ V (} t_d = 1 \mu \text{s, } t_1 = 200 \text{ ms})$
- $E_2 = 0.40 \text{ V}$
- $E_3 = -1.00 \text{ V (} t_3 = 200 \text{ ms})$
- $t_i = 1 \text{ s}$
- $\Delta E = 30 \text{ mV}$

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

Regions:
- [A] 0.20 M NaOH
- [B] 0.50 M NaOH
- [C] 1.0 M NaOH
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 M NaOH in a 0.20 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 mM glucose in 0.20 M 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 M NaOH.

4. Calibration

Normalized calibration plots of $N_1 I_p/C^b$ and $N_q q_p/C^b$ for thiourea in 0.25 M NH$_4$NO$_3$ by PAD and PS-PCD, respectively, are shown in Fig. X-12. The normalization constants $N_1$ 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 ($t_d = 1$ $\mu$s, $t_1 = 100$ ms)
- $E_2 = 0.40$ V or varied
- $E_3 = -1.00$ V ($t_3 = 200$ ms)
- $t_1 = 1$ s
- $\Delta E = 30$ mV

**Conditions:**
- 0.50 mL min$^{-1}$ flow rate
- 100 $\mu$L sample injected

**Curves:**
- (•) Peak height as a function of $E_1$.
- (▲) Background as a function of $E_1$.
- (*) Peak height as a function of $E_2$.
- (o) Background as a function of $E_2$. 
Figure X-11B. Peak height and background optimization for the PS-PCD of 0.20 mM glucose in 0.20 M 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)
$t_1 = 1$ 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)

q(μC)
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 µM. The region of linearity for PAD is ca. 0.6 decade, i.e., 15-200 µM. 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 mM. 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 mM. Errors from the variation in potential of maximum current are
Figure X-12. Calibration data for thiourea in 0.25 M NH₄NO₃ by PS-PCD and PAD

PS-PCD waveform (1B):  
E₁ = 0.15 V (t₁ = 300 ms)  
E₂ = 1.2 V (t₂ = 400 ms)  
E₃ = -0.6 V (t₃ = 500 ms)

PAD waveform:  
E₁ = 1.0 V (t₁ = 400 ms)  
E₂ = 1.2 V (t₂ = 300 ms)  
E₃ = -0.6 V (t₃ = 500 ms)

Conditions:  
0.50 mL min⁻¹ flow rate  
100 μL sample injected

Curves:  
[●] PS-PCD (N = 1.90 x 10¹ μM μcoul⁻¹)  
[▲] PAD (N = 1.71 x 10⁴ μM μA⁻¹)  
[*] PAD with post-peak dips
not expected for PS-PCD if $E_2 \gg E_p$ 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\textsuperscript{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 N₂ saturated 0.25 M NH₄NO₃ at a Au RED (0.005 cm²; 900 rev min⁻¹)

Conditions: scan rate 4.8 V min⁻¹

Concentration of thiourea:

[A] 0.0 mM
[B] 0.1 mM
[C] 0.3 mM
[D] 0.5 mM
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. Sensitivity is higher and, consequently, the detection limits are decreased by at least 20x for carbohydrates 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 mM glucose in 0.20 M NaOH
II) 0.10 mM thiourea in 0.20 M NaOH

Conditions: 0.40 mL min⁻¹ flow rate
100 μL sample injected

I) Glucose
A) Waveform 1A:

\[
E_1 = -0.20 \text{ V } (t_d = 1 \mu s, \quad t_1 = 100 \text{ ms}) \\
E_2 = 0.40 \text{ V} \\
E_3 = -1.0 \text{ V } (t_3 = 200 \text{ ms}) \\
t_1 = 1 \text{ s} \\
\Delta E = 30 \text{ mV}
\]

B) Waveform 1B:

\[
E_1 = -0.20 \text{ V } (t_d = 100 \text{ ms}, \quad t_1 = 300 \text{ ms}) \\
E_2 = 0.40 \text{ V } (t_2 = 1000 \text{ ms}) \\
E_3 = -1.0 \text{ V } (t_3 = 200 \text{ ms})
\]

II) Thiourea
A) Waveform 1A:

\[
E_1 = -0.20 \text{ V } (t_d = 1 \mu s, \quad t_1 = 200 \text{ ms}) \\
E_2 = 0.50 \text{ V} \\
E_3 = -1.0 \text{ V } (t_3 = 500 \text{ ms}) \\
t_1 = 1 \text{ s} \\
\Delta E = 35 \text{ mV}
\]

B) Waveform 1B:

\[
E_1 = -0.20 \text{ V } (t_d = 100 \text{ ms}, \quad t_1 = 200 \text{ ms}) \\
E_2 = 0.50 \text{ V } (t_2 = 1000 \text{ ms}) \\
E_3 = -1.0 \text{ V } (t_3 = 500 \text{ ms})
\]
Figure X-15. Comparison of detectability of thiourea in 0.25 M NH$_4$NO$_3$ 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 ($t_d = 1$ $\mu$s, $t_1 = 400$ 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 $\mu$L 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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G. References


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\textsuperscript{12} and constant potential pulse polarography,\textsuperscript{13} and others have resolved the problem by removal of dissolved oxygen.\textsuperscript{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.\textsuperscript{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, Paneth and Hevesy, Herzfeld, Haissinsky and Rogers et al. 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. Compilations of the underpotential shifts observed for a variety of adatoms on several electrode substrates have recently appeared in the literature. 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 H₂ 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, 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, chrono-coulometric 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\textsuperscript{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 $t_1$ 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 $t_d + t_1$, 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;  
(0) sampling time for signal output;  
(S) shorting time of integrator.
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 (EGG Princeton Applied Research, Princeton, NJ). 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 cm²; 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. The flow-through detector cell for FIA studies (Dionex Corp.) was of the sandwich-type and contained a Au working (0.05 cm²), 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 HNO₃. 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 HNO₃

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);
Figure XI-3. Current-potential curves for Bi(III) in nitrogen saturated 0.20 M HNO₃

- 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).
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; $t_1 = 167$ 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 $\mu$M for 50 $\mu$L 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:  
- $E_1 = 0.9\,\text{V for Bi(III)}$ (t$_1 = 200\,\text{ms}$),  
- $E_1 = 1.05\,\text{V for Hg(II)}$ (t$_1 = 200\,\text{ms}$),  
- $E_2 = -0.3\,\text{V (t}_2 = 800\,\text{ms)}$,  
- $t_i = 167\,\text{ms}$,  
- $t_d = 4\,\text{ms}$.

Curves:  
- [●] Hg(II)  
- [▲] Bi(III)

Volume injected: 50 µL

Carrier stream: $0.20\,\text{M KNO}_3$ at 0.5 mL min$^{-1}$

Dispersion coefficient ($D_p = C_p/C_b$): 0.56
Table XI-I. Detection limits of metals obtained with FI-PCD at a Au electrode with the waveform $E_1 = 0.90 \, V \, (t_j = 167 \, ms, \, t_d = 4 \, ms, \, t_1 = 200 \, ms)$, $E_2 = -0.30 \, V \, (t_2 = 800 \, ms)$. Nitrâte salts were used for all metal ion solutions unless otherwise noted.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$c^b , (\mu M)$</th>
<th>Amount injected (pmoles)</th>
<th>$\Delta E_p , (V)^b$</th>
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<tr>
<td>Hg(I)$^c$</td>
<td>0.3</td>
<td>15</td>
<td>0.43</td>
</tr>
<tr>
<td>Hg(II)$^c$</td>
<td>0.3</td>
<td>15</td>
<td>0.43</td>
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<tr>
<td>Cu(II)</td>
<td>3</td>
<td>150</td>
<td>0.21</td>
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<tr>
<td>Bi(III)</td>
<td>4</td>
<td>200</td>
<td>0.25</td>
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<tr>
<td>Pb(II)</td>
<td>12</td>
<td>600</td>
<td>0.40</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>8</td>
<td>400</td>
<td>0.50</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>15</td>
<td>750</td>
<td>-</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>8</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>Tl(III)$^d$</td>
<td>0.7</td>
<td>35</td>
<td>0.68</td>
</tr>
</tbody>
</table>

$^a$Volume injected: 50 $\mu$L
Carrier stream: 0.20 $M$ KNO$_3$ at 0.5 mL min$^{-1}$
Dispersion coefficient ($D_p = C_p/C^b$): 0.56.

$^b$Reprinted from Ref. 31.
$^cE_1 = 1.05 \, V$.
$^d$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).

$t_j = 167$ ms,

$t_d = 4$ ms.

**Conditions:** Same as Fig. XI-4.

**Curves:**

- [●] 100 μM Bi(III),
- [▲] 100 μM Cu(II).
Figure XI-6. Selective detection of \( \text{Hg(II)} \) and \( \text{Bi(III)} \) by variation of \( E_2 \) in PCD waveform

Waveform:
- \( E_1 = 1.05 \text{ V} \) \((t_1 = 200 \text{ ms})\),
- \( E_2 \) varied \((t_2 = 800 \text{ ms})\),
- \( t_i = 167 \text{ ms} \),
- \( t_d = 4 \text{ ms} \).

Conditions: Same as Fig. 4.

Injection Peaks:
- [I] \( E_2 = 0.60 \text{ V} \),
- [II] \( E_2 = 0.25 \text{ V} \),
- [III] \( E_2 = -0.30 \text{ V} \).

- [A] 50 \( \mu \text{M} \) \( \text{Hg(II)} \);
- [B] 100 \( \mu \text{M} \) \( \text{Bi(III)} \);
- [C] 50 \( \mu \text{M} \) \( \text{Hg(II)} \) and 100 \( \mu \text{M} \) \( \text{Bi(III)} \);
- [D] 50 \( \mu \text{M} \) \( \text{Hg(II)} \), 100 \( \mu \text{M} \) \( \text{Bi(III)} \), 100 \( \mu \text{M} \) \( \text{Cd(II)} \), 100 \( \mu \text{M} \) \( \text{Cu(II)} \), and 100 \( \mu \text{M} \) \( \text{Zn(II)} \).
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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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 \( \mu M \) for glucose and sucrose, respectively, in 0.20 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 \( \mu M \) 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 encountered 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 μM 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 baseline 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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XVII. ACKNOWLEDGEMENTS

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XVIII. APPENDIX

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A. Extended Bibliography for Underpotential Deposition Summary


69. Cadle, S. H.; Bruckenstein, S. "Rotating Ring-Disk Study of the Underpotential Deposition of Copper at Platinum in 0.5M Hydrochloric Acid", Anal. Chem. 1971, 43, 932 {ca78(18):118404y}.


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),
     PROFILES[10],FILES(150)[10],T$[60]
110    DIM ARRAYFILES[10],J1$[5],J2$[5],C1$[5],C2$[5],CUR(20)
120    ON ERROR GOSUB 1770
130    CLEAR @ DISP "A) Run program ARRAY CREATE" @
     DISP "B) Chain Autost"
140    IF T$[1,1]="A" OR T$[1,1]="a" THEN 160 ELSE CHAIN "Autost"
150    CLEAR @ DISP "Enter the file prefix." @ INPUT PROFILES
160    CLEAR @
170    DISP "Enter file names Individually or by Limits <I,L> [I] :
180    INPUT T$ @ IF LEN (T$)=0 THEN 430
190    IF T$[1,1]="I" OR T$[1,1]="i" THEN 430
200    CLEAR @ DISP "Enter the lower row limit "; @ INPUT 11$
210    DISP @ DISP "Enter the upper row limit "; @ INPUT 12$
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$)
330    INC=INC+1 @ FILES(INC)=VAL$(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$)
390    INC=INC+1 @ FILES(INC)=VAL$(I)&VAL$(J)
400    NEXT J
410    NEXT I @ NF=INC
```
GOTO 470
CLEAR @ DISP "Enter the file names (numbers)." @ DISP "Press <END LINE> when all have been entered."
FOR J=1 TO 60 @ INPUT FILE$(J)
IF LEN (FILE$(J))=0 THEN NF=J-1 @ GOTO 470
NEXT J
CLEAR @ DISP "Drive number <0,1> [1]" @ INPUT DRIVES
IF LEN (DRIVES)=0 THEN DRIVE$="1"
IF VAL (DRIVE$)=0 OR VAL (DRIVE$)=1 THEN 500 ELSE 470
CLEAR @ DISP "Eat the Whole file or Just Parts <W,P> [W] :" @ INPUT T$
IF LEN (T$)=0 THEN PARTS=0 @ GOTO 760
IF T$[1,1]="W" OR T$[1,1]="w" THEN PARTS=0 @ GOTO 760 ELSE PARTS=1
CLEAR @ DISP "Which current elements do you want <1,N> :"
FOR I=1 TO 50
INPUT T$
IF LEN (T$)=0 THEN T0TCUR=I-1 @ GOTO 590 ELSE CUR(I)=VAL (T$) GOTO 580
GOTO 550
NEXT I
PTYPE,CFLAG,RFLAG,KFLAG=0 @ DIVIDE=1
CLEAR @ DISP "Divide all elements by Column or Row values or a Konstant <C,R,K> [K] :
PTYPE=0 @ INPUT T$ @ IF LEN (T$)=0 THEN PTYPE=3 @ GOTO 760
IF T$[1,1]="" " THEN 660
IF T$[1,1]="C" THEN CFLAG=1 @ GOTO 660
IF T$[1,1]="R" THEN RFLAG=1 @ GOTO 660
IF T$[1,1]="K" THEN KFLAG=1
IF LEN (T$)>1 THEN T$=T$[2,LEN (T$)] @ GOTO 620
IF CFLAG=0 AND RFLAG=0 AND KFLAG=0 THEN 600
IF CFLAG=1 THEN PTYPE=1
IF RFLAG=1 THEN PTYPE=2
IF KFLAG=1 THEN PTYPE=3
IF CFLAG=1 AND RFLAG=1 THEN PTYPE=4
IF CFLAG=1 AND KFLAG=1 THEN PTYPE=5
IF RFLAG=1 AND KFLAG=1 THEN PTYPE=6
IF CFLAG=1 AND RFLAG=1 AND KFLAG=1 THEN PTYPE=7
IF PTYPE=1 OR PTYPE=2 OR PTYPE=4 THEN 810
DISP @
DISP "Enter the constant divisor <any non-zero value> [1] :"
INPUT T$ @ IF LEN (T$)=0 THEN DIVIDE=1 @ GOTO 810 ELSE DIVIDE=VAL (T$) @ GOTO 790
GOTO 760
IF DIVIDE=0 THEN 770
CLEAR @ DISP "Enter the minimum row header, e.g., beginning potential."
INPUT T$ @ IF LEN (T$)=0 THEN 810 ELSE RMIN=VAL (T$) @ GOTO 840
GOTO 810
DISP @ DISP @ DISP "Enter the maximum row header, e.g., final potential."
INPUT T$ @ IF LEN (T$)=0 THEN 840 ELSE RMAX=VAL (T$) @ GOTO 870
GOTO 840
870 DISP @ DISP @ DISP "Enter the row header increment, e.g., potential increment."
INPUT T$ @ IF LEN (T$)=0 THEN 870 ELSE RINC=VAL (T$) @ GOTO 900
GOTO 870
900 T=(RMAX-RMIN)/RINC+1 @ IF PARTS=1 THEN 910 ELSE 940
910 IF 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 the minimum column header, e.g., conc., w(1/2), etc."
INPUT T$ @ IF LEN (T$)=0 THEN 950 ELSE CMIN=VAL (T$) @ GOTO 980
GOTO 950
960 DISP @ DISP "Enter the maximum column header, e.g., conc., w(1/2), etc."
INPUT T$ @ IF LEN (T$)=0 THEN 980 ELSE CMAX=VAL (T$) @ GOTO 1010
GOTO 980
970 DISP @ DISP "Enter the column header increment, e.g., conc.,
(1/2), etc."
INPUT T$ @ IF LEN (T$)=0 THEN 1010 ELSE CINC=VAL (T$) @ GOTO 1040
GOTO 1010
1000 T=(CMAX-CMIN)/CINC+1 @ IF PARTS=0 THEN 1050 ELSE 1080
1030 IF T<NF THEN INC=1 @ GOTO 1060 ELSE 1080
1040 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 PREFILES$&FILES$(INC)&F$
1180 DISP "Reading":PREFILES$&FILES$(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$
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 TO ARRAYFILE$&F$
1550 PRINT# 1 ; RMIN,RMAX
1560 PRINT# 1 ; 0,0
1570 PRINT# 1 ; 0,0
1580 PRINT# 1 ; "m1111",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 @
1730 PRINT# 1 ; 0 @ FOR J=1 TO NF @ PRINT# 1 ; N @ NEXT J @
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 ! FOR I=1 TO 14 @ ON KEY# I GOTO menu @ NEXT I @ RETURN
40 Ti$="" @ FOR L=1 TO LEN (T$) @ Ti$[L,L]=CHR$ (NUM (T$[L,L])+128) @ NEXT L
50 RETURN
60 ! ASSIGN# 1 TO "CHARSET"
80 FOR I=1 TO 46
90 READ# 1 : CHAR$(I)
100 NEXT I @ ASSIGN# 1 TO *
110 RETURN
120 ! 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) @
260 DAT$(35)=VAL$ (YCLICK)
270 DAT$(36)=TYPE$ @ DAT$(37),DAT$(38)="" @ DAT$(39)=ZPRINT$
280 DAT$(40),DAT$(41)=""
290 ! 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$="YES"
370 GOTO menu
380 CLEAR @ DISP "Enter storage file name <10 characters> [TEST] :" @
390 INPUT FILE2$
400 IF LEN (FILE2$)=0 THEN FILE2$="TEST"
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 YMAX<-100 OR YMAX>100 THEN 430 ELSE GOTO menu
450 DISP @ DISP @ 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 T$[1,1]="B" OR T$[1,1]="b" THEN T$="B" @ GOTO 530
510 IF VAL (T$)=0 OR VAL (T$)=1 THEN 530 ELSE 490
520 IF CRSR=5 AND T$[1,1]="B" THEN 490
530 IF CRSR=4 THEN DATADRIVE$=T$[1,1] ELSE GRAPHDRIVE$=T$[1,1]
540 GOTO menu
550 CLEAR @ DISP "Enter the file name" @ INPUT T$
560 IF T$[1,1]="B" THEN FILES="" ELSE FILE$="NULL"
570 IF T$[1,1]="B" THEN FILES="NULL" ELSE T$[1,1]="" @ GOTO 630
580 FILE$=T$
590 GOSUB fileinput @ LOCK$="" @ GOTO 630
600 ! Row NR+1 is minimum or NR(1,J) for each column, row NR+2 is maximum or NR(2,J) for each column.
610 ! A similar assignment is also made for NC+1 and NC+2 columns.
620 IF Y(0,0)=0 THEN FILETYPE$="time base"
630 ELSE FILETYPE$="conc. base"
640 GOTO menu
650 IF T$[1,1]="B" THEN DRIVE=1 ELSE DRIVE=0 @ 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" ELSE ZPRINT$="NO" @ PRINTER IS 705,90 ELSE ZPRINT$="NO" @ PRINTER IS 1
710 GOTO menu
720 IF PLOTLINES$="NO" THEN PLOTLINES$="YES" ELSE PLOTLINES$="NO"
730 GOTO menu
740 !
750 IF SCALING$="Man" THEN SCALING$="Auto" ELSE SCALING$="Man"
760 GOTO menu
770 IF PENSIZE$="Man" THEN PENSIZE$="Auto" ELSE PENSIZE$="Man"
780 GOTO menu
790 IF PLOTTEXT$="NO" THEN PLOTTEXT$="YES" ELSE PLOTTEXT$="NO"
800 GOTO menu
810 CLEAR @ DISP "Enter the x-axis labels as literal strings <10 max> ;"
FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN XCLICK=I-1 @ GOTO 840
XCLICK(I)=VAL (T$) @ NEXT I @ XCLICK=10
GOTO menu
CLEAR @
 DISP "Enter the y-axis labels as literal strings <10 max> ;"
FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN YCLICK=I-1 @
YCLICK(I)=VAL (T$) @ NEXT I @ YCLICK=10
GOTO menu

! fileinput:
IF DATADRIVE$="B" OR DATADRIVE$="b" THEN DRIVES$=VAL$ (1) ELSE
ASSIGN# 1 TO FILES$&":D70"&DRIVES$
READ# 1 ; E1,E2  ! beginning detection pot., ending detection pot.
READ# 1 ; E3,E4  ! anodic limit, cathodic limit
READ# 1 ; T1,T2  ! beginning detection time, ending detection time
READ# 1 ; _RANGE,I_TYPE$,$RANGE
READ# 1 ; T3,T4  ! cleaning time, adsorption time
READ# 1 ; EXTDATAS,T5
FOR I=0 TO NR+2
FOR J=0 TO NC+2
READ# 1 ; Y(I,J)
NEXT J
NEXT I
ASSIGN# 1 TO *
RETURN
IF FILE$="NULL" THEN CLEAR @ DISP "No master file on board" @
DISP "Press <END LINE> to continue." @ INPUT T$ @ GOTO menu
IF CAL=1 AND LOCK$="*" THEN RETURN
IF CAL=0 AND LOCK$="*" THEN menu
CLEAR @ AWRITE 10,33,"calculating"
ON TYPE GOSUB
4850,4860,4900,5040,5140,5290,5150,5220,5360,4970,5430 @
LOCK$="*
IF CAL=1 THEN RETURN
GOTO menu
plotting:
Graphics routine
CAL=1 @ GOSUB calculations @ CAL=0
IF DSPCRT$="NO" AND DSPXY$="NO" THEN 2810
CLEAR @ AWRITE 10,33,"Plotting"
MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
PFLAG=0 @ IF PLOTTYPE=2 THEN 1380
FOR I=1 TO NR @ IF ROW(I)=0 THEN 1360
IF Y(I,0)<MINX THEN MINX=Y(I,0)
IF Y(I,0)>MAXX THEN MAXX=Y(I,0)
FOR J=1 TO NC @ IF COL(J)=0 THEN 1350
PFLAG=1
IF Y(I,J)<MINY THEN MINY=Y(I,J)
IF Y(I,J)>MAXY THEN MAXY=Y(I,J)
NEXT J
NEXT I
GOTO 1470
FOR J=1 TO NC @ IF COL(J)=0 THEN 1460
IF Y(0,J)<MINX THEN MINX=Y(0,J)
IF Y(0,J)>MAXX THEN MAXX=Y(0,J)
FOR I=1 TO NR @ IF ROW(I)=0 THEN 1450
PFLAG=1
IF Y(I,J)<MINY THEN MINY=Y(I,J)
IF Y(I,J)>MAXY THEN MAXY=Y(I,J)
NEXT I
NEXT J
IF PFLAG<> 0 THEN 1500
AWRITE 20,0,"Improper boundary selection" @ AWRITE 21,0,"Press <END LINE> to continue ." @ AWRITE 22,0,"
RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD @ GOTO menu
IF DSPCRT$ <> "YES" THEN 1770
GRAPHALL @ FRAME
LOCATE 30,200,25,95
XEXP=ABS ((MAXX-MINX)/200 @ YEXP=ABS ((MAXY-MINY)/20)
IF PLOTTYPE=2 THEN SCALE MINX-XEXP,MAXX+XEXP,MINY-YEXP,MAXY+YEXP
ELSE SCALE MAXX+XEXP,MINX-XEXP,MINY-YEXP,MAXX,YEXP
FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
LAXES -((MAXX-MINX)/60),(MAXY-MINY)/4/5,0,0,10,5,3
MOVE MINX,MINY
X$=CHR$ (46)
FOR J=1 TO NC @ IF COL(J)=0 THEN 1640
FOR I=1 TO NR @ IF ROW(I)=0 THEN 1630
MOVE Y(I,0),Y(I,J) @ LABEL X$
NEXT I
NEXT J
GOTO 1710
FOR I=1 TO NR @ IF ROW(I)=0 THEN 1700
FOR J=1 TO NC @ IF COL(J)=0 THEN 1690
MOVE Y(0,J),Y(I,J) @ LABEL X$
NEXT J
NEXT I
CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
LABEL "millamps"
LDIR 0 @ MOVE RATIO *100/2-10,15
LABEL " "
IF DSPFLAGS="YES" THEN GSTORE FILE2$&":D70"&GRAPHDRIVES$
INPUT T$ @ ALPHALL
IF DSPXY$ <> "YES" THEN 2810
!
! Mechanical plotting routine
!
GOSUB label check
XSCALE=8.5 @ YSCALE=7
IF PLOTTYPE=1 THEN A=MINX @ MINX=MAXX @ MAXX=A
XSCALING=XSCALE/(MAXX-MINX)
YSCALING=YSCALE/(MAXY-MINY)
XCENTER=MAXX-(MAXX-MINX)/2
YCENTER=MAXY-(MAXY-MINY)/2
OUTPUT 723 ;"GP"
TAKE KEYBOARD
CLEAR @ DISP "Set zero positions now !" @ 
DISP "Press <END LINE> to continue"
OUTPUT 723 ;"OP 7 0T OP 12 50T OP 14 50T"
KYY=NUM (KEY$ ) @ IF NOT KYY THEN 1910
WAIT 1000
IF PLOTAXES$="NO" THEN 2510
X=MINX*XSCALING-XCENTER*XSCALING+XSCALE/2
Y=MAXY*YSCALING-YCENTER*YSCALING+YSCALE/2
IF PLOTLABELS="YES" THEN 2080
OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 OT OP 14 50T"
WAIT 2000
OUTPUT 723 ;"OP 7 7.0T OP 11 1500 14 50T WA .2T OP 7 ";X;"T OP 12 50T"
OUTPUT 723 ;"OP 7 0.0T OP 11 1500 14 50T"
WAIT 3100
OUTPUT 723 ;"OP 7 ";Y;"T OP 14 50T OP 7 ";0;"T OP 12 50T"
WAIT 750
OUTPUT 723 ;"OP 7 8.5T OP 11 1500 12 50T WA .2T OP 7 ";Y;"T OP 14 50T"
OUTPUT 723 ;"OP 7 0.0T OP 11 1500 12 50T"
WAIT 3100
Y=INT (Y*10000)/10000 @ X=INT (X*10000)/10000
WAIT 1000
XPOS=XSCALE/6
YP0S=YSCALE/5
IF Y-YSCALE/6<0 THEN Y1=0 ELSE Y1=Y-YSCALE/60
IF Y+YSCALE/60>YSCALE THEN Y2=YSCALE ELSE Y2=Y+YSCALE/60
Y1=INT (Y1*10000)/10000 @ Y2=INT (Y2*10000)/10000
LXSCALING=550
FOR I=1 TO XCLICK
IF SCALING$ <> "Man" THEN 2190
X1=XCLICK(I)*XSCALING-XCENTER*XSCALING+4.25 @ GOTO 2210
X1=INT (I*(XSCALE/XCLICK)*10000)/10000
IF X1>XSCALE THEN 2300
Y3=INT ((Y2-Y1)*10000)/10000
OUTPUT 723 ;"OP 7 ";X1;"T OP 12 50T OP 7 ";Y1;"T OP 14 50T"
WAIT 1500
OUTPUT 723 ;"OP 11 500 7 ";Y1+Y3:" 14 50T"
WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (XCLICK(I)) @
GOTO 2270
LA$=VAL$ ((MAXX-MINX)/XCLICK*I+MINX+.0001)*1000)/1000)
XIN=X1-8.5/LXSCALING*LEN (LA$)*7/2
YIN=7.25 @ GOSUB xylabel
NEXT I
IF X-XSCALE/73<0 THEN X1=0 ELSE X1=X-XSCALE/73
IF X+XSCALE/73>XSCALE THEN X2=XSCALE ELSE X2=X+XSCALE/73
X1=INT (X1*10000)/10000 @ X2=INT (X2*10000)/10000
FOR I=1 TO YCLICK
IF SCALING$ <> "Man" THEN 2360
Y1=YCLICK(I)*YSCALING-YCENTER*Y$CALING+.35 @ GOTO 2390
Y1=INT (Y1*(YSCALE/5)*10000)/10000
IF Y1>YSCALE THEN 2510
IF Y1=Y THEN 2470
X3=INT ((X2-X1)*10000)/10000
OUTPUT 723 ;"OP 7 ";Y1;"T OP 14 50T OP 7 ";X1;"T OP 12 50T"
WAIT 1000
OUTPUT 723 ;"OP 11 500 7 ";X1+X3;" 12 50T"
WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (YCLICK(I)) @
GOTO 2450
LA$=VAL$ ((MAXY-MINY)/YCLICK*I+MINY+.000001)*10000)/10000)
XIN=8.75
YIN=Y1+.12 § GOSUB xylabel
NEXT I
IF PENSWITCH$="Auto" THEN 2510
CLEAR @ DISP "Change pen color ? Press <END LINE> to continue."
RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
WAIT 1000
PFLAG=0 @ IF PLOTTYPE=2 THEN 2670
FOR J=1 TO NC @ IF COL(J)=0 THEN 2650
FOR I=1 TO NR @ IF ROW(I)=0 THEN 2610
PFLAG=1
X=Y(I,0)*XSCALING-XCENTER*XSCALING+4.25
Y=Y(I,J)*YSCALING-YCENTER*YSCALING+3.5
OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
OUTPUT 723 ;"OP 11 100T"
NEXT I
IF PENSWITCH$="Auto" THEN 2650
CLEAR @ DISP "Change pen color ? Press <END LINE> to continue."
RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
NEXT J
GOTO 2800
FOR I=1 TO NR @ IF ROW(I)=0 THEN 2790
FOR J=1 TO NC @ IF COL(J)=0 THEN 2750
PFLAG=1
X=Y(0,J)*XSCALING-XCENTER*XSCALING+4.25
Y=Y(I,J)*YSCALING-YCENTER*YSCALING+3.5
441

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(IO),DROPTYPE(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),
2891 DATADRIVE$,GRAPHDRIVE$,DRIVE$[5]
2900 DIM DSPFLAG$(3),DSPCRT$(3),DSPXY$(3),
2910 CHAR$(46)[35],LA$(80),TYPE$(30)
2920 ON ERROR GOTO 3730 @ AWRITE 0,0
2930 DSPFLAG$="NO" @ FILE2$="TEST" @ DATADRIVE$="B" @ GRAPHDRIVE$="0"
2940 FLAG=1 @ TOTAL=10 @ SETMILLI=0 @ SETMICR0=0 @ PRODUCT=0 @
2950 YMIN,YMAX=0
2960 FILE$="NULL" @ E1,E4=0 @ PLOTTYPE=1 @ FILETYPE$="" @
2970 ZPRINT$="NO"
2980 LOCK$="" @ N=1 @ TYPE=5 @ CAL=0 @ PLOTAXES="YES" @
2990 SCALING$="Auto"
3000 PENSWITCH$="Man" @ PLOTLABEL$="NO" @ XCLICK=6 @ YCLICK=5 @
3010 TYPE2=1
3020 DSPCRT$="YES" @ DSPXY$="NO" @ TYPE$="i vs. x [j]" @ XMIN,XMAX=0
3030 FOR I=1 TO NRMAX @ ROW(I)=0 @ NEXT I
3040 FOR J=1 TO NCMAX @ COL(J)=0 @ NEXT J
3050 FOR I=1 TO 10 @ XCLICK(I),YCLICK(I)=100000000000000000 @ NEXT I
3060 TAKE KEYBOARD @ GOSUB 30 @ GOSUB 70
3070 A$(1)="Filler directory"
3080 A$(2)="Mass storage directory"
3090 A$(3)="Plotting directory"
3095 A$(4)="Start plotting"
3096 A$(5)="Chain Autost"
3100 A$(6)="End program"
3105 A$(7)="NULL"
1,000 A$(8)="Exit to main menu"
1,100 A$(9)="Store graph on disk"
1,110 A$(10)="Graph storage file name"
1,120 A$(11)="Numeric data drive number"
1,130 A$(12)="Graphic data drive number"
1,140 A$(13)="Catalog of disk"
1,150 A$(14)="NULL"
1,160 A$(15)="NULL"
1,170 A$(16)="NULL"
1,180 A$(17)="NULL"
1,190 A$(18)="NULL"
1,200 A$(19)="NULL"
1,210 A$(20)="Exit to main menu"
1,220 A$(21)="Master array file <type>"
1,230 A$(22)="Re-enter master file"
1,240 A$(23)="Set min and max for y-axis only"
1,250 A$(24)="Set min and max for x-axis only"
1,260 A$(25)="NULL"
1,270 A$(26)="Exit to main menu"
1,280 A$(27)="Plot on CRT"
1,290 A$(28)="Plot on printer"
1,300 A$(29)="Plot on X-Y recorder"
1,310 A$(30)="Manual or Automatic scaling"
1,320 A$(31)="Manual or Automatic pen switching"
1,330 A$(32)="Plot axes (including labels)"
1,340 A$(33)="Plot ticks and labels only"
1,350 A$(34)="X-axis labels"
1,360 A$(35)="Y-axis labels"
1,370 A$(36)="Curves plotted"
1,380 A$(37)="Set intervals for plotting"
1,390 A$(38)="Least squares calculation"
1,400 A$(39)="Activate printer"
1,410 A$(40)="Do calculations"
1,420 A$(41)="NULL"
1,430 PERIOD$=".
1,440 FOR I=1 TO 41 @ T$=A$(I) @ GOSUB 40 @ B$(I)=T1$ @ NEXT I
1,450 SCRn=3 @ A1=1 @ A2=6
1,460 menu: TAKE KEYBOARD @ GOSUB 130 @ PAGEFLAG=0
1,470 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
1,480 AWRITE 1,8,B$(A1) @ CRSR=1
1,490 AWRITE 21,2, "Change any parameters ?" @ AWRITE 22,2, "Press the indicated letters or use the ',' and ',' keys for slewing "
1,500 AWRITE 23,2, "Press '4' to change any parameters or to start experiment "
1,510 TAKE KEYBOARD
1,520 KYY=NUM (KEY$ ) @ IF NOT KY$ THEN 3520
1,530 IF KY$>64 AND KY$<65+A2-A1+1 THEN AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=KYY-64 @ AWRITE CRSR,8,B$(A1+CRSR-1)
1,540 IF KY$< 46 THEN 3570
443

3550  AWRITE CRSR,8,A$(Al+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
       CRSR=A2-A1+1
3560  AWRITE CRSR,8,B$(Al+CRSR-1)
3570  IF KYY<> 44 THEN 3600
3580  AWRITE CRSR,8,A$(Al+CRSR-1) @ CRSR=CRSR+1 @ IF CRSR>A2-A1+1 THEN
       CRSR=1
3590  AWRITE CRSR,8,B$(Al+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 LOADDIN "UTIL/1" @ GOTO 3840
3790  IF ERRN =67 AND (DRIVES$="O" OR DRIVES$="1") THEN CLEAR @
       DISP "Place correct disk in drive" @ WAIT 5000 @ GOTO menu
3800  IF ERRN =67 AND (DATADRIVES$="B" OR DATADRIVES$="b") THEN
       DRIVES$=VAL$ (ABS (VAL (DRIVES$)-1)) @ GOTO 930
3810  IF ERRN =130 AND DATADRIVES$="B" THEN
       DRIVES$=VAL$ (ABS (VAL (DRIVES$)-1)) @ GOTO 930
3820  IF ERRN =130 THEN BEEP 300,1000 @ RELEASE KEYBOARD @ CLEAR @
       DISP "Place disk in drive and then press <END LINE>" @ INPUT T$
       @ 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
LYSCALING = INT ((LXSCALING/CLRATIO)*10000)/10000

IF LXSCALING > 400 THEN LSPACE = 2 ELSE LSPACE = 1

LX = (-((5 + LSPACE)*8.5/LXSCALING) + XIN

OUTPUT 723;"OP 7";XIN;"T OP 12 50T OP 7";YIN;"T OP 14 50T"

WAIT 500

FOR LI = 1 TO LEN (LA$)
    LT = NUM (LA$[LI,LI])
    IF LT = 32 THEN LT = 47
    LY = YIN
    LP0INT = 0
    LX = LX + (LSPACE + 5)*8.5/LXSCALING

    FOR LJ = 1 TO 7
        LY = INT ((LY - 7/LYSCALING)*10000)/10000
        LX1 = LX
        FOR LK = 1 TO 5
            LP0INT = LP0INT + 1
            LX2 = INT ((LX1 + LK*8.5/LXSCALING)*10000)/10000
            IF CHAR$(LT - 44)[LP0INT,LP0INT] <> "1" THEN 4170
            OUTPUT 723;"OP 7";LX2;"T OP 12 50T OP 7";LY;"T OP 14 50T"
        ENDIF
        WAIT 200
        OUTPUT 723;"OP 11 100T"
    ENDIF
    WAIT 200
    NEXT LJ
    NEXT LI
    NEXT LI
    RETURN

FILELABEL:

CLEAR @ DISP "Set zero positions now!" @
DISP "Press <END LINE> to continue"

OUTPUT 723;"OP 7 OT OP 12 50 14 50T"

KYY = NUM (KEYS) @ IF NOT KYY THEN 4250

LYSCALING = 550

LA$ = "FILES" @ XIN = 0 @ YIN = 0 @ GOSUB xylabel

LA$ = "-----" @ XIN = 0 @ YIN = -0.14 @ GOSUB xylabel

X = 1

FOR I = 1 TO TOTAL
    IF FILES = "NULL" THEN 4410
    X = X + 1
    LA$ = UPC$ (FILES)
    FOR J = 1 TO LEN (FILES)
        TS = FILES[J,J]
        IF TS = "_" THEN LA$[J,J] = "_"
    ENDIF
    NEXT J
    XIN = 0 @ YIN = -X*.1875
    GOSUB xylabel
    NEXT I
    RETURN
4450 | Plotting type
4460 |
4470 IF FILE$="NULL" THEN CLEAR @ DISP "No master file on board" @
4480  DISP "$Press <END LINE> to Continue." @  INPUT T$ @ GOTO menu
4490 CLEAR @ DISP "Enter number corresponding to type of curve
4500  plotted" 4490 DISP "Note, 'j' refers to rows, 'k' refers to
4510 column;"
4520 DISP "i.e., j implies that the data is plotted vs. to zeroeth
4530 row."
4540 AWRITE 8,20,"1) 1 vs. X [k]"
4550 AWRITE 9,20,"2) 1 vs. 1/x [k]"
4560 AWRITE 10,20,"3) ln(i) vs. ln(x) [k]"
4570 AWRITE 11,20,"4) d(i)/d(1/y) vs. x [j]"
4580 AWRITE 12,20,"5) i vs. x [j]"
4590 AWRITE 13,20,"6) 1/i vs. 1/x [k]"
4600 AWRITE 14,20,"7) (1-1/1(o))/1 vs. x [k]"
4610 AWRITE 15,20,"8) 1 vs. x [j]"
4620 AWRITE 16,20,"9) 1/i vs. 1/x [k]"
4630 AWRITE 17,19,"10) ln(i) vs. ln(x) [j]"
4640 AWRITE 18,19,"11) i vs. sqr(x) [j]"
4650 AWRITE 20,2,"" @ INPUT T$  
4660 IF LEN (T$)=0 THEN menu ELSE TYPE=VAL (T$) @ GOTO 4660
4670 GOTO menu
4680 IF TYPE<1 OR TYPE>11 THEN 4470
4690 IF TYPE=4 OR TYPE=5 OR TYPE=9 OR TYPE=10 OR TYPE=11 THEN TYPE2=1
4700 ELSE TYPE2=2
4710 IF TYPE2=1 THEN PLOTTYPE=1 ELSE PLOTTYPE=2
4720 ON TYPE GOSUB  
4730 4710,4720,4730,4740,4750,4760,4770,4780,4790,4800,4810
4740 GOTO menu
4750 TYPES$="i vs. x [k]" @ RETURN
4760 TYPES$="i vs. 1/x [k]" @ RETURN
4770 TYPES$="ln(i) vs. ln(x) [k]" @ RETURN
4780 TYPES$="d(i)/d(1/y) vs. x [j]" @ RETURN
4790 TYPES$="i vs. x [j]" @ RETURN
4800 TYPES$="1/R vs. x [k]" @ RETURN
4810 TYPES$="1/R/R vs. x [k]" @ RETURN
4820 ! Calculations as per type selected for plotting
4830 !
4840 !
4850 RETURN
4860 FOR J=1 TO NC
4870 Y(0,J)=1/Y(0,J)
4880 NEXT J
4890 RETURN
4900 FOR I=0 TO NR
4910 FOR J=1 TO NC
4920 IF NOT Y(I,J) THEN 4940
4930 Y(I,J)=LOG (ABS (Y(I,J)))
4940 NEXT J
4950 NEXT I
4960 RETURN
4970 FOR I=1 TO NR
4980 FOR J=0 TO NC
4990 IF NOT Y(I,J) THEN 5010
5000 Y(I,J)=LOG (ABS (Y(I,J)))
5010 NEXT J
5020 NEXT I
5030 RETURN
5040 GOSUB 4860
5050 PLOTYPE=2
5060 FOR I=1 TO NR @ IF ROW(I)=0 THEN 5100
5070 RLOW,RHIGH=I
5080 LSCALE=2 @ GOSUB leastsquares
5090 Y(I,1)=SLOPE
5100 NEXT I
5110 PLOTYPE=1 @ CLOW,CHIGH=1
5120 FOR J=2 TO NC @ COL(J)=0 @ NEXT J @ COL(1)=1
5130 RETURN
5140 RETURN
5150 FOR I=1 TO NR
5160 FOR J=2 TO NC
5170 Y(I,J)=Y(I,1)/Y(I,J)
5180 NEXT J
5190 Y(I,1)=1
5200 NEXT I
5210 RETURN
5220 GOSUB 5150
5230 FOR I=1 TO NR
5240 FOR J=2 TO NC
5250 Y(I,J)=(1-Y(I,J))/Y(I,J)
5260 NEXT J
5270 NEXT I
5280 RETURN
5290 FOR I=0 TO NR
5300 FOR J=1 TO NC
5310 IF NOT Y(I,J) THEN 5330
5320 Y(I,J)=1/Y(I,J)
5330 NEXT J
5340 NEXT I
5350 RETURN
5360 FOR I=1 TO NR
5370 FOR J=0 TO NC
5380 IF NOT Y(I,J) THEN 5400
5390 Y(I,J)=1/Y(I,J)
5400 NEXT I
5410 NEXT I
5420 RETURN
5430 FOR I=1 TO NR
5440 Y(I,0)=SQR(Y(I,0))
5450 NEXT I
5460 RETURN
5470 !
5480 limits:
5490 !
5500 ! Setting limits
5510 !
5520 IF FILE$="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)&"columns or "&CHR$ (128+82)&"rows, or perhaps "&CHR$ (128+69)&"xiting?"
5540 KYY=NUM (KEYS ) @ IF NOT KYY THEN 5540
5550 IF KYY=69 TEEN 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 CODES @ IF LEN (CODE$)=0 THEN 5530
5600 FOR J=1 TO NC @ COL(J)=0 @ NEXT J
5610 GOSUB decode @ IF error=1 THEN J=1
5620 CLEAR @ AWRITE 2,0,"Column numbers to be defined." @ AWRITE 3,0,"" @ DISP
5630 FOR J=1 TO NC @ IF CODE(J)=1 THEN J=1
5640 NEXT J @ DISP
5650 FOR J=1 TO NC @ IF CODE(J)=1 THEN COL(J)=1
5660 NEXT J @ AWRITE 20,0,"Press <END LINE> to continue" @ AWRITE 21,0,"" @ INPUT T$ @ 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 CODES @ IF LEN (CODE$)=0 THEN 5530
5690 FOR I=1 TO NR @ ROW(I)=0 @ NEXT I
5700 GOSUB decode @ IF error=1 THEN 5670
5710 CLEAR @ AWRITE 2,0,"Row numbers to be defined." @ AWRITE 3,0,"" @ DISP
5720 FOR I=1 TO NR @ IF CODE(I)=1 THEN I=1
5730 NEXT I @ DISP
5740 FOR I=1 TO NR @ IF CODE(I)=1 THEN ROW(I)=1
5750 NEXT I @ AWRITE 20,0,"Press <END LINE> to continue" @ AWRITE 21,0,"" @ INPUT T$ @ GOTO 5530
5760 !
5770 decode:
5780 !
5785 IF KYY=82 THEN NDMAX=NRMAX ELSE NDMAX=NCMAX
ON ERROR GOTO error3 @ err=0 @ FOR I=1 TO NDMAX @ CODE(I)=0 @ NEXT I

FOR I=1 TO LEN (CODE$) @ IF CODE$(1,1)=CHR$ (32) THEN 
CODE$=CODES[2,LEN (CODE$)] @ GOTO 5800

IF CODE$(1,1) <= "*" THEN 5830

FOR I=1 TO NDMAX @ CODE(I)=1 @ NEXT I @ GOTO 5940

T$="1"

FOR I=0 TO 9 @ IF CODE$(1,1)=VAL$(I) THEN T$="-1"

NEXT I @ IF T$ <> THEN 5830

FOR I=1 TO NDMAX @ CODE(I)=1 @ NEXT I @ GOTO 5940

TS="1"

FOR 1=0 TO 9 @ IF CODE$(1,1)=VAL$(I) THEN T$="-1"

NEXT I @ IF TS <> VAL$(I) THEN CODE$=CODES[2,LEN (CODE$)] ELSE 5870

IF LEN (CODE$)=0 THEN error3 ELSE 5840

T=VAL$(CODE$) @ IF T<0 OR T>NDMAX THEN error2 ELSE CODE(T)=1

IF LEN (VAL$(T))=LEN (CODE$) THEN 5940 

CODES=CODES[1+LEN (VAL$(T)),LEN (CODE$)] @ IF T="" OR T="-" THEN 5910 ELSE error1

T1=VAL (CODE$) @ IF T1<0 OR T1>NDMAX THEN T=T1 @ GOTO error2

IF T="" THEN CODE(T1)=1 @ GOTO 5940

FOR I=T+1 TO T1 @ CODE(I)=1 @ NEXT I @ GOTO 5870

ON ERROR GOTO 3730 @ RETURN

error1: error=1

DISP "Character ";T$; " not allowed." @ DISP @ 

DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN

error2: error=1

DISP "The value ";T; " is to large." @ DISP @ 

DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN

error3: error=1

DISP "String does not follow syntax." @ DISP @ 

DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN

ls_select:

IF FILES="NULL" OR LOCKS="" THEN menu

IF TYPE=4 THEN 6230

IF TYPE2=1 THEN 6110 ELSE 6170

CLEAR @ AWRITE 1,0,"Column number ?" @ AWRITE 2,0,"" 

RELEASE KEYBOARD @ INPUT T$ @ IF LEN (T$)=0 THEN menu

IF VAL (T$)<1 OR VAL (T$)>NC THEN 6110 ELSE 6150

GOTO 6110

GOTO 6110

CLOW,CHIGH=VAL (T$)

LSCAL=1 @ GOSUB leastsquares @ GOTO 6110

CLEAR @ AWRITE 1,0,"Row number ?" @ AWRITE 2,0,""

RELEASE KEYBOARD @ INPUT T$ @ IF LEN (T$)=0 THEN menu

IF VAL (T$)<1 OR VAL (T$)>NR THEN 6170 ELSE 6210

GOTO 6170

RLOW,RHIGH=VAL (T$)
449

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 ((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_INTERCEPT = ";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 ;"OP" @ 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$="YES" THEN STATIC=8 @ STATIC2=32768 ELSE
160 STATIC=8+ROT(ROT) @ STATIC2=32768+ ROT(ROT)
170 FOR I=1 TO T6
180 OUTPUT 723 ;"OP 7 ";E3;" 14 ";T3;"T OP 7 ";E2;" 14 ";T2;"T"
190 NEXT I
200 OUTPUT 723 ;"OP 7 ";E8;" 14 ";T9;" 13 ";STATIC;"T OP 7 ";E6;" 11 ";PTYME;" 13 ";STATIC 2 ;"T"
210 INTEGRATE=32768
220 WAIT T6*(T2+T3+100)+T1+T9+100
230 DISP "Continuing"
240 OUTPUT 723 ;"WF 11.2 OT"
250 INTEGRATE=8 @ GOSUB 20
260 !
270 ! Input data from memory cards
280 !
290 SEND 7 ; UNL MLA TALK 23 SCG 5
300 FOR I=0 TO N
310 ENTER 7 USING ",.K" ; TEMP(I)
320 NEXT I
330 !
340 IF SCANS=1 THEN 360
350 FOR I=0 TO N @ Y(I)=Y(I)+TEMP(I) @ NEXT I @ GOTO 370
360 FOR I=0 TO N @ Y(I)=TEMP(I) @ NEXT I
370 SCANS=SCANS+1 @ IF SCANS<TOTALSCANS+1 THEN GOTO experiment2
380 COUNTER=COUNTER+1
390 !
400 FOR I=0 TO INT (N/SAMPLE)
410 X(I)=T5*I*SAMPLE
420 Y(I)=Y(I*SAMPLE)/TOTALSCANS
430 NEXT I
440 N=INT (N/SAMPLE)
445 DISP Y(1),Y(N)
450 IF COULOMB$="q" THEN 500
FOR I=1 TO N
Y(I)=-(Y(I)/10*ADVOLTE*I RANGE/V RANGE)
NEXT I
GOTO 540
FOR I=1 TO N
Y(I)=-(1000000^2.000001*Y(I)/ADVOLTE*I RANGE/(V RANGE*100))
NEXT I
SCANFLAG=1 @ GOSUB datastore @ SCANFLAG=0 @ IF T4=T7 THEN 580
T9=T9+T8 @ IF T9>T7 THEN T9=T4 @ GOTO 580
SCANS=1 @ GOTO experiment2
IF E4=E7 THEN 630
E8=E8+INCPR2 @ IF E8>E7 THEN E8=E4 @ GOTO 630
SCANS=1 @ GOTO experiment2
IF E1=E5 THEN 665
E6=E6+INCPR @ IF E6>E5 THEN E6=E1 @ GOTO 665
SCANS=1 @ GOTO experiment2
IF STATIC$="YES" THEN 710
IF ROTMIN=0 THEN 710
ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN @ GOSUB 20 @ GOTO 710
GOSUB 20 @ SCANS=1 @ GOTO experiment2
IF PLOTFIG$="NO" THEN menu
plotter: ! Graphics routine

LOW=1 @ HIGH=N
MINX=0 @ MAXX=0 @ MINY=YMIN @ MAXY=YMAX
IF X(N)>X(0) THEN MAXX=X(N) @ MINX=X(0) ELSE MAXX=X(0) @ MINX=X(N)
FOR I=LOW TO HIGH
IF Y(I)<MINY THEN MINY=Y(I)
IF Y(I)>MAXY THEN MAXY=Y(I)
NEXT I
GRAPHALL @ FRAME
LOCATE 30,200,25,95
SCALE MINX,MAXX,MINY,MAXY
FRAME @ CSIZE 4 @ FXD 0,4 @ LINE TYPE 1
LAXES -((MAXX-MINX)/50),(MAXY-MINY)/4/5,0,0,10,5,3
MOVE MINX,MINY
LORG 4 @ X$=CHR$ (46)
FOR I=LOW TO HIGH
MOVE X(I),Y(I)
LABEL X$
NEXT I
CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
LABEL I TYPE$&"amps"
453

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$="YES" THEN GSTORE FIGUREFILES&FD$ @ GOTO 1030 ELSE 1030
1020  GSTORE FIGUREFILES&FD$
1030  GSTORE: IF DATASTORE$="YES" THEN 1040 ELSE 1130
1040  DDS=VAL$ (COUNTER)&":D70"&VAL$ (DATADRIVE)
1050  PURGE DATAFILES&DDS
1060  CREATE DATAFILES&DDS,20+N*2,10
1070  ASSIGN# 1 TO DATAFILES&DDS
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 @
1250  DISP "Enter the anodic cleaning potential <-10,+10> [1.3] :
1260  INPUT T$ @ IF LEN (T$)=0 THEN E2=1.3 @ GOTO 1270 ELSE E2=VAL (T$) @ GOTO 1270
1270  GOTO 1240
1280  IF E2<-10 OR E2>10 THEN 1240
1290  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
1340  !
1350  CLEAR @ DISP "Enter the detection time <0,600000 msec> [200] :" @
1360  INPUT T$
1370  IF LEN (T$)=0 THEN T1=200 @ GOTO 1390 ELSE T1=VAL (T$) @
1370  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  CLEAR @ DISP "Enter the anodic cleaning time <0,600000 msec> [200] :"
1440  INPUT T$ @ IF LEN (T$)=0 THEN T2=200 @ GOTO 1460 ELSE T2=VAL (T$)
1450  @ GOTO 1430
1460  GOTO 1430
1470  IF T2<0 OR T2>600000 THEN 1430
1480  IF T2=0 THEN T2=.001
1490  GOTO menu
1500  CLEAR @ DISP "Enter the initial reduction/adsorption time <0,600000> [500] :"
1510  INPUT T$ @ IF LEN (T$)=0 THEN T4=500 @ GOTO 1530 ELSE T4=VAL (T$)
1520  @ GOTO 1500
1530  IF T4<0 OR T4>600000 THEN 1500
1540  IF T4=0 THEN T4=.001
1550  GOTO menu
1560  CLEAR @ DISP "Enter the data file name <7 characters> [PADTEST] :"
1580  INPUT T$ @ IF LEN (T$)=0 THEN DATAFILES="PADTEST" ELSE DATAFILES=T$
1590  IF LEN (T$)<8 OR DATAFILES="PADTEST" THEN 1630
1600  DISP @ DISP @ DISP "File name is longer than 7 characters."
1610  DISP "Do you wish to change it? <Y,N> [N] ;" @ INPUT T$
1615  IF LEN (T$)=0 THEN menu
1620  IF T$[1,1]="Y" OR T$[1,1]="y" THEN 1570
1630  GOTO menu
1640  CLEAR @ DISP "Enter the figure file name <10 characters> [TEST_PAD] :"
1660  INPUT T$ @ IF LEN (T$)=0 THEN FIGUREFILES="TEST_PAD" ELSE FIGUREFILES=T$
1670  IF LEN (T$)<11 OR FIGUREFILES="TEST_PAD" THEN 1710
1680  DISP @ DISP @ DISP "File name ";T$;" 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$[1,1]="y" THEN 1650
1710  GOTO menu
1720  IF DATADRIVE=1 THEN DATADRIVE=0 ELSE DATADRIVE=1
1740  GOTO menu
1750  IF Statics="YES" THEN Static$="NO" ELSE Statics="YES"
1770  GOTO menu
1780 IF FIGUREDRI VE=1 THEN FIGUREDRI VE=0 ELSE FIGUREDRI VE=1
1790 GOTO menu
1800 GOTO menu
1810 IF DATASTORE$="YES" THEN DATASTORE$="NO" ELSE DATASTORE$="YES"
1820 GOTO menu
1830 IF FIGSTORE$="YES" THEN FIGSTORE$="NO" ELSE FIGSTORE$="YES"
1840 GOTO menu
1850 IF COULOMB$="i" THEN COULOMB$="q" ELSE COULOMB$="i"
1860 GOTO menu
1870 CLEAR @ DISP "Enter the drive number <0,1> [1] :" @ INPUT T$
1880 IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 1940 ELSE DRIVE=VAL (T$) @
1890 GOTO 1940
1900 GOTO 1910
1910 IF DRIVE=0 OR DRIVE=1 THEN 1950 ELSE 1910
1920 CAT ":D70"&VAL$ (DRIVE)
1930 DISP "Press <END LINE> to continue ;" @ INPUT T$
1940 GOTO menu
1950 IF PLOTFIG$="YES" THEN PLOTFIG$="NO" ELSE PLOTFIG$="YES"
1960 GOTO menu
1970 CLEAR @ DISP "Enter the cathodic cleaning potential <-10,+10> [-0.25] :"
1980 INPUT T$ @ IF LEN (T$)=0 THEN E3=-.25 @ GOTO 2050 ELSE E3=VAL
1990 (T$) @ GOTO 2050
2000 GOTO 2020
2010 IF E3<-10 OR E3>10 THEN 2020
2020 GOTO menu
2030 CLEAR @ DISP "Enter the cathodic cleaning time <0,600000 msec> [200] :"
2040 INPUT T$ @ IF LEN (T$)=0 THEN T3=200 @ GOTO 2110 ELSE T3=VAL
2050 (T$) @ GOTO 2110
2060 GOTO 2080
2070 IF T3<0 OR T3>600000 THEN 2080
2080 IF T3=0 THEN T3=.001
2090 GOTO menu
2100 CLEAR @ DISP "Enter the sampling time for i vs. t <0.1,600000 msec> [2] :"
2110 INPUT T$ @ IF LEN (T$)=0 THEN T5=2 @ GOTO 2180 ELSE T5=VAL
2120 (T$) @ GOTO 2180
2130 GOTO 2150
2140 IF T5<.1 OR T5>600000 THEN 2150
2150 GOTO menu
2160 CLEAR @ DISP "Enter the minimum on Y <-50,max Y> [0] :" @ INPUT T$
456

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>1000 THEN GOTO 2530
2520 GOTO menu
2530 CLEAR @ DISP "Enter the ending detection potential <0, 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
CLEAR @ DISP "Enter the potential increment, E-d <-2, 2 [.005 min]> [0.05] :"
INPUT T$ @ IF LEN (T$)=0 THEN INCPOT=.05 @ GOTO 2660 ELSE INCPOT=VAL (T$) @ GOTO 2610
GOTO 2580
IF INCPOT>ABS (E5-E2) THEN 2580
IF INCPOT<-.005 AND INCPOT<0 THEN 2580
IF INCPOT<.005 AND INCPOT>0 THEN 2580
IF INCPOT<-2 OR INCPOT>2 THEN 2580
IF INT (INCPOT*1000)/.005 <> INCPOT*1000/.005 THEN 2580
GOTO menu
CLEAR @ DISP "Enter the A/D voltage range <1, 10> [10] :") @ INPUT T$
IF LEN (T$)=0 THEN ADV0LTAGE=10 @ GOTO 2710 ELSE ADV0LTAGE=VAL (T$) @ GOTO 2700
GOTO 2670
GOTO menu
CLEAR @ DISP "Enter the number of signal averaged scans <1, --> [1] :")
INPUT T$ @ IF LEN (T$)=0 THEN TOTALSCANS=1 @ GOTO 2750 ELSE TOTALSCANS=VAL (T$) @ GOTO 2750
GOTO 2690
GOTO menu
CLEAR @ DISP "Enter the final reduction/adsorption time <0,600000> [500] :")
INPUT T$ @ IF LEN (T$)=0 THEN T7=500 @ GOTO 1530 ELSE T7=VAL (T$) @ GOTO 2810
GOTO 2780
GOTO menu
CLEAR @ DISP "Enter the reduction/adsorption time increment <0,600000> [0] :")
INPUT T$ @ IF LEN (T$)=0 THEN T8=0 @ GOTO 1530 ELSE T8=VAL (T$) @ GOTO 2870
GOTO menu
CLEAR @ DISP "Enter the potential increment, E-r/a <-2, 2 [.005 min]> [0.05] :"
INPUT T$ @ IF LEN (T$)=0 THEN INCPOT2=.05 @ GOTO 2980 ELSE INCPOT2=VAL (T$) @ GOTO 2980
GOTO 2900
IF INCPOT2>ABS (E5-E2) THEN 2900
IF INCPOT2<-.005 AND INCPOT2<0 THEN 2900
IF INCPOT2<.005 AND INCPOT2>0 THEN 2900
IF INCPOT2<-2 OR INCPOT2>2 THEN 2900
458

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) &"\"&PERIODS[1,5-LEN (VAL$ (I))] &ROTS(I)&ROTS(I) @ NEXT I
3060 FOR I=1 TO 7 @ AWRITE I+7,30,VAL$ (I+10) &"\"&PERIODS[1,3]&ROTS(I+10)&ROTS(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$(I)="*-" THEN
ROT(J)=ROT2(I) @ J=J+1
3100 NEXT I @ ROTMAX=J-1 @ IF ROTMAX=0 THEN ROTMIN=0 @ ROT=0 ELSE
ROTMIN=1 @ ROT=1
3120 GOTO 3040
3130 IF ZPRINT$="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$(50)[25],
DATAFILES[20],FIGUREFILES[20]
3200 DIM T$[50],TI$[50],PERIODS[50],DATASTORES[10],FIGSTORES[10]
3210 DIM FLOTFIGS[10],I_TYPES[5],FD$[15],DDS[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 @ DATAFILES="PADTEST" @ FIGUREFILES="TEST_PAD" @
DATADRIVE=1
3260 FIGUREDROME=1 @ DATASTORES="YES" @ FIGSTORES="NO" @ DRIVE=1 @
E3=-.25
3270 ROT,ROT(0),ROTMAX,ROTMIN=0 @ ZPRINTS="NO" @ PRINTER IS 1 @
INTEGRATE=8
3280 PLOTFI$="YES" @ YMIN,YMAX=0 @ I_RANGE=5 @ I_TYPE$="milli" @
INCPOT=.05
3290 SCANFLAG=0 @ ADVOLUTE=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 ROTS$(3)="1400" @ FOR I=10 TO 70 STEP 10 @
ROTS$(I/10+10)=VAL$(I') @ NEXT I
3320 FOR I=1 TO 17 @ READ T @ ROT2(I)=T @ ROT(I)=0 @ NEXT I
3330 COULOMB$="1" @ 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$(16)="Detection time (msec), T1"
3510 A$(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$(26)="Sampling frequency"
3610 A$(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$[1:1] & A$(I) & PERIOD$[1:45 - LEN(A$(I))] & " & DAT$(I) @ NEXT I
3860  AWRITE 1, 8, B$(A1) @ CR$ = 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(KEYS) @ 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 3990
4000  IF SCR$ = 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, 2900, 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
4100  ELSE ON CRSR GOTO 4100, 1990, 2200, 3130
4110  TAKE KEYBOARD @ SCRN = 1 @ A1 = 1 @ A2 = 6 @ GOTO 3850
4120  TAKE KEYBOARD @ SCRN = 5 @ A1 = 22 @ A2 = 32 @ GOTO 3850
4130  TAKE KEYBOARD @ SCRN = 2 @ A1 = 7 @ A2 = 21 @ GOTO 3850
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$(INCP0T2)
4230 DAT$(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)=COULOMBS
4300 DAT$(32)=STATIC$ @ DAT$(33),DAT$(34)="
4310 DAT$(35)=DATAFILES $ @ DAT$(36)=FIGUREFILES $ @ DAT$(37)=VAL$
(DATADRIVE)
4320 DAT$(38)=VAL$ (FIGUREDRAIVE) @ DAT$(39)=DATASTORES
4330 DAT$(40)=FIGSTORES $ @ DAT$(41)=VAL$ (DRIVE) @ DAT$(42)=""
4340 DAT$(43)="" @ DAT$(44)=PLOTFIGS $ @ DAT$(45)=VAL$(YMIN)&", 
&VALS
(YMAX)
4350 DAT$(46)=ZPRINTS
4360 RETURN
4370 I
4380 !
4390 ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN
4400 GOSUB 20 @ RETURN
4410 ROT=0 @ GOSUB 20 @ RETURN
4420 decode:
4430 ON ERROR GOTO error2 @ error=0 @ FOR I=1 TO 20 @ CODE(I)=0 @ 
NEXT I
4450 FOR I=1 TO LEN(CODES$) @ IF CODES$[1,1]=CHR$(32) THEN CODES=
CODES[2,LEN(CODES$)] @ GOTO 4450
4460 IF CODES$[1,1]<>"*" THEN 4480
4470 FOR I=0 TO 9 @ IF CODES$[1,1]=VAL$(I) THEN T$="-1"
4480 NEXT I @ IF T$ <> VAL$(I) THEN CODES=CODES[2,LEN (CODES$)]
ELSE 4520
4490 FOR I=0 TO 9 @ IF CODES$[1,1]=VAL$(I) THEN T$="-1"
4500 NEXT I @ IF T$ <> VAL$(I) THEN CODES=CODES[2,LEN (CODES$)]
ELSE 4520
4510 IF LEN (CODES$)=0 THEN error3 ELSE 4490
4520 T=VAL $(CODES$) @ IF T<0 OR T>99 THEN error2 ELSE CODE(T)=1
4530 IF LEN (VAL$(T))=LEN (CODES) THEN 4590
4540 CODES=CODES[1+LEN (VAL$(T)),LEN (CODES)] @ IF LEN (CODES$)=0 THEN
CODE(T)=1 @ GOTO 4590
4550 T$=CODES$[1,1] @ CODES=CODES[2,LEN (CODES$)] @ IF T$=""," OR T$="-"
THEN 4560 ELSE error1
4560 t1=VAL $(CODES$) @ IF t1<0 OR t1>99 THEN T=t1 @ GOTO error2
4570 IF T$="" THEN CODE(t1)=1 @ GOTO 4520
4580 FOR I=T+1 TO t1 @ CODE(I)=1 @ NEXT I @ GOTO 4520
4590 ON ERROR GOSUB 4720 @ RETURN
4620 DISP "Character ";T$;" 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
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

GOTO beginning
FOR I=1 TO 14 @ ON KEY# I GOTO menu @ NEXT I @ RETURN
T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128) @ NEXT L @ RETURN

ASSIGN# 1 TO"CHARSET"
FOR I=1 TO 46
READ# 1 : CHAR$(I)
NEXT I @ ASSIGN# 1 TO * @ RETURN

DAT$(1),DAT$(2),DAT$(3),DAT$(4), DAT$(5),DAT$(6),DAT$(7),DAT$(8)="
DAT$(9)=DSPFLAGS $@ DAT$(10)=FILE2$ @ DAT$(11)=DATADRIVE$
DAT$(12)=GRAPHDRIVE$ @ DAT$(13)=VAL$ (DRIVE) @ DAT$(14)="
FOR I=15 TO 24
DAT$(I)=FILE$(I-14)&LOCK$(I-14)&" (<"&VAL$ (E4(I-14))&") >" @ NEXT I @

CLEAR @ DISP "Plot on CRT <Y/N> [Y] :" @ INPUT T$ @ IF LEN (T$)=0 THEN DSPCRT$="YES" @ GOTO 90
IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPCRT$="YES" ELSE DSPCRT$="NO"
GOTO menu
CLEAR @ DISP "Store graph on disk <Y/N> [Y]:" @ INPUT T$
IF T$[1,1]="N" OR T$[1,1]="n" THEN DSPFLAGS="NO" ELSE DSPFLAGS="YES"
GOTO menu
CLEAR @ DISP "Plot on X-Y recorder <Y/N> [N] :"); INPUT T$ @ IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPXY$="YES" ELSE DSPXY$="NO"
GOTO menu
CLEAR @ DISP "Enter storage file name <10 characters> [TEST] :"); INPUT FILE2$
IF LEN (FILE2$)=0 THEN FILE2$="TEST"
GOTO menu
CLEAR @ DISP "Enter the minimum on X <-100,100> [0] :"); INPUT T$ @ IF T$[1,1]="Y" OR T$[1,1]="y" THEN YMIN=0 ELSE YMIN=VAL (T$)
IF YMIN<-100 OR YMIN>100 THEN 138
DISP @ DISP @ DISP "Enter the maximum on X <-100,100> [0] :"); INPUT T$ @ IF T$[1,1]="Y" OR T$[1,1]="y" THEN XMAX=0 ELSE XMAX=VAL (T$)
IF XMAX<−100 OR XMAX>100 THEN 140 ELSE GOTO menu
CLEAR @ DISP "Enter the minimum on Y <-100,100> [0] :" @ INPUT T$ @ IF LEN (T$)=0 THEN YMIN=0 ELSE YMIN=VAL (T$)
IF YMIN<-100 OR YMIN>100 THEN 145
DISP @ DISP @ DISP "Enter the maximum on Y <-100,100> [0] :" @ INPUT T$ @ IF LEN (T$)=0 THEN YMAX=0 ELSE YMAX=VAL (T$)
IF YMAX<-100 OR YMAX>100 THEN 155 ELSE GOTO menu
CLEAR @ DISP "Enter the drive number <0,1 or both--data read only> [0] :" @ INPUT T$
IF T$(1,1)="B" OR T$(1,1)="b" THEN FLAG=0 @ GOTO 185
IF VAL (T$)=0 OR VAL (T$)=1 THEN 185 ELSE 165
IF CRSR=5 AND (T$(1,1)="B" OR T$(1,1)="b") THEN 165
IF CRSR=4 THEN DATADRIVES$=T$(1,1) ELSE GRAPHDRIVES$=T$(1,1)
GOTO menu
CLEAR @ DISP "Enter the file name" @ INPUT T$
IF LEN (T$)=0 THEN FILES$(CRSR-1)="NULL" @ LOCKS$(CRSR-1)="" @ LOW(CRSR-1),HIGH(CRSR-1)= 1 @ GOTO 235
FILES$(CRSR-1)=T$ @ LOCKS$(CRSR-1)="
J=CRSR-1 @ GOSUB fileinput
GOTO menu
CLEAR @ DISP "Enter the drive number <0,1> [1] :" @ INPUT T$
IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 255
DRIVE=VAL (T$) @ IF DRIVE=0 OR DRIVE =1 THEN 255 ELSE 240
CLEAR @ CAT :":D70"&VAL$(DRIVE)
DISP "Press <END LINE> to continue:" @ INPUT T$
GOTO menu
CLEAR @ DISP "Enter the raw data filenames [10] :" @ DISP "Press <END LINE> when the last name has been entered."
FOR J=1 TO TOTAL
INPUT FILES$(J)
N=J @ LOCKS$(J)="" @ LOW(J),HIGH(J)=1
IF LEN (FILES$(J))=0 THEN FILES$(J)="NULL" @ LOCKS$(J)="" @ N=J-1 @ J=TOTAL
NEXT J
FOR J=1 TO N
GOSUB fileinput
NEXT J
GOTO menu
fileinput:
IF DATADRIVES$="b" OR DATADRIVES$="b" THEN DRIVES$=VAL$(0) ELSE DRIVES$=DATADRIVES$
ASSIGN# 1 TO FILES$(J)&":D70"&DRIVE$
READ# 1 ; E1(J),E2(J),E3(J),E4(J),T1(J),T2(J),I_RANGE(J)
READ# 1 ; I_TYPE$(J),T3(J),T4(J),EXTDATA$(J),N(J)
READ# 1 ; T5(J),A,A,A,A,A,A
FOR I=1 TO N(J) @ READ# 1 ; X(I,J),Y(I,J) @ NEXT I
IF DATADRIVES$="b" OR DATADRIVES$="b" THEN FLAG=0
IF ERRN =67 OR ERRN =66 THEN 430
ASSIGN# 1 TO *
HIGH(J)=N(J) @ RETURN
FOR J=1 TO TOTAL
FILE$(J)="NULL" @ LOCKS$(J)="" @ LOW(J),HIGH(J)=1 @ E1(J),E4(J)=0
NEXT J
GOTO menu
FOR J=1 TO TOTAL
LOCKS$(J)="" @ LOW(J),HIGH(J)=1
IF FILE$(J)="NULL" THEN 510
GOSUB fileinput
NEXT J
GOTO menu
plotting:
Graphics routine
CLEAR @ AWRITE 10,33,"Calculating"
ON TYPE GOSUB 3800,3850,3900,3950,4000,4050
IF DSPCRT$="NO" AND DSPXY$="NO" THEN 1200
CLEAR @ AWRITE 10,33,"Plotting"
SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @ FACTOR=1
FOR J=1 TO TOTAL
IF FILE$(J)="NULL" THEN 615
IF I TYPE$(J)="milli" THEN SETMILLI=1 ELSE SETMICR0=1
NEXT J
IF SETMILLI=1 AND SETMICRO=1 THEN PRODUCT=1
MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
FOR J=1 TO TOTAL
IF FILE$(J)="NULL" THEN 720
IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE FILE$(J)="null" THEN 840
LOW=LOW(J) @ HIGH=HIGH(J)
IF X(Low,J)>MAXX THEN MAXX=X(Low,J)
IF X(HIGH,J)>MAXX THEN MAXX=X(HIGH,J)
IF X(LOW,J)<MINX THEN MINX=X(LOW,J)
IF X(HIGH,J)<MINX THEN MINX=X(HIGH,J)
FOR I=LOW TO HIGH
IF Y(I,J)*FACTOR<MINY THEN MINY=Y(I,J)*FACTOR
IF Y(I,J)*FACTOR>MAXY THEN MAXY=Y(I,J)*FACTOR
NEXT I
NEXT J
IF DSPCRT$ <> "YES" THEN 870
GRAPHALL @ FRAME
LOCATE 30,200,25,95
XEXP=ABS ((MAXX-MINX)/20) @ YEXP=ABS ((MAXY-MINY)/20)
SCALE MINX-XEXP,MAXX+XEXP,MINY-YEXP,MAXY+YEXP
FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
LAXES -((MAXX-MINX)/60),(MAXY-MINY)/4/5,0,0,10,5,3
MOVE MINX,MINY
LONG 4 @ XS=CHR$ (46)
FOR J=1 TO TOTAL
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 @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20, 80
850 IF PRODUCT = 1 THEN LABEL "microamps" ELSE LABEL I_TYPE$(J) & "amps"
855 LDIR 0 @ MOVE RATIO -100/2-10, 15 @ LABEL "time (msec)"
860 IF DSPFLAGS = "YES" THEN GSTORE FILE2$ &":D70" & GRAPHDRIVES$
865 INPUT T$ @ ALPHALL
870 IF DSPXY$ <> "YES" THEN 1200
875 ! Mechanical plotting routine
880 !
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 OT OP 12 50T OP 14 50T"
925 KYY = NUM (KEYS) @ 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 OT 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
1030 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+.00001)*1000)/1000)
1040 XIN=X1+.85/LXScaling*LEN (LA$)*7/2
1041 YIN=7.25 @ GOSUB xlabel
1045 NEXT I
1050 IF X-XScale/73<0 THEN X1=0 ELSE X1=X-XScale/73
1055 IF X+XScale/73>XScale THEN X2=XScale ELSE X2=X+XScale/73
1057 X1=INT (X1*10000)/10000 @ X2=INT (X2*10000)/10000
1060 FOR I=1 TO 5
1065 Y1=INT ((I*YScale/5)*10000)/10000
1070 IF Y1>YScale THEN 1095
1075 IF Y1=Y THEN 1090
1078 X3=INT ((X2-X1)*10000)/10000
1080 OUTPUT 723 ;"OP 7 ";Y1;"T OP 14 50T OP 7 ";X1;"T OP 12 50T"
1081 WAIT 1000
1082 OUTPUT 723 ;"OP 11 500 7 ";X1+X3;" 12 50T"
1085 WAIT 550
1086 LA$=VAL$ (INT (((MAXY-MINY)/5*I+MINY+.000001)*10000)/10000)
1087 XIN=8.75
1088 YIN=Y1+.12 @ GOSUB xlabel
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
1105 IF FILE$(J)="NULL" THEN 1195
1110 IF PRODUCT=1 AND I_TYPE$(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 continue."
1190 RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
1195 NEXT J
1197 GOSUB filelabel
GOTO menu

beginning:

CLEAR

DIM Y(300,10), X(300,10), EXPMT(10), FINPOT(10)
DIM SCANS(10), DROPTIME(10), I_RANGE(10), I_TYPE$(10)
DIM INCPT(10), PTYME1(10), EXTDATA$(10)[10], N(10)
DIM AS$(36)[50], BS$(36)[50], FILES$(10)[15], FILE2$(15), DAT$(36)[25]
DIM T$(50), T1$(50), PERIOD$(50), DATADRIVE$(5), GRAPHDRIVE$(5), DRIVES$(5)

DIM DSPFLAGS$[3], DSPCRT$[3], DSPXY$[3], CHAR$(46)[35], ISA$(80), TYPS$(30)
DIM LOW(IO), HIGH(IO), LOCK$(IO)(1)

SMOOTH=0 @ ON ERROR GOSUB 1715 @ AWRITE 0, 0
DSPFLAGS$="NO" @ FILE2$="TEST" @ DATADRIVE$="B" @ GRAPHDRIVE$="O"
@ DRIVE=1
FLAG=1 @ TOTAL=10 @ SETMILLI=0 @ SETMICRO=0 @ PRODUCT=0 @ YMIN=0
@ YMAX=0
FOR J=1 TO TOTAL @ FILES$(J)="NULL" @ E1(J), E4(J)=0
LOW(J), HIGH(J)=1 @ LOCK$(J)="" @ NEXT J @ N(1)=1
DSPCRT$="YES" @ DSPXY$="NO" @ TYPE=1 @ TYPS$="i vs. t" @
XMIN, XMAX=0
TAKE KEYBOARD @ GOSUB 10 @ GOSUB 26
A$(1)="File directory"
A$(2)="Mass storage directory"
A$(3)="Plotting directory"
A$(4)="Start plotting"
A$(5)="Chain Autost"
A$(6)="End program"
A$(7)="NULL"
A$(8)="Exit to main menu"
A$(9)="Store graph on disk"
A$(10)="Graph storage file name"
A$(11)="Numeric data drive number"
A$(12)="Graphic data drive number"
A$(13)="Catalog of disk"
A$(15)="File <detection potential> <ads. potential>"
A$(23)="Enter all files"
A$(26)="Re-enter all files"
A$(27)="Clear all files"
A$(28)="Set min and max for y-axis only"
A$(29)="Set min and max for x-axis only"
A$(30)="Exit to main menu"
A$(31)="Plot on CRT"
A$(32)="Plot on printer"
A$(33)="Plot on X-Y recorder"
A$(34)="Curves plotted"
A$(35)="Set intervals for plotting"
A$(36)="Least squares calculation"
PERIODS$=".............................................................................."
FOR I=1 TO 13 @ T$=A$(I) @ GOSUB 15 @ BS$(I)=T1$ @ NEXT I
469

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-Al+1,2,CHR$ (64+I-Al+1)&CHR$(41)&PERIOD$(1,4)&A$(I)&PERIOD$(1,45-LEN(A$(I)))&" &DAT$(I) @ NEXT I
1600  AWRITE 1,8,B$(A1) @ CR$=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  KY=NUM (KEY$ ) @ IF NOT KY THEN 1620
1625  IF KY>64 AND KY<65+A2-A1+1 THEN AWRITE CR$R,8,A$(A1+CR$R-1) @ CR$R=KY-64 @ AWRITE CR$R,8,B$(A1+CR$R-1)
1630  IF KY< 46 THEN 1645
1635  AWRITE CR$R,8,A$(A1+CR$R-1) @ CR$R=CR$R-1 @ IF CR$R=A2-A1+1 THEN CR$R=CR$R-1
1640  AWRITE CR$R,8,B$(A1+CR$R-1)
1645  IF KY> 44 THEN 1660
1650  AWRITE CR$R,8,A$(A1+CR$R-1) @ CR$R=CR$R+1 @ IF CR$R=A2-A1+1 THEN CR$R=CR$R+1
1655  AWRITE CR$R,8,B$(A1+CR$R-1)
1660  IF KY> 52 THEN 1615
1665  IF SCRN> 3 THEN 1690
1670  IF CR$R=1 THEN SCRN=1 @ A1=14 @ A2=29 @ GOTO 1595
1675  IF CR$R=2 THEN SCRN=2 @ A1=8 @ A2=13 @ GOTO 1595
1680  IF CR$R=3 THEN SCRN=4 @ A1=30 @ A2=36 @ GOTO 1595
1685  IF CR$R=4 THEN 565
1687  RELEASE KEYBOARD @ IF CR$R=5 THEN CHAIN "Autost" ELSE GOTO 1710
1690  PAGEFLAG=1 @ RELEASE KEYBOARD
1695  IF SCRN=1 THEN ON CR$R GOTO
1700  IF SCRN=2 THEN ON CR$R GOTO 1705,95,130,165,165,240 ELSE ON CR$R GOTO 1705,80,1615,115,3500,4300,7500
1705  TAKE KEYBOARD @ SCRN=3 @ A1=1 @ A2=6 @ GOTO 1595
1710  CLEAR @ END
1715  ! Error trap subroutine
1720  IF ERRN =71 THEN 1775
1725  IF ERRN =66 OR ERRN =12 THEN 1775
1730  IF ERRN =11 THEN menu
1735  IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 1775
1740  IF FLAG=1 AND ERRN =67 AND (DATADRIVES="B" OR DATADRIVES="b") THEN FLAG=0 @ GOTO 390
1745  IF FLAG=1 AND ERRN =67 THEN CLEAR @ DISP "Place correct disk in drive and press <END LINE>, " @ RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
1750  IF ERRN =67 AND (DATADRIVES="B" OR DATADRIVES="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$,LXSCALING
3090  RATIO=230/190 ! X/Y
3095  LYSCALING=INT (LXSCALING/LRATIO*10000)/10000
3105  IF LXSCALING>400 THEN LSPACE=2 ELSE LSPACE=1
3110  LX=-(5+LSPACE)*8.5/LXSCALING)+XIN
3112  OUTPUT 723 ;"0P 7 ";XIN;"T OP 12 50T OP 7 ";YIN;"T OP 14 50T"
3113  WAIT 500
3115  FOR LI=1 TO LEN (LA$)
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 OT 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 xlabel
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
3650 GOTO menu
3700 TYPES$="1 vs. t" @ RETURN
3705 TYPES$="1 vs. 1/t" @ RETURN
3710 TYPES$="ln(i) vs. t" @ RETURN
3715 TYPES$="ln(i) vs. 1/t" @ RETURN
3720 TYPES$="ln(i) vs. t" @ RETURN
3725 TYPES$="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$(J)&" <"&
4330 0 = (LOW(J))&"> <"&VAL$ (HIGH(J))&">
4340 NEXT J
4345 AWRITE 19,20,CHR$ (64+TOTAL+1)&").....Interval for all files"
4350 AWRITE 20,20,CHR$ (64+TOTAL+2)&").....Exit to plotting menu"
4355 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
4400 not exist" @ WAIT 2000 @ GOTO 4300
4410 CLEAR @ AWRITE 10,20,"" @ DISP "Enter interval for ",&FILE$(T)
4420 DISP @ DISP "Enter lower bound of interval <lower, upper> [1] :
4440 " @ INPUT T$
4450 IF LEN (T$)=0 THEN LOW(T)=1 @ GOTO 4460 ELSE LOW(T)=VAL (T$) @
4460 GOTO 4450
4470 GOTO 4410
4480 IF LOW(T)>N(T)-3 THEN DISP "Value to large" @ GOTO 4420
4490 DISP "Enter upper bound of interval <lower, total> [total] :
4510 @ INPUT T$
4470 IF LEN (T$)=0 THEN HIGH(T)=N(T) @ GOTO 4600 ELSE HIGH(T)=VAL (T$)
4480 GOTO 4490
4490 GOTO 4460
4500 GOTO 4300
4510 CLEAR @ DISP @
4520 IF LEN (T$)=0 THEN LOW=1 @ GOTO 4530 ELSE LOW=VAL (T$) @
4530 DISP "Enter lower bound of interval <l,upper> [1] :" @ INPUT T$
4540 IF LEN (T$)=0 THEN HIGH=N(1) @ GOTO 4550 ELSE HIGH=VAL (T$) @
4550 FOR J=1 TO TOTAL
4560 IF FILES(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$)=0 THEN menu
7570 IF T<1 OR T>T0TAL+1 THEN menu
7590 IF FILE$(T="NULL" THEN AWRITE 21,2,"File &CHR$ (64+T)&" does not exist" @ WAIT 2000 @ GOTO 7550
7600 GOSUB leastsquares
7610 GOTO 7500
7999 !
8000 leastsquares: ! Linear least squares subroutine
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 @
8060 FOR I=LOW(T) TO HIGH(T) @
8061 VARIANCE=VARIANCE+(Y(I,T)-INTERCEPT-SLOPE*X(I,T))^2 @ NEXT I
8070 VARIANCE=VARIANCE/(N-2)
8080 SLOPESDERR=SQR (VARIANCE/N*VARIANCE/CONSTANT)
8090 INTERCEPTSDEERR=SQR (VARIANCE/N*(1+SUMX^2/CONSTANT))
8100 CORRCEFF=SQR (SLOPE*((SUMXY-SUMX*SUMY)/(SUMXSQRD-SUMX^2/N)))
8110 DISP "CORRELATION COEFFICIENT = ";VAL$ (CORRCEFF)
8120 DISP "SLOPE = ":SLOPE @ DISP " Y-INTERCEPT = ";INTERCEPT
8130 DISP "SD ERROR IN SLOPE IS = ";SLOPESDERR
8140 DISP "SD ERROR IN Y-INTERCEPTY = ";INTERCEPTSDEERR
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 !
100     CSIZE 4 @ FXD 0,4 @ LINE TYPE 1
110     MAXY=10 @ MINY=-10 @ X$=CHRS (46)
120 !
130 experiment1:
140 !
150      CLEAR 723 @ WAIT 4000 @ SCALE E2,E3,MINY,MAXY @ C0UNTER=1
160      GOSUB 20 @ XX=E2-(E2-E3)/2 @ YY=MINY+(MAXY-MINY)/20
170      FRAME @ AXES -.2,(MAXY-MINY)/2,0,0,2,1,3 @ I=1 @ SCANS=0 @ T3=T1 @ TSCANS=0
180      OUTPUT 723 ;"OP 7 ";VOLT(I);"T OP 12 ";T3;"T OP 14 .03 12 18 T IP 4T"
190      SEND 7 ; UNL MLA TALK 23 SCG 1
200      ENTER 7 ; Y(I)
210      MOVE VOLT(I),-Y(I) @ LABEL X$
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 @ GOSUB 20 @ GOTO menu
250      IF SCANS=INTSCAN THEN SCANFLAG=1 @ GOSUB calculation @ SCANFLAG=0 ELSE 1=1 @ GOTO 180
260      C0UNTER=C0UNTER+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
475

95  CLEAR @ DISP "Store graph on disk <Y/N> [Y]:" @ INPUT T$
100  IF LEN (T$)=0 THEN DSPFLAGS="YES"
105  IF T$[1,1]="N" OR T$[1,1]="n" THEN DSPFLAGS="NO" ELSE
110     DSPFLAGS="YES"
115  GOTO menu
120  CLEAR @ DISP "Plot on X-Y recorder <Y/N> [N] :" @ INPUT T$ @
125  IF LEN (T$)=0 THEN DSPXY$ ="NO" @ GOTO 125
130  IF T$[1,1]="Y" OR T$[1,1]="y" THEN DSPXY$="YES" ELSE DSPXY.MAXY
150  FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
160  LAXES -((MAXX-MINX)/50),(MAXY-MINY)/4,5,0,0,10,5,3
170  MOVE MINX,MINY
180  LORG 4 @ X$=CHR$ (46)
190  FOR I=LOW TO HIGH
200      MOVE VOLT(I),Y(I)
210  LABEL X$
220  NEXT I
230  CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
240  LABEL I_TYPE$&"amps"
250  LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "volts (V)"
260  !
270  ! Store data on disk
280  !
290  IF FIGSTORE$="Y" THEN GSTORE FILE$&":D70"&VAL$ (FIGUREDRIVE) @
300      GOTO 730 ELSE 730
310  GSTORE FILE$&"D70"&VAL$ (FIGUREDRIVE)
320  !
330  storedata:
340  !
350  IF DATASTORE$="Y" THEN 760 ELSE 850
360  DDS$=DATAFILES&VAL$ (COUNTER)&":D70"&VAL$ (DATADRIVE)
370  PURGE DDS @ GOTO 780
380  CREATE DDS,20fN*2,10
390  ASSIGN# 1 TO DDS
400  PRINT# 1 ; E1,E2,E3,E4,T1,T2,I_RANGE
410  PRINT# 1 ; I_TYPE$[1,5],INCTIME,0,"NULL"
420  PRINT# 1 ; N,V_RANGE,ADVOLTAGE,INTSCAN,TOTALSCANS,0,0,0,0
430  FOR I=1 TO N @ PRINT# 1 ; VOLT(I),Y(I) @ NEXT I
440  ASSIGN# 1 TO *
450  IF SCANFLAG=1 THEN RETURN
460  IF PLOTCTR$="N" THEN 870 ELSE RELEASE KEYBOARD @ INPUT T$ @
470      ALPHALL
480  GOSUB xyplot
490  GOTO menu
500  !
510  ! inputs
520  !
530  CLEAR @ DISP "Enter the beginning potential <-10,+10> [0.2] :" @
540      INPUT T$
550  IF LEN (T$)=0 THEN E1=.2 @ GOTO 950 ELSE E1=VAL (T$) @ GOTO 950
560  GOTO 920
570  IF E1<-10 OR E1>10 THEN 920
IF FLAG=1 THEN RETURN
GOTO menu

CLEAR @ DISP "Enter the anodic potential limit <-10,+10> [1.3] :"
INPUT T$ @ IF LEN (T$)=0 THEN E2=1.3 @ GOTO 1020 ELSE E2=VAL (T$) @ GOTO 1020
GOTO 990
IF E2<-10 OR E2>10 THEN 990
IF E2<E3 THEN 990
IF FLAG=1 THEN RETURN
GOTO menu

CLEAR @ DISP "Enter the cathodic potential limit <-10,10> [-0.25] :
INPUT T$ @ IF LEN (T$)=0 THEN E3=-.25 @ GOTO 1100 ELSE E3=VAL (T$) @ GOTO 1100
GOTO 1070
IF E3<-10 OR E3>10 THEN 1070
IF E3>E2 THEN 1070
IF FLAG=1 THEN RETURN
GOTO menu

CLEAR @ DISP "Enter the beginning current sampling delay time <0.001, 600000 msec> [0.001] :" @ INPUT T$
IF LEN (T$)=0 THEN T1=.001 @ GOTO 1180 ELSE T1=VAL (T$) @ GOTO 1180
GOTO 1150
IF T1=0 THEN T1=.001
IF TK.001 OR T1>600000 THEN 1150
GOTO menu

CLEAR @ @
DISP "Enter the data file name <7 characters> [DTESTSC] :
INPUT T$ @ IF LEN (T$)=0 THEN DATAFILE$="DTESTSC" ELSE DATAFILE$=T$
IF LEN (T$)<8 OR DATAFILE$="DTESTSC" THEN 1300
DISP @ DISP @ DISP "File name is longer than 7 characters."
DISP "Do you wish to change it? <Y,N> [N] :" @ INPUT T$
IF LEN (T$)<0 THEN menu
IF LEN (T$)<0 AND (T$[1,1]="Y" OR T$[1,1]="y") THEN 1230
GOTO menu

CLEAR @
DISP "Enter the figure file name <10 characters> [TEST_SC],"
INPUT T$ @ IF LEN (T$)=0 THEN FIGUREFILE$="TEST_SC" ELSE FIGUREFILE$=T$
IF LEN (T$)<11 OR FIGUREFILE$="TEST_SC" THEN 1390
DISP @ DISP @ DISP "File name ";T$; is longer than 10 characters."
DISP "Do you wish to change it? <Y,N> [N] :" @ INPUT T$
IF LEN (T$)=0 THEN menu
IF LEN (T$)<> 0 AND (T$[1,1]="Y" OR T$[1,1]="y") THEN 1320
GOTO menu
1400 !
IF DATADRIVE=0 THEN DATADRIVE=1 ELSE DATADRIVE=0
GOTO menu
1430 !
IF FIGUREDRIVE=0 THEN FIGUREDRIVE=1 ELSE FIGUREDRIVE=0
GOTO menu
1460 !
IF DATASTORE$="Y" THEN DATASTORE$="N" ELSE DATASTORE$="Y"
GOTO menu
1490 !
IF FIGSTORE$="Y" THEN FIGSTORE$="N" ELSE FIGSTORE$="Y"
GOTO menu
1520 !
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
GOTO 1530
1560 IF DRIVE=0 OR DRIVE=1 THEN 1570 ELSE 1530
CAT ":D70"&VAL$ (DRIVE)
1580 DISP "Press <END LINE> to continue:" @ INPUT T$
GOTO menu
1600 !
IF PLOTFIG$="Y" THEN PLOTFIG$="N" ELSE PLOTFIG$="Y"
GOTO menu
1630 !
CLEAR @ DISP "Enter the potential increment, dE, <-10,+10> [0.01] :
1650 INPUT T$ @ IF LEN (T$)=0 THEN E4=.01 @ GOTO 1670 ELSE E4=VAL (T$) @ GOTO 1670
GOTO 1640
1670 IF E4<-10 OR E4>10 THEN 1640
1680 IF FLAG=1 THEN RETURN
GOTO menu
1700 !
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
GOTO 1710
1740 IF T3<0 OR T3>600000 THEN 1710
1750 IF T3=0 THEN T3=.001
GOTO menu
1770 !
IF AXISS$="Y" THEN AXISS$="N" ELSE AXISS$="Y"
GOTO menu
1800 !
CLEAR @ DISP "Enter the minimum on Y <-50,max Y> [0] :
1810 INPUT T$
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>10 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"
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2190  GOTO menu
2200  !
2210  IF PLOTXS$="Y" THEN PLOTXS$="N" ELSE PLOTXS$="Y"
2220  GOTO menu
2230  !
2240  CLEAR @ DISP "Enter the A/D voltage range <1 & 10 only> [10] :" @
2250  INPUT T$
2260  GOTO 2220
2270  IF ADV0LTAGE=1 OR ADV0LTAGE=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  V0LT(0)=E1-E4
2320  FOR I=1 TO N
2330  V0LT(I)=V0LT(I-1)+E4
2340  IF V0LT(I)>E2 THEN E4=-E4 @ V0LT(I)=V0LT(I)+2*E4
2350  IF V0LT(I)<E3 THEN E4=-E4 @ V0LT(I)=V0LT(I)+2*E4
2360  NEXT I
2370  RETURN
2380  CLEAR @ DISP "Enter the ending current sampling delay time <0.001 ,
2390  600000 msec> [0.00 1] :" @ INPUT T$
2400  GOTO 2210
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
2450  <0.0001 ,100000 msec> [1] :" @ INPUT T$
2460  GOTO 2240
2470  IF INCTIME<.0001 OR INCTIME>100000 THEN 2440
2480  GOTO menu
2490  CLEAR @ DISP "Enter the number of scans per file <1,total
2500  scans--> [1] " @
2510  INPUT T$ @ IF LEN (T$)=0 THEN INTSCAN=1 @ GOTO 2520 ELSE
2520  INTSCAN=VAL (T$) @ GOTO 2520
2530  GOTO 2490
2540  IF INTSCAN<1 OR INTSCAN>TOTALSCANS THEN 2490
2550  GOTO menu
2560  CLEAR @ DISP "Enter the total number of scans <1,--> [100] :
2570  INPUT T$ @ IF LEN (T$)=0 THEN TOTALSCANS=100 @ GOTO 2570
2580  ELSE TOTALSCANS=VAL (T$) @ GOTO 2570
2590  GOTO 2490
2590  CLEAR @ AWRITE 1,0,"Rotation speed(s) -- e.g., 1,2,3,... , 1-5, *
for all

FOR \( I = 1 \) TO \( 10 \) @ AWRITE \( I+7,12,VAL\$(I)\)"
   
   &PERIODS[1,5-LEN(VAL\$(I))]&ROTS(I)&ROTI$ (I) @ NEXT I

FOR \( I = 1 \) TO \( 7 \) @ AWRITE \( I+7,30,VAL\$(I+10)\)"
   
   &PERIODS[1,3]&ROTS(I+10)&ROTI$ (I+10) @ NEXT I

AWRITE 20,2," @ LINPUT CODE$ @ IF LEN(CODE$)=0 THEN menu

GOSUB decode IF error=1 THEN 2590

FOR I=1 TO 17 @ ROT$ (I)=" @ IF CODE (I)<> 0 THEN ROT$ (I)="*

NEXT I @ J=1

FOR I=1 TO 17 @ IF ROT$ (I)="*" THEN ROT (J)=ROT2(I) @ J=J+1

NEXT I

ROTMAX=J-1 IF ROTMAX=0 THEN ROTMIN=0 @ ROT=0 ELSE ROTMIN=1 @

ROTL=1

GOTO 2590

I 

beginning:

CLEAR

DIM \( Y(1000), VOLT(1000), SMTHDATA(300) \)

DIM \( A$(40), B$(40), FILE$(15), FILE2$(15), DAT$(40)(30) \)

DIM \( T[50], T1[50], PERIODS[50], DATADRIVES[5], GRAPHDRIVES[5], DRIVES[5] \)

DIM \( DSPFLAGS[3], DSPCRTS[3], AXISS[3], PLOTCRTS[3], PLOTXY[3] \)

DIM \( CODE(20), ROT2(20), ROT1S(20)[1], ROT1S(20)[4] \)

ON ERROR GOSUB 4140 @ AWRITE 0,0

FOR \( I = 1 \) TO \( 10 \) @ ROT$ (I)=VAL\$(I*500) @ ROT1$ (I), ROT1$ (I+10)=" @

NEXT I

ROW$(3)="1400" @ FOR I=10 TO 70 STEP 10 @

ROT$ (I/10+10)=VAL\$(I) @ NEXT I

FOR \( I = 1 \) TO \( 17 \) @ READ T @ ROT2(I)=T @ ROT(I)=0 @ NEXT I

DATADRIVE=1 @ FIGUREDRIVE=1 @ DATAFILE$="DTESTSC" @

FIGUREFILES="TEST_SC"

E1=.2 @ E2=1.3 @ E3=-.25 @ E4=.01 @ T1=.001 @ DATASTORE$="Y" @

FIGSTORES="N"

PLOTFIG$="Y" @ I_RANGE=1 @ I_TYPE$="milli" @ FLAG=0 @ YMIN, YMAX=0

XMIN, XMAX=0 @ PLOTCRTS="Y" @ PLOTXY$="N" @ AXISS="Y" @ V_RANGE=10

DRIVE=1 @ ADV0LTAGE=10 @ INCTIME=1 @ T2=T1 @ SCANFLAG=0 @

INTSCAN=1

TOTALSCANS=100 @ ROT, ROT1(0), ROTMAX, ROTMIN=0 @ ZPRINT$="NO" @

PRINTER IS 1

TAKE KEYBOARD @ GOSUB 3770

A$(1)="Experimental directory"

A$(2)="Mass storage directory"

A$(3)="Plotting directory"

A$(4)="Begin experiment"

A$(5)="Chain Autost"

A$(6)="End program"

A$(7)="NULL"

A$(8)="Exit to main menu"

A$(9)="Beginning potential, E1"

A$(10)="Anodic limit, E2"
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3000 A$(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 @ Al=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)&PERI0D$[1,4]&A$(I)&PERI0D$[1,48-LEN (A$(I))]&" &DAT$(I) @ NEXT I
3330 AWRITE 1,8,BS(A1) @ CRSR=1
3340 AWRITE 21,2,"Change any parameters ?" @ AWRITE 22,2,"Press the indicated letters or use the the '...' and ',,' keys for slewing :"
3350 AWRITE 23,2,"Press '4' to change any parameters or to start experiment "
3360 AWRITE 24,2,"Asterisks indicate precedence, * being the highest"
3370 TAKE KEYBOARD
3380 KYY=NUM (KEYS ) @ IF NOT KYY THEN 3380
3390 IF KYY>64 AND KYY<65+A2-A1+1 THEN AWRITE CRSR,8,A$(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
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3450 AWRITE CRSR,8,B$(A1+CRSR-1)
3460 IF KYY<>52 THEN 3370
3470 IF SCN<>1 THEN 3530
3480 IF CRSR=1 THEN SCN=2 @ A1=8 @ A2=22 @ GOTO 3320
3490 IF CRSR=2 THEN SCN=3 @ A1=24 @ A2=31 @ GOTO 3320
3500 IF CRSR=3 THEN SCN=4 @ A1=33 @ A2=38 @ GOTO 3320
3510 IF CRSR=5 THEN RELEASE KEYBOARD @ CHAIN "Autost"
3520 IF CRSR=4 THEN experiment ELSE RELEASE KEYBOARD @ GOTO 3570
3530 PAGEFLAG=1 @ RELEASE KEYBOARD
3540 IF SCN=2 THEN ON CRSR GOTO
3550 IF SCN=3 THEN ON CRSR GOTO
3560 ,920,990,1070,1460,1150,2380,2440,1900,2240,2540,2490
3570 CLEAR @ END
3580 T1$="" @ FOR L=1 TO LEN (T$) @ T1$[L,L]=CHR$ (NUM (T$[L,L])+128)
3590 @ NEXT L
3600 RETURN
3610 DAT$(1)="" @ DAT$(2)="" @ DAT$(3)="" @ DAT$(4)="" @ DAT$(5)=""
3620 DAT$(6)="" @ DAT$(7)="" @ DAT$(8)="
3630 DAT$(9)=VAL$ (E1) @ DAT$(10)=VAL$ (E2) @ DAT$(11)=VAL$ (E3)
3640 DAT$(12)=VAL$ (E4) @ DAT$(13)=VAL$ (T1) @ DAT$(14)=VAL$ (T2)
3650 DAT$(15)=VAL$ (INCTIME) @ DAT$(17)=VAL$ (ADVOLTAGE)
3660 DAT$(16)=VAL$ (I_RANGE)&"amps/"& VAL$(V_RANGE)&"V"
3670 DAT$(17)=VAL$ (ADVOLTAGE)
3680 DAT$(18)=VAL$ (TOTALSCANS) @ DAT$(19)=VAL$ (INTSCAN)
3690 DAT$(20)=VAL$ (YMIN)&",&VAL$ (YMAX)
3690 DAT$(21)=VAL$ (XMIN)&",&VAL$ (XMAX)
3700 DAT$(22),DAT$(23),DAT$(24)="" @ DAT$(25)=DATAFILES
3710 DAT$(26)=FIGUREFILES @ DAT$(27)=VAL$ (DATADRIVE)
3720 DAT$(28)=VAL$ (FIGUREDRIVE) @ DAT$(29)=DATASTORES @
3730 DAT$(30)=FIGSTORES
3740 DAT$(31)=VAL$ (DRIVE) @ DAT$(32)="" @ DAT$(33)="" @
3750 DAT$(34)=PLOTFIGS
3760 DAT$(35)=PLOTCRTS @ DAT$(36)=PLOTXYs @ DAT$(37)=AXISS @
3770 DAT$(38)=ZPRINTS
3780 RETURN
3790 ON KEY# 1 GOTO 3920
3780 ON KEY# 2 GOTO 3930
3790 ON KEY# 3 GOTO 3940
3800 ON KEY# 4 GOTO 3950
3810 ON KEY# 5 GOTO 3970
3820 ON KEY# 6 GOTO 3990
3830 ON KEY# 7 GOTO 4010
3840 ON KEY# 8 GOTO 4020
3850 ON KEY# 9 GOTO 4040
3860 ON KEY# 10 GOSUB 4060
ON KEY# 11 GOSUB 4080
ON KEY# 12 GOSUB 4100
ON KEY# 13 GOSUB 4120
ON KEY# 14 GOSUB 4130
RETURN
ALPHALL @ GOTO menu
GOTO calculation
MAXY=MAXY/2 @ MINY=MINY/2 @ GCLEAR @ GOTO experiment1
MAXY=MAXY*2 @ MINY=MINY*2
GCLEAR @ GOTO experiment1
ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1900
TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @ I=1 @ GOTO experiment1
GCLEAR @ GOTO experiment1
ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 920
TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @ GOTO experiment1
ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 990
TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @ GOTO experiment1
ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1070
TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @ GOTO experiment1
ALPHALL @ FLAG=1 @ RELEASE KEYBOARD @ GOSUB 1470
TAKE KEYBOARD @ FLAG=0 @ GOSUB calculate @ GRAPHALL @ GOTO experiment1
ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=1
OUTPUT 723 ;"OP 13 ";ROT(ROT);"T" @ RETURN
OUTPUT 723 ;"OP 13 OT" @ RETURN
PRINT CHR$ (12) @ FOR K=1 TO 37 @ PRINT CHR$ (64+K)&CHR$(41)&PERIOD$(1,4)&AS$(K)&PERIOD$(1,45-LEN (AS$(K)))&" 
&DAT$(K) @ NEXT K @ PRINT CHR$(12) @ RETURN
! Error trap subroutine
IF ERRN =67 OR ERRN =66 THEN 4200
IF ERRN =11 THEN menu
IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 4200
IF ERRN =130 THEN BEEP 300,1000 @ RELEASE KEYBOARD @ DISP "Place 
disk in drive and then press <END LINE>" @ INPUT T$ @ TAKE 
KEYBOARD @ GOTO 4200
DISP ERRN ,ERRL @ WAIT 2000
RETURN
END
xyplot:
IF PLOTXY$="N" THEN 4640
IF PLOTXY$="Y" THEN 4230
IF PLOTXY$="N" THEN 4640
IF PLOTXY$="Y" THEN 4230
! Mechanical plotting routine
RELEASE KEYBOARD
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 OT OP 12 50T OP 14 50T"
4390 KYY=NUM (KEY$ ) @ IF NOT KYY THEN 4380
4400 WAIT 1000
4410 IF AXISS="N" THEN 4560
4420 X=8.5-(-XCENTER*XSCALING)+XSCALE/2
4430 OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 OT 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-(VOLTd)*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 (CODES$) @ IF CODES$[1,1]=CHR$ (32) THEN
        CODES$=CODES$[2,LEN (CODES$)] @ GOTO 4690
4700 IF CODES$[1,1] <> "" THEN 4720
4710 FOR I=1 TO 100 @ CODE(I)=1 @ NEXT I @ GOTO 4830
4720 T$="1"
4730 FOR I=0 TO 9 @ IF CODES$[1,1]=VAL$ (I) THEN T$="1"
4740 NEXT I @ IF TS <> VAL$ (-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$=""," THEN CODE(t1)=1 @ GOTO 4760
4820 FOR I=T+1 TO t1 @ CODE(I)=1 @ NEXT I @ GOTO 4760
4830 ON ERROR GOSUB 4140 @ RETURN
4840 I
4850 error1: error=1
4860 DISP "Character ";T$;" not allowed." @ DISP @
   DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
4870 I
4880 error2: error=1
4890 DISP "The value ";T;" is too large." @ DISP @
   DISP "Press <END LINE> to continue." @ INPUT T$ @ RETURN
4900 I
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),
120 DAT$(5),DAT$(6),DAT$(7),DAT$(8)=""
130 DAT$(9)=DSPFLAGS @ DAT$(10)=FILE2$ @ DAT$(11)=DATADRIVE$ @
140 FOR I=15 TO 19
150 DAT$(I)=FILE$(I-14)&" <"&VAL$(E2(I-14))&"> <"&
160 NEXT I
170 DAT$(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) @
230 DAT$(34)=VAL$ (YCLICK)
240 RETURN
250 !
260 IF DSPCRT$="YES" THEN DSPCRT$="NO" ELSE DSPCRT$="YES"
270 GOTO menu
280 IF DSPFLAGS="YES" THEN DSPFLAGS="NO" ELSE DSPFLAGS="YES"
290 GOTO menu
300 IF DSPXY$="YES" THEN DSPXY$="NO" ELSE DSPXY$="YES"
310 GOTO menu
320 CLEAR @ DISP "Enter storage file name <10 characters> [TEST] : " @
330 INPUT FILE2$
340 IF LEN (FILE2$)=0 THEN FILE2$="TEST"
350 GOTO menu
360 CLEAR @ DISP "Enter the minimum on X <-100,100> [0] : " @
370 INPUT T$ @ IF LEN (T$)=0 THEN XMIN=0 ELSE XMIN=VAL (T$)
380 IF YMIN<-100 OR YMIN>100 THEN 350
390 DISP @ DISP @ DISP "Enter the maximum on X <-100,100> [0] : " @
400 IF YMIN<100 OR YMIN>100 THEN 370
```
DISP @ DISP @ DISP "Enter the maximum on Y <-100,100> [0] :" @
INPUT T$ @ IF LEN (T$)= 0 THEN YMAX=0 ELSE YMAX=VAL (T$)
IF YMAX<-100 OR YMAX>100 THEN 410 ELSE GOTO menu
CLEAR @ DISP "Enter the drive number <0,1 or both> " data read only> [0] :" @ INPUT T$
IF LEN (T$)=0 THEN T$="0" @ GOTO 480
IF T$[1,1]="B" OR T$[1,1]="b" THEN FLAG=0 @ GOTO 470
IF VAL (T$)=0 OR VAL (T$)=1 THEN 470 ELSE 430
IF CRSR=4 THEN DATADRIVE$=T$[1,1] ELSE GRAPHDRIVE$=T$[1,1]
GOTO menu
CLEAR @ DISP "Enter the file name" @ INPUT T$
IF LEN (T$)=0 THEN FILES(CRSR-1)="NULL" @ GOTO 540
FILES(CRSR-1)=T$
J=CRSR-1 @ GOSUB fileinput
GOTO menu
CLEAR @ DISP "Drive number <0,1> [1]" @ INPUT T$
IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 580
DRIVE=VAL (T$) @ IF DRIVE=0 OR DRIVE=1 THEN 580 ELSE 550
CLEAR @ CAT "D70"&VAL$ (DRIVE)
DISP "Press <END LINE> to continue :" @ INPUT T$
GOTO menu
CLEAR @ DISP "Enter the raw data filenames [10] :" @
DISP "Press <END LINE> when the last name has been entered."
FOR J=1 TO TOTAL
INPUT FILES(J)
N=J
IF LEN (FILES(J))=0 THEN FILES(J)="NULL" @ N=J-1 @ J=TOTAL
NEXT J
FOR J=1 TO N
GOSUB fileinput
NEXT J
GOTO menu
IF ZPRINT$="NO" THEN ZPRINT$="YES" @ PRINTER IS 705,90 ELSE
ZPRINT$="NO" @ PRINTER IS 1
GOTO menu
IF PLOTAXES$="NO" THEN PLOTAXES$="YES" ELSE PLOTAXES$="NO"
GOTO menu
IF SCALING$="Man" THEN SCALING$="Auto" ELSE SCALING$="Man"
GOTO menu
IF PENSWITCH$="Man" THEN PENSWITCH$="Auto" ELSE PENSWITCH$="Man"
GOTO menu
IF PLOTLABEL$="NO" THEN PLOTLABEL$="YES" ELSE PLOTLABEL$="NO"
GOTO menu
CLEAR @
DISP "Enter the x-axis labels as literal strings <10 max> :"
FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN XCLICK=I-1 @
GOTO 840
XCLICK(I)=VAL (T$) @ NEXT I @ XCLICK=10
GOTO menu
CLEAR @
DISP "Enter the y-axis labels as literal strings <10 max> :"
FOR I=1 TO 10 @ INPUT T$ @ IF LEN (T$)=0 THEN YCLICK=I-1 @
GOTO 880
YCLICK(I)=VAL (T$) @ NEXT I @ YCLICK=10
GOTO menu

fileinput:

IF DATADRIVES$="B" OR DATADRIVES$="b" THEN DRIVES=VAL$ (0) ELSE
DRIVES=DATADRIVES$
ASSIGN# 1 TO FILE$(J)&":D70"&DRIVES
READ# 1 ; E1(J),E2(J),E3(J),E4(J),T1(J),A,I_RANGE(J)
READ# 1 ; I_TYPE$(J),A,A,EXTDAS(J),N(J)
READ# 1 ; V_RANGE(J),ADVOLTAGE(J),A,A,A,A,A
FOR I=1 TO N(J) @ READ# 1 ; X(I,J),Y(I,J) @ NEXT I
IF ERRN =67 OR ERRN =66 THEN 1040
ASSIGN# 1 TO *
RETURN

plotting:

IF DSPCRT$="NO" AND DSPXY$="NO" THEN 2430
CLEAR @ AWRITE 10,33,"Plotting"
SETMILLI=0 @ SETMICR0=0 @ PRODUCT=0 @ FACT0R=1
FOR J=1 TO TOTAL
IF FILE$(J)="NULL" THEN 1160
IF I_TYPE$(J)="mlli" THEN SETMILLI=1 ELSE SETMICR0=1
NEXT J
MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
FOR J=1 TO TOTAL
IF ERRX=1 THEN 1290
IF PRODUCT=1 AND I_TYPE$(J)="mlli" THEN FACTOR=1000 ELSE FACT0R=1
LOW=1 @ HIGH=N(J)
IF E2(J)>MAXX THEN MAXX=E2(J)
IF E3(J)<MINX THEN MINX=E3(J)
FOR I=LOW TO HIGH
IF Y(I,J)*FACTOR<MINY THEN MINY=Y(I,J)*FACTOR
IF Y(I,J)*FACTOR>MAXY THEN MINY=Y(I,J)*FACTOR
NEXT I
LOCATE 30,200,25,95
XEXP=ABS {(MAXX-MINX)/20) @ YEXP=ABS ((MAXY-MINY)/20)
SCALE MAXX+XEXP,MINX-XEXP,MINY-YEXP,MAXY+YEXP

Graphics routine

IF DSPCRT$="NO" AND DSPXY$="NO" THEN 2430
CLEAR @ AWRITE 10,33,"Plotting"
SETMILLI=0 @ SETMICR0=0 @ PRODUCT=0 @ FACT0R=1
FOR J=1 TO TOTAL
IF FILE$(J)="NULL" THEN 1160
IF I_TYPE$(J)="mlli" THEN SETMILLI=1 ELSE SETMICR0=1
NEXT J
MINX=XMIN @ MAXX=XMAX @ MINY=YMIN @ MAXY=YMAX
FOR J=1 TO TOTAL
IF ERRX=1 THEN 1290
IF PRODUCT=1 AND I_TYPE$(J)="mlli" THEN FACTOR=1000 ELSE FACT0R=1
LOW=1 @ HIGH=N(J)
IF E2(J)>MAXX THEN MAXX=E2(J)
IF E3(J)<MINX THEN MINX=E3(J)
FOR I=LOW TO HIGH
IF Y(I,J)*FACTOR<MINY THEN MINY=Y(I,J)*FACTOR
IF Y(I,J)*FACTOR>MAXY THEN MINY=Y(I,J)*FACTOR
NEXT I
LOCATE 30,200,25,95
XEXP=ABS {(MAXX-MINX)/20) @ YEXP=ABS ((MAXY-MINY)/20)
SCALE MAXX+XEXP,MINX-XEXP,MINY-YEXP,MAXY+YEXP
FRAME @ CSIZE 4 @ FXD 2,4 @ LINE TYPE 1
LAKES -((MAXX-MINX)/60),(MAXY-MINY)/4/5,0,0,10,5,3
MOVE MINX,MINY
LORG 4 @ X$=CHR$ (46)
FOR J=1 TO TOTAL
    IF FILE$(J)="NULL" THEN 1470
    IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE FACTOR=1
    LOW=1 @ HIGH=N(J)
    FOR I=LOW TO HIGH
        MOVE X(I,J),Y(I,J)*FACTOR
        LABEL X$
    NEXT I
    NEXT J
CSIZE 5 @ LORG 2 @ DEG @ LDIR 270 @ SETGU @ MOVE 100*RATIO -20,80
IF PRODUCT=1 THEN LABEL "microamps" ELSE LABEL I_TYPE$(1)&"amps"
LDIR 0 @ MOVE RATIO *100/2-10,15 @ LABEL "volts (V)"
IF DSPFLAGS$="YES" THEN GSTORE FILE2$&":D70"&GRAPHDRIVES
INPUT T$ @ ALPHALL
IF DSPXY$ <> "YES" THEN 2430
Mechanical plotting routine
GOSUB label_check
XSCALE=8.5 @ YSCALE=7 @ A=MINX @ MINX=MAXX @ MAXX=A
XSCALING=XSCALE/(MAXX-MINX)
YSCALING=YSCALE/(MAXY-MINY)
XCENTER=MAXX-(MAXX-MINX)/2
YCENTER=MAXY-(MAXY-MINY)/2
OUTPUT 723 ;"GP"
TAKE KEYBOARD
CLEAR @ DISP "Set zero positions now !" @ DISP "Press <END LINE> to continue"
OUTPUT 723 ;"OP 7 OT OP 12 50T OP 14 50T"
KYY=NUM (KEY$) @ IF NOT KYY THEN 1660
WAIT 1000
IF PLOTAXES$="NO" THEN 2260
X=MINX*XSCALING-XCENTER*XSCALING+XSCALE/2
Y=MAXY*YSCALING-YCENTER*YSCALING+YSCALE/2
IF PLOTLABEL$="YES" THEN 1830
OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 OT OP 14 50T"
WAIT 2000
OUTPUT 723 ;"OP 7 ";Y;"T OP 12 50T OP 7 OT OP 14 50T"
WAIT 3100
OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 OT OP 14 50T"
OUTPUT 723 ;"OP 7 7.0T OP 11 1500 14 50T WA .2T OP 7 ";X;"T OP 12 50T"
OUTPUT 723 ;"OP 7 0.0T OP 11 1500 14 50T"
WAIT 3100
OUTPUT 723 ;"OP 7 ";Y;"T OP 14 50T OP 7 ";0;"T OP 12 50T"
WAIT 750
OUTPUT 723 ;"OP 7 8.5T OP 11 1500 12 50T WA .2T OP 7 ";Y;"T OP 14 50T"
OUTPUT 723 ;"OP 7 0.0T OP 11 1500 12 50T"
WAIT 3100
Y=INT (Y*10000)/10000 @ X=INT (X*10000)/10000
WAIT 1000
XP0S=XSCALE/6
YPbS=YSCALE/5
IF Y-YSCALE/60<0 THEN Y1=0 ELSE Y1=Y-YSCALE/60
IF Y+YSCALE/60>YSCALE THEN Y2=YSCALE ELSE Y2=Y+YSCALE/60
Y1=INT (Y1*10000)/10000 @ Y2=INT (Y2*10000)/10000
LXSCALING=550
FOR I=1 TO XCLICK
IF SCALING$ <> "Man" THEN 1940
Xl=XCLICK(I)*XSCALING-XCENTER*XSCALING+4.25 @ GOTO 1960
X1=INT (I*(XSCALE/6)*10000)/10000
IF X1>XSCALE THEN 2050
Y3=INT ((Y2-Y1)*10000)/10000
OUTPUT 723 ;"OP 7 ";X1;"T OP 12 50T OP 7 ";Y1;"T OP 14 50T"
WAIT 1500
OUTPUT 723 ;"OP 11 500 7 ";Y1+Y3:" 14 50T"
WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (XCLICK(I)) @ GOTO 2020
LA$=VAL$ (INT (((MAXX-MINX)/6*I+MINX+.001)*1000)/1000)
XIN=X1-8.5/LXSCALING*LEN (LA$)*7/2
YIN=7.25 @ GOSUB xylabel
NEXT I
IF X-XSCALE/73<0 THEN XI=0 ELSE Xl=X-XSCALE/73
IF X+XSCALE/73>XSCALE THEN X2=XSCALE ELSE X2=X+XSCALE/73
X1=INT (Xl*10000)/10000 @ X2=INT (X2*10000)/10000
FOR 1=1 TO YCLICK
IF SCALING$ <> "Man" THEN 2110
Yl=YCLICK(I)*YSCALING-YCENTER*YSCALING+3.5 @ GOTO 2140
Y1=INT (I*(YSCALE/5)*10000)/10000
IF Y1=Y THEN 2220
Y1=Y THEN 2220
X3=INT ((X2-X1)*10000)/10000
OUTPUT 723 ;"OP 7 ";Y1;"T OP 14 50T OP 7 ";X1;"T OP 12 50T"
WAIT 1000
OUTPUT 723 ;"OP 11 500 7 ";X1+X3:" 12 50T"
WAIT 550 @ IF SCALING$="Man" THEN LA$=VAL$ (YCLICK(I)) @ GOTO 2200
LA$=VAL$ (INT (((MAXY-MINY)/5*I+MINY+.000001)*10000)/10000)
XIN=8.75
YIN=Y1+.12 @ GOSUB xylabel
NEXT I
IF PENSWITCH$="Auto" THEN 2260
CLEAR @ DISP "Change pen color ? Press <END LINE> to continue."
RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
WAIT 1000
FOR J=1 TO TOTAL
IF FILE$(J)="NULL" THEN 2410
IF PRODUCT=1 AND I_TYPE$(J)="milli" THEN FACTOR=1000 ELSE FACTOR=1

LOW=1 @ HIGH=N(J)
FOR I=LOW TO HIGH
X=X(I,J)*XSCALING-XCENTER*XSCALING+4.25
Y=Y(I,J)*FACTOR*YSCALING-YCENTER*YSCALING+3.5
OUTPUT 723 ;"OP 7 ";X;"T OP 12 50T OP 7 ";Y;"T OP 14 50T"
IF I=LOW THEN WAIT 500 ELSE WAIT 150
OUTPUT 723 ;"OP 11 100T"
NEXT I
IF PENVSWITCH$="Auto" THEN 2410
CLEAR @ DISP "Change pen color ? Press <END LINE> to continue."
RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD
NEXT J
GOSUB filelabel
GOTO menu
!
beginning:
CLEAR
DIM Y(800,5),X(800,5),EXPMT(5),INTPOT(5),FINPOT(5),V_RANGE(5)
DIM SCAN(5),DROPTIME(5),I_RANGE(5),I_TYPE$(5)[10],C(25)
DIM INCPTOT(5),PTYME(5),EXTDATA(5)[4],N(5),GP(25),ADVOLTAGE(5)
DIM A$(36)[50],B$(36)[50],FILE$(5)[15],FILE2$(15),DAT$(36)[40]
DIM T$(50),TI$(50),PERIODS$(50),
DATADRIVE$(5),GRAPHDRIVE$(5),DRIVE$(5)
DIM DSPFLAG$(3),DSPCRT$(3),DSPXY$(3),CHAR$(46)[35],LA$(80)
DIM XCLICK(IO),YCLICK(IO)
ON ERROR GOSUB 3210 @ AWRITE 0,0
DSPFLAG$="NO" @ FILE2$="TEST" @ DATADRIVE$="B" @ GRAPHDRIVE$="0"
@ DRIVE=1
FLAG=1 @ TOTAL=5 @ SETMILLI=0 @ SETMICR0=0 @ PRODUCT=0 @ YMIN=0 @
YMAX=0
FOR J=1 TO TOTAL @ FILE$(J)="NULL" @ E2(J),E3(J)=0 @ NEXT J
DSPCRT$="YES" @ DSPXY$="NO" @ XMIN,XMAX=0 @ PLOTAXES$="YES"
SCALING$="Auto" @ PENVSWITCH$="Man" @ PLOTLABEL$="NO" @ XCLICK=G
YCLICK=5 @ ZPRINT$="NO"
TAKE KEYBOARD @ GOSUB 20 @ GOSUB 60
A$(1)="Filer directory"
A$(2)="Mass storage directory"
A$(3)="Plotting directory"
A$(4)="Start plotting"
A$(5)="Chain Autost"
A$(6)="End program"
A$(7)="NULL"
A$(8)="Exit to main menu"
A$(9)="Store graph on disk"
A$(10)="Graph storage file name"
A$(11)="Numeric data drive number"
A$(12)="Graphic data drive number"
A$(13)="Catalog of disk"
A$(15)="File <anodic limit> <cathodolimit>"
A$(20)="Enter all files"
A$(21)="Set min and max for y-axis only"
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A$(22)="Set min and max for x-axis only"
A$(23)="NULL"
A$(24)="NULL"
A$(25)="Exit to main menu"
A$(26)="Plot on CRT"
A$(27)="Plot on printer"
A$(28)="Plot on X-Y recorder"
A$(29)="Manual or Automatic scaling"
A$(30)="Manual or Automatic pen switching"
A$(31)="Plot axes (including labels"
A$(32)="Plot ticks and labels only"
A$(33)="X-axis labels"
A$(34)="Y-axis labels"
A$(35)="Activate printer"

PERIOD$=" 
FOR I=1 TO 13 @ T$=A$(I) @ GOSUB 30 @ B$(I)=T1$ NEXT I
FOR I=16 TO 19 @ A$(I)=A$(15) @ B$(I)=B$(15) NEXT I
FOR I=20 TO 35 @ T$=A$(I) @ GOSUB 30 @ B$(I)=T1$ NEXT I
SCRN=3 @ A1=1 @ A2=6
menu: TAKE KEYBOARD @ GOSUB 110 @ PAGEFLAG=0
CLEAR @ FOR I=A1 TO A2 @ AWRITE I-A1+1,2,CHR$(64+I-A1+1)&"&PERIOD$[1,45-LEN (A$(I))]&"&DAT$(I) @
AWRITE 1,8,B$(A1) @ CRSR=1
AWRITE 20,2,"Change any parameters ?" @ AWRITE 21,2,"Press the indicated letters or use the the "." and "," keys for slewing ;"
AWRITE 22,2,"Press '4' to change any parameters or to start experiment :"
TAKEN KEYBOARD
KYY=NUM (KEY$) @ IF NOT KYY THEN 3010
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)
IF KYY< 46 THEN 3060
AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR-1 @ IF CRSR<1 THEN
AWRITE CRSR,8,B$(A1+CRSR-1)
IF KYY< 44 THEN 3090
AWRITE CRSR,8,A$(A1+CRSR-1) @ CRSR=CRSR+1 @ IF CRSR>A2-A1+1 THEN
CRSR=1
IF SCRN< 52 THEN 3000
IF SCRN< 3 THEN 3160
IF CRSR=1 THEN SCRN=1 @ A1=14 @ A2=22 @ GOTO 2960
IF CRSR=2 THEN SCRN=2 @ A1=8 @ A2=13 @ GOTO 2960
IF CRSR=3 THEN SCRN=4 @ A1=25 @ A2=35 @ GOTO 2960
IF CRSR=4 THEN 1060
RELEASE KEYBOARD @ IF CRSR=5 THEN CHAIN "Autost" ELSE GOTO 3200
PAGEFLAG=1 @ RELEASE KEYBOARD
IF SCRN=1 THEN ON CRSR GOTO 3190,500,500,500,500,500,610,390,350
IF SCRN=2 THEN ON CRSR GOTO 3190,280,320,430,430,550
ELSE ON CRSR GOTO 3190, 260, 3000, 300, 750, 770, 730, 790, 810, 850, 710
3190 TAKE KEYBOARD @ SCRN=3 @ A1=1 @ A2=6 @ GOTO 2960
3200 CLEAR @ END
3210 ! Error trap subroutine
3220 IF ERRN =71 THEN 3330
3230 IF ERRN =66 OR ERRN =12 THEN 3330
3240 IF ERRN =11 THEN menu
3250 IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 3330
3260 IF FLAG=1 AND ERRN =67 AND (DATADRIVES="B" OR DATADRIVES="b")
3270 THEN FLAG=0 @ GOTO 960
3280 IF ERRN =67 THEN CLEAR @
3290 IF ERRN =67 AND (DATADRIVES="B" OR DATADRIVES="b") THEN
3300 THEN DRIVE$=VAL$ (ABS (VAL (DRIVES )-1)) @ FLAG=1 @ GOTO 960
3310 IF ERRN =130 THEN BEEP 300, 1000 @ RELEASE KEYBOARD @
3320 DISP "Place disk in drive and then press & END LINE&" @
3330 INPUT T$ @ TAKE KEYBOARD
3340 IF ERRN =130 AND ERRLL =390 THEN 960
3350 IF ERRN =130 AND ERRLL =860 THEN 1510
3360 DISP ERRN,ERRLL @ WAIT 5000
3370 RETURN
3380 xylabel:
3390 ! Beginning of labeling subroutine
3400 ! Range of characters is defined by LXSCALING and should be within
3410 ! the interval 100 to 600 inclusive, where the larger the number the
3420 ! smaller the character.
3430 ! Inputs LA$, LXSCALING
3440 LRATIO=230/190 ! X/Y
3450 LYSCLING=INT (LXSCALING/LRATIO*10000)/10000
3460 IF LXSCALING>400 THEN LSPACE=2 ELSE LSPACE=1
3470 LX=-(5+LSPACE)*8.5/LXSCALING+XIN
3480 OUTPUT 723 ;"OP 7 ";XIN;"T OP 12 50T OP 7 ";YIN;"T OP 14 50T"
3490 WAIT 500
3500 FOR LI=1 TO LEN (LA$)
3510 LT=NUM (LA$[LI,LI])
3520 IF LT=32 THEN LT=47
3530 LY=YIN
3540 LPOINT=0
3550 LX=LY+(LSPACE+5)*8.5/LXSCALING
3560 FOR LJ=1 TO 7
3570 LY=INT ((LY-7/LYSCALING)*10000)/10000
3580 LX1=LX
3590 FOR LK=1 TO 5
3600 LX2=INT ((LX1+LK*8.5/LXSCALING)*10000)/10000
3610 IF CHAR$(LT-44)[LPOINT,LPOINT] <> "1" THEN 3630
3620 OUTPUT 723 ;"OP 7 ";LX2;"T OP 12 50T OP 7 ";LY;"T OP 14 50T"
3630 WAIT 200
3640 OUTPUT 723 ;"OP 11 100T"
3650 WAIT 200
filelabel:

1 CLEAR @ DISP "Set zero positions now!" @
   DISP "Press <END LINE> to continue"

OUTPUT 723 ;"OP 7 0T OP 12 50 14 50T"

KY$=NUM (KEY$ ) @ IF NOT KY$ THEN 3700

LXSCALING=550

LA$="FILES" @ XIN=0 @ YIN=0 @ GOSUB xlabel

LA$="-----" @ XIN=0 @ YIN=-.14 @ GOSUB xlabel

X=1

FOR I=1 TO TOTAL

IF FILE$(I)="NULL" THEN 3860

X=X+1

LA$=UPC$ (FILE$(I))

FOR J=1 TO LEN (FILE$(I))

T$=FILE$(I)[J,J]

IF T$="." THEN LA$(J,J)="." 

NEXT J

NEXT I

RETURN

label_error:

DISP @ DISP "Assigned labels for plotting out of data range"

DISP "Re-enter values via menu" @
   DISP "Press <END LINE> to continue."

RELEASE KEYBOARD @ INPUT T$ @ TAKE KEYBOARD @ GOTO menu

label_check:

IF SCALING$="Auto" THEN RETURN

FOR I=1 TO XCLICK @
   IF XCLICK(I)<MINX OR XCLICK(I)>MAXX THEN label_error

NEXT I

FOR I=1 TO YCLICK @
   IF YCLICK(I)<MINY OR YCLICK(I)>MAXY THEN label_error

NEXT I

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" @ ON TIMER# 2,T21 GOTO 50 @ ON RET GOTO 550,560
50 OFF TIMER# 2 @ ON I=0 @ BEEP 100,200 @ OUTPUT 723 ;"OP 13 ";INTEGRATE","T" @ ON TIMER# 3,T22 GOTO 90 @
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" @ ON TIMER# 2,T21 GOTO 50 @ ON RET GOTO 550,560
80 OFF TIMER# 2 @ ON I=0 @ BEEP 100,200 @ OUTPUT 723 ;"OP 13 ";INTEGRATE","T" @ ON TIMER# 3,T22 GOTO 90 @
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 @ I=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 FIAFLAGS="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$="Active" THEN 390
310 FOR I=1 TO T6
320 OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1;"T OP 7 ";E6;" 12 ";T27;"T OP 12 ";T9;" 13 ";N2;"T"
330 OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3;"T OP 11 .02T OP 7 ";E12;" 12 ";T25;"T"
340 NEXT I @ I=0
350 OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1;"T OP 7 ";E6;" 12 ";T27;"T OP 12 ";T9;" 13 ";N2;"T"
360 OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3;"T OP 11 .02T OP 7 ";E12;" 12 ";T25;"T"
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370   E6=E6+INC@T @ T9=T9+T5 @ T12=T12+T11 @ E12=E12+E11 @ E15=E15+E14
      @ T25=T25+T24 @ DISP A+C*I @ I=I+1 @ IF I<N THEN 350
380   GOSUB 120 @ GOTO 640
390   FOR I=1 TO T6
400   DISP "Waveform not applicable for batch work" @ WAIT 5000 @ GOTO menu
410 !
420 ! NEXT I @ I=0
430 !
440 !
450   E6=E6+INC@T @ T9=T9+T5 @ T12=T12+T11 @ E12=E12+E11 @ E15=E15+E14
      @ T25=T25+T24 @ DISP A+C*I @ I=I+1 @ IF I<N THEN 430
460   GOSUB 120 @ GOTO 640
470   OUTPUT 723 ;"MI 2 ";4096;"T"
480   OUTPUT 723 ;WF 3.0 ";4096;"T WF 11.2 OT"
490   T=(T12+T9+T2+18)/1000
500   IF UPD$="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+O1;"T OP 7 ";E6;" 12 ";T27;"T OP 12 ";T9;" 13 ";N2+O1;"T"
560   OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3+O1;"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+EI @ 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+O1;"T OP 7 ";E6;" 12 ";T27;"T OP 13 ";N2+O1;"T"
625   FOR K=1 TO 20 @ OUTPUT 723 ;"OP 7 ";E0;" 12 ";T0;"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+O1;" 12 20T
      OP 11 .02T" @ DISP EO,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

IF C0UL0MB$="q" THEN 890
FOR I=1 TO N
Y(I)=Y(I)/TOTALSCANS
Y(I)=-(Y(I)/10*ADV0LTAGE*I RANGE/V RANGE)
NEXT I
GOTO 940
FOR I=1 TO N
Y{I)=Y(I)/TOTALSCANS
Y(I)=-(1000000*2*.000001*Y{I)/ADVOLTAGE*I RANGE/(V_RANGE*100))
NEXT I
SCANFLAG=1 @ GOSUB datastore @ SCANFLAG=0
PRINT "I(E1)= ";Y(IMAX)
PRINT "E(det)= ";E6,"E(ads)= ";E15,"E(a)= ";E12
PRINT "T(det)= ";T9+18,"T(ads)= ";T12,"T(a)= ";T25
PRINT
IF FIAFLAG$ <> "YES" THEN 1070
IF E1=E5 THEN 1070
E6=E6+INCP0T @ IF SGN (INCP0T)=1 AND E6>E5 THEN E6=E1 @ GOTO 1070
IF SGN (INCP0T)=-1 AND E6<E5 THEN E6=E1 @ GOTO 1070
SCANS=1 @ GOTO experlment2
IF T1=T4 THEN 1120
T7=T7+T5 @ IF SGN (T5)=1 AND T7>T4 THEN T7=T1 @ GOTO 1120
IF SGN (T5)=-1 AND T7<T4 THEN T7=T1 @ GOTO 1120
SCANS=1 @ GOTO experlment2
IF T10=T3 THEN 1170
T12=T12+T11 @ IF SGN (T11)=1 AND T12>T10 THEN T12=T3 @ GOTO 1170
IF SGN (T11)=-1 AND T12<T10 THEN T12=T3 @ GOTO 1170
SCANS=1 @ GOTO experlment2
IF E2=E10 THEN 1220
E12=E12+E11 @ IF SGN (E11)=1 AND E12>E10 THEN E12=E2 @ GOTO 1220
IF SGN (E11)=-1 AND E12<E10 THEN E12=E2 @ GOTO 1220
SCANS=1 @ GOTO experlment2
IF E3=E13 THEN 1270
E15=E15+E14 @ IF SGN (E14)=1 AND E15>e13 THEN E15=E3 @ GOTO 1270
IF SGN (E14)=-1 AND E15<E13 THEN E15=E3 @ GOTO 1270
SCANS=1 @ GOTO experlment2
IF T2=T23 THEN 1320
T25=T25+T24 @ IF SGN (T24)=1 AND T25>T23 THEN 1320
IF SGN (T24)=-1 AND T25<T23 THEN 1320
SCANS=1 @ GOTO experlment2
IF ROTMIN=0 THEN 1360
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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 @ LDUR 270 @ SETGU @ MOVE 100*RATIO -20,80
1590 LABEL I_TYPE$&"amps"
1600 LDUR 0 @ MOVE RATIO *.100/2-10,15 @ LABEL "volts (V)"
1610 GOTO 1790
1620 !
1630 ! Store data on disk
1640 !
1650 FD$=":D70"&VAL$ (FIGUREDRIVE)
1660 IF FIGSTORE$="YES" THEN GSTORE FIGUREFILE$&FD$ @ GOTO 1680 ELSE
1680 GSTORE FIGUREFILE$&FD$
1670 "Store data on disk"
1680 !
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,O.T1,T2,I_RANGE
1740 PRINT# 1 ; I_TYPE$[1,5],T3,0,"00"
1750 PRINT# 1 ; N,O,E2,O,0,V_RANGE,ADVOLTAGE,TOTALSCANS,0
1760 FOR I=1 TO N @ PRINT# 1 ; X(I),Y(I) @ NEXT I
1770 ASSIGN# 1 TO *
1780 IF SCANFLAG=1 THEN RETURN
1790 WAIT 1000 @ RELEASE KEYBOARD @ INPUT T$ @ ALPHALL @ GOTO menu
1800 !
1810 ! inputs
CLEAR @ DISP "Enter the beginning detection potential <-10,+10> [-1.0] :"
INPUT T$ @ IF LEN (T$)=0 THEN E1=-1 @ GOTO 1860 ELSE E1=VAL (T$)
@ GOTO 1860
GOTO 1830
1860 IF E1<-10 OR E1>10 THEN 1830
1870 IF E1=E5 THEN INCROT=0
1880 GOTO menu
1890 CLEAR @ DISP "Enter the beginning anodic cleaning potential
<-10,+10> [0.8] :"
INPUT T$ @ IF LEN (T$)=0 THEN E2=.8 @ GOTO 1930 ELSE E2=VAL (T$)
@ GOTO 1930
GOTO 1900
1900 IF E2<-10 OR E2>10 THEN 1900
1940 IF E2=E10 THEN E11=0
1950 GOTO menu
1960 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 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 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$[1,1]="y" THEN 2140
2210 GOTO menu
2220 CLEAR @ DISP "Enter the figure file name <10 characters>
[TEST_PAD] :"
INPUT T$ @ IF LEN (T$)=0 THEN FIGUREFILES="TEST_PAD" ELSE FIGUREFILES=T$

IF LEN (T$)<11 OR FIGUREFILES="TEST_PAD" THEN 2300

DISP @ DISP @ DISP "File name ":T$;" is Longer than 10
characters." 2270 DISP "Do you wish to change it? <Y,N> [N] ": @ INPUT T$

IF LEN (T$)=0 THEN menu

IF LEN (T$)<> 0 AND (T$[1,1]="Y" OR T$[1,1]="Y") THEN 2230

GOTO menu

IF DATADRIVE=0 THEN DATADRIVE=1 ELSE DATADRIVE=0

GOTO menu

IF FIGUREDRIVE=0 THEN FIGUREDRIVE=1 ELSE FIGUREDRIVE=0

GOTO menu

IF COULOMB$="q" THEN COULOMB$="1" ELSE COULOMB$="q"

GOTO menu

IF DATASTORE$="yES" THEN DATASTORE$="NO" ELSE DATASTORE$="yES"

GOTO menu

IF FIGSTORE$="YES" THEN FIGSTORE$="NO" ELSE FIGSTORE$="YES"

GOTO menu

IF UPD$="Active" THEN UPD$="Not active" ELSE UPD$="Active"

GOTO menu

CLEAR @ DISP "Enter the drive number <0 1> [1] :": @ INPUT T$

IF LEN (T$)=0 THEN DRIVE=1 @ GOTO 2530 ELSE DRIVE=VAL (T$) @

GOTO 2530

GOTO 2500

IF DRIVE=0 OR DRIVE=1 THEN 2540 ELSE 2500

CAT ":D70"&VAL$ (DRIVE)

DISP "Press <END LINE> to continue." @ INPUT T$

GOTO menu

IF PLOTFIG$="YES" THEN PLOTFIG$="NO" ELSE PLOTFIG$="YES"

GOTO menu

CLEAR @ DISP "Enter the beginning cathodic cleaning potential
<-10,+10> [-1.0] :":

INPUT T$ @ IF LEN (T$)=0 THEN E3=-1 @ GOTO 2640 ELSE E3=VAL (T$)

GOTO 2640

GOTO 2610

IF E3<-10 OR E3>10 THEN 2610

IF E3=E13 THEN E14=0

GOTO menu

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=T10 THEN T11=0
2730 GOTO menu
2740 !
2750 CLEAR @ DISP "Enter the minimum on Y <-50,max Y> [0] :" @ INPUT T$
2760 IF LEN (T$)=0 THEN YMIN=0 @ GOTO 2790 ELSE YMIN=VAL (T$) @ GOTO 2790
2770 GOTO 2760
2780 IF YMIN<-50 OR YMIN>50 THEN 2760
2790 DISP @ DISP @ DISP @ DISP "Enter the maximum on Y <min Y, 50> [0] :" @ 2790 INPUT T$ @ IF LEN (T$)=0 THEN YMAX=0 @ GOTO 2830 ELSE YMAX=VAL (T$) @ GOTO 2830
2800 GOTO 2800
2810 IF YMAX<YMIN OR YMAX>50 THEN 2880
2820 GOTO menu
2830 IF YMAX<YMIN OR YMAX>50 THEN 2880
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 2860
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
2940 ELSE 2900
2950 IF I_RANGE<.02 OR I_RANGE>10 THEN 2860
2960 GOTO Disp
2970 DISP @ DISP @ DISP I_RANGE;"amps, per what voltage range <0.5000> [10] :" @ INPUT T$
2980 IF LEN (T$)=0 THEN V_RANGE=10 @ GOTO 2970 ELSE V_RANGE=VAL (T$) @ GOTO 2970
2990 GOTO 2960
3000 IF V_RANGE<0 OR V_RANGE>5000 THEN 2970
3010 GOTO menu
3020 CLEAR @ DISP "Total number of cleaning pulses <1,-> [5] :
3030 INPUT T$ @ IF LEN (T$)=0 THEN T6=5 @ GOTO 3020 ELSE T6=VAL (T$) @ GOTO 3020
3040 IF T6<1 THEN 2990
3050 CLEAR @ DISP "Enter the ending detection potential <-10,+10> [0.60] :
3060 INPUT T$ @ IF LEN (T$)=0 THEN E5=.6 @ GOTO 3070 ELSE E5=VAL (T$) @ GOTO 3070
3070 GOTO 3040
502

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$)=0 THEN INCPOT=.05 @
3115 ELSE INCPOT=VAL (T$) @ 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] :" @
3210 INPUT T$ @ IF LEN (T$)=0 THEN ADVOLTAGE=10 @ GOTO 3240 ELSE
3215 ADVOLTAGE=VAL (T$) @ GOTO 3230
3220 GOTO 3200
3230 IF ADVOLTAGE=10 OR ADVOLTAGE=1 THEN 3240 ELSE 3200
3240 GOTO menu
3250 CLEAR @
3255 DISP "Enter the number of signal averaged scans <1, ---> [1] :"
3260 INPUT T$ @ IF LEN (T$)=0 THEN TOTALSCANS=1 @ GOTO 3280 ELSE
3265 TOTALSCANS=VAL (T$) @ 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$)=0 THEN T4=1000 @ GOTO 3340 ELSE T4=VAL (T$) @
3325 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] :");
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
503

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 too 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$="YES" @ PRINT " PRINTER IS 705,90 ELSE ZPRINT$="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$)=0 THEN T21=300000 @ GOTO 3820 ELSE T21=VAL (T$) @ 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$="NO"
3950 GOTO menu
3960 CLEAR @ DISPCENTER "Enter the ending anodic cleaning potential <-10,10> [.8] :
3970 INPUT T$ @ 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 @ DISPCENTER "Enter then anodic cleaning potential increment
<-2,2 [.005 min] [.05] :"
4030 INPUT T$ @ IF LEN (T$)=0 THEN E11=.05 @
     GOTO 4050 ELSE E11=VAL (T$) @ 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 @ DISPCENTER "Enter the ending cathodic cleaning 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 @ DISPCENTER "Enter then cathodic cleaning potential increment
<-2,2 [.005 min] [.05] :"
4190 INPUT T$ @ IF LEN (T$)=0 THEN E14=.05 @
     GOTO 4270 ELSE E14=VAL (T$) @ GOTO 4270
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
505

GOTO menu

CLEAR @ DISP "Enter the ending anodic cleaning time <0,600000 msec> [200] :"

INPUT T$ @ IF LEN (T$)=0 THEN T23=200 @
GOTO 4310 ELSE T23=VAL (T$) @ GOTO 4310

GOTO 4280

IF T23<0 OR T23>600000 THEN 4280

IF T23=0 THEN T23=.001

IF T23=T2 THEN T24=0

GOTO menu

CLEAR @ DISP "Enter the Anodic cleaning time increment <600000,600000 msec> [50] :" @ INPUT T$

IF LEN (T$)=0 THEN T24=50 @ GOTO 4380 ELSE T24=VAL (T$) @ GOTO 4380

GOTO 4350

IF T24<-600000 OR T24>600000 THEN 4350

T24=INT(T24*1000)/1000

IF T2=T23 THEN T24=0

GOTO menu

CLEAR @ AWRITE 1.0,"Rotation speed(s) -- e.g., 1,2,3..., 1-5, * for all"

FOR I=1 TO 10 @ AWRITE I+7,12,VAL$ (I)&")"&PERIOD$[1,5-LEN (VAL$ (I))]&ROTS(I)&ROT1$(I) @ NEXT I

FOR I=1 TO 7 @ AWRITE I+7,30,VAL$ (I+10)&")"&PERIOD$[1,3]&ROTS(I+10)&ROT1$(I+10) @ NEXT I

AWRITE 20,2,"" @ LINPUT CODES @ IF LEN (CODES)=0 THEN menu

GOSUB decode @ IF error=1 THEN 4420

FOR I=1 TO 17 @ ROT1S(I)="" @ IF CODE(I)<> 0 THEN ROT1S(I)="*

NEXT I @ J=1 @ FOR I=1 TO 17 @ IF ROT1S(I)="*" THEN

ROT(J)=ROTS(I) @ J=J+1

NEXT I @ ROTMAX=J-1 @ IF ROTMAX=0 THEN ROTMIN=0 @ ROT=0 ELSE

ROTMIN=1 @ ROT=1

GOTO 4420

CLEAR @ DISP "Enter the delay time before charge measurement <.001, 99999999> [0.001] :"

INPUT T$ @ IF LEN (T$)=0 THEN T27=.001 @
GOTO 4540 ELSE T27=VAL (T$) @ GOTO 4540

GOTO 4510

IF T27<.001 OR T27>99999999 THEN 4510

GOTO menu

CLEAR @ DISP "Enter the beginning integration potential <-10, 10> [-.20] :"

INPUT T$ @ IF LEN (T$)=0 THEN E30=-.2 @ GOTO 4557 ELSE E30=VAL (T$) @ GOTO 4557

GOTO 4551

IF E30<-10 OR E30>10 THEN 4551

GOTO menu

BEGINNING:

CLEAR @ ON ERROR GOSUB 6030 @ AWRITE 0,0
**Alternate waveform selection** (*indicates loaded upon execution)*

1) Zero-background, surface controlled (sulfurs), 3-step, FIA work only
2) *Zero-background, mt controlled (carbohydrates), 3-step, FIA work only*
3) UPD stripping beginning at deposition potential, batch and FIA
4) Zero-background, surface controlled (sulfurs), 4-step, FIA work only
5) Continue with program

**Waveform <1,5> [1]**

Position cursor over get statement with cursor controls and press <END LINE>.

Press RUN to restart program and select option 5 in the previous menu

If T=1 then
   AWRITE 10,0,"GET "&CHR$(34)&"WFM_1"&CHR$(34) @ AWRITE 11,0 @ DISP @ PAUSE

If T=2 then
   AWRITE 10,0,"GET "&CHR$(34)&"WFM_2"&CHR$(34) @ AWRITE 11,0 @ DISP @ PAUSE

If T=3 then
   AWRITE 10,0,"GET "&CHR$(34)&"WFM_3"&CHR$(34) @ AWRITE 11,0 @ DISP @ PAUSE

If T=4 then
   AWRITE 10,0,"GET "&CHR$(34)&"WFM_4"&CHR$(34) @ AWRITE 11,0 @ DISP @ PAUSE

CLEAR

DIM Y(3000),X(3000),TEMP(3000)

DIM

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
4610 DIM T$[50],T1$[50],PERIODS$[50],DATASTORES$[10],FIGSTORES$[10]
4620 DIM PLOTFIGS$[10],I_TYPES$[5],FD$[15],DD$[15]
4630 DIM CODE$[20],ROT$[20],ROT2$[20],ROT1$[20][1],ROT$[20][4]
4640 DIM 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)=VAL$(I-2) @ NEXT I
4670 FOR I=1 TO 17 @ READ T @ ROT2$(I)=T @ ROT$(I)=0 @ NEXT I
4680 E1=-1 @ E3=-.6 @ R2=-.8 @ T1=100 @ T2=200 @ T4=100 @ T3=500 @ T5=0 @ T6=5
4690 DATAFILES$="PADTEST" @ FIGUREFILES$="TEST_PAD" @ DATADRIVE=1 @ T8=0
4700 FIGUREDRIVE=1 @ DATASTORES$="YES" @ FIGSTORES$="NO" @ DRIVE=1 @ E3=-1 @ E7=0 @
   E10=.8 @ E13=-1 @ E11=.8 @ E14=.8 @ E24=.8 @ E17=.8 @ E18=.8 @
   E21=.8 @ E22=.8 @ E23=.8 @ E25=.8 @ E27=.8 @ E28=.8 @
   E29=.8 @ E30=.8 @ E31=.8 @ E32=.8 @ E33=.8 @ E34=.8 @
   E35=.8 @ E36=.8 @ E37=.8 @ E38=.8 @ E39=.8 @ E40=.8 @
   E41=.8 @ E42=.8 @ E43=.8 @ E44=.8 @ E45=.8 @ E46=.8 @
   E47=.8 @ E48=.8 @ E49=.8 @ E50=.8 @ E51=.8 @ E52=.8 @
   E53=.8 @ E54=.8 @ E55=.8 @ E56=.8 @ E57=.8 @ E58=.8 @
   E59=.8 @ E60=.8 @ E61=.8 @ E62=.8 @ E63=.8 @ E64=.8 @
   E65=.8 @ E66=.8 @ E67=.8 @ E68=.8 @ E69=.8 @ E70=.8 @
   E71=.8 @ E72=.8 @ E73=.8 @ E74=.8 @ E75=.8 @ E76=.8 @
   E77=.8 @ E78=.8 @ E79=.8 @ E80=.8 @ E81=.8 @ E82=.8 @
   E83=.8 @ E84=.8 @ E85=.8 @ E86=.8 @ E87=.8 @ E88=.8 @
   E89=.8 @ E90=.8 @ E91=.8 @ E92=.8 @ E93=.8 @ E94=.8 @
   E95=.8 @ E96=.8 @ E97=.8 @ E98=.8 @ E99=.8 @
   DATAFILE$="PADTEST" @ FIGUREFILES$="TEST_PAD" @ DATADRIVE=1 @ T8=0
4710 DATAFILE$="PADTEST" @ FIGUREFILES$="TEST_PAD" @ DATADRIVE=1 @ T8=0
4720 SCANFLAG=0 @ ADVOLTAGE=10 @ TOTALSCANS=1 @ V_RANGE=10 @ IMAX=1
4730 T10=500 @ T11=0 @ FIAFLAGS$="NO" @ ZPRINT$="NO" @ PRINTER IS 1 @
4740 Z30=.2 @ E30=-.2 @ T20=300000 @ T21=300000 @ T22=600000 @ INJECT=5 @ SKIPFLAGS$="NO"
4750 E10=.8 @ E13=-1 @ T23=200 @
   E11,E14,T24,ROT,ROT(0),ROTMAX,ROTMIN=0
4760 COULOMBS$="1" @ T27=.001 @ RINSE$="NO" @ INTEGRATE=8
GOSUB 5750 @ TAKE KEYBOARD
A$(1)="Experimental directory"
A$(2)="Mass storage directory"
A$(3)="Plotting directory"
A$(4)="Begin experiment"
A$(5)="Chain Autost"
A$(6)="End program"
A$(7)="Exit to main menu"
A$(8)="Beginning detection potential, E1...i"
A$(9)="Ending detection potential, E5...i"
A$(10)="Potential increment, E-d...i"
A$(11)="Beginning detection time (msec), T1...ii"
A$(12)="Ending detection time (msec), T4...ii"
A$(13)="Detection time increment (msec), T5...ii"
A$(14)="Beginning adsorption time (msec), T3...iii"
A$(15)="Ending Adsorption time (msec), T10...iii"
A$(16)="Adsorption time increment (msec), T11...iii"
A$(17)="Cleaning pulses, T6"
A$(18)="Delay time before charge measurement, T27"
A$(19)="Continuance of experimental directory"
A$(20)="Activate alternate waveform"
A$(21)="UPD beginning integration potential, E30"
A$(22)="Continuance of experimental directory"
A$(23)="Exit to previous experimental menu"
A$(24)="Current range"
A$(25)="Number of signal averaged decays"
A$(26)="Waiting reduction time"
A$(27)="Potential NUMBER of voltage monitoring"
A$(28)="Hold detection potential constant"
A$(29)="Delsy time before injections, T20"
A$(30)="Injection time, T21"
A$(31)="Delay time between injections, T22"
A$(32)="Number of injections"
A$(33)="Converting to current or charge"
A$(34)="Continuance of experimental directory"
A$(35)="Exit to main menu"
A$(36)="Data file name"
A$(37)="Figure file name"
A$(38)="Data file drive number"
A$(39)="Figure file drive number"
A$(40)="Store data on disk"
A$(41)="Store figure on disk"
A$(42)="Catalog of disk"
A$(43)="NULL"
A$(44)="Exit to main menu"
A$(45)="Plot raw data curve"
A$(46)="Enter max and min on Y only"
A$(47)="Activate printer"
A$(48)="Conversion override"
A$(49)="NULL"
5280 \text{A$(50)="Exit to previous experimental menu"}
5290 \text{A$(51)="Beginning anodic potential, E2...iv"
5300 \text{A$(52)="Ending anodic potential, E10...iv"
5310 \text{A$(53)="Anodic potential increment, E11...iv"
5320 \text{A$(54)="Beginning cathodic potential, E3...v"
5330 \text{A$(55)="Ending cathodic potential, E13...v"
5340 \text{A$(56)="Cathodic potential increment...v"
5350 \text{A$(57)="Beginning cleaning time, T2...vi"
5360 \text{A$(58)="Ending cleaning time, T23...vi"
5370 \text{A$(59)="Cleaning time increment, T24...vi"
5380 \text{A$(60)="Rotation speeds...vii"
5390 \text{A$(61)="Activate automatic rinse for FIA"
5400 \text{PERIOD$="...""
5410 \text{FOR I=1 TO 61 @ T$=A$(I) @ GOSUB 5770 @ B$(I)=T1$ @ NEXT I
5420 SCRN=1 @ A1=1 @ A2=6
5430 \text{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) @ CR$=1
5460 AWRITE 20,2,"Change any parameters ?" @ AWRITE 21,2,"Press the indicated letters or use the the "." and "," keys for slewing :"
5470 AWRITE 22,2,"Press '4' to change any parameters or to start experiment :"
5480 AWRITE 23,2,"Lower case Roman numerals indicate precedence, vi being the lowest."
5490 \text{T AKE KEYBOARD}
5500 KY$=NUM (KEY$) @ IF NOT KY$ THEN 5500
5510 IF KY$>64 AND KY$<65+A2-A1+1 THEN AWRITE CR$=A$(A1+CR$-1) @ CR$=KY$-64 @ AWRITE CR$=A$(A1+CR$-1) @&DAT$(I) @ NEXT I
5520 IF KY$< 46 THEN 5550
5530 AWRITE CR$=A$(A1+CR$-1) @ CR$=CR$=CR$-1 @ IF CR$<1 THEN CR$=A2-A1+1
5540 AWRITE CR$=A$(A1+CR$-1) @ CR$=CR$=CR$+1 @ IF CR$>A2-A1+1 THEN CR$=1
5550 IF KY$< 44 THEN 5580
5560 AWRITE CR$=A$(A1+CR$-1) @ CR$=CR$=CR$+1 @ IF CR$>A2-A1+1 Then
5570 AWRITE CR$=A$(A1+CR$-1)
5580 IF KY$< 52 THEN 5490
5590 IF SCRN< 1 THEN 5650
5600 IF CR$=1 THEN SCRN=2 @ A1=7 @ A2=21 @ GOTO 5440
5610 IF CR$=2 THEN SCRN=3 @ A1=35 @ A2=42 @ GOTO 5440
5620 IF CR$=3 THEN SCRN=4 @ A1=44 @ A2=48 @ GOTO 5440
5630 IF CR$=5 THEN RELEASE KEYBOARD @ CHAIN "Autost"
5640 IF CR$=4 THEN singlevariable ELSE RELEASE KEYBOARD @ GOTO 5740
5650 PAGEFLAG=1 @ RELEASE KEYBOARD
5660 IF SCRN=2 THEN ON CR$ GOTO
5700,1830,3040,3100,1980,3310,3370,2680,3560,3630,2990,
4510,2470,4551,5710
5670 IF SCRN=5 THEN ON CR$ GOTO
5720,2850,3200,3250,3440,3490,3700,3740,3790,3840,3890,2380,5730
5680 IF SCRN=6 THEN ON CRSR GOTO 5700,1900,3960,4020,2610,4120,4180,2050,4280,4350,4420,6690
5690 IF SCRN=3 THEN ON CRSR GOTO 5700,2140,2230,2320,2350,2410,2440,2500,2410,2440,2500 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)&" \\
5870 "&I_TYPE$[1,5]&"amps"&/ "&VAL$ (V_RANGE)&" V"
5880 DAT$(24)=VAL$ (ADVOLTAGE) @ DAT$(25)=VAL$ (TOTALSCANS)
5890 DAT$(26)=VAL$ (T8) @ DAT$(27)=VAL$ (IMAX) @ DAT$(28)=FIAFLAGS
5900 DAT$(29)=VAL$ (T20) @ DAT$(30)=VAL$ (T21) @ DAT$(31)=VAL$ (T22)
5910 DAT$(32)=VAL$ (INJECT) @ DAT$(33)=COULOMBS @ DAT$(34)=""
5920 DAT$(35)="" @ DAT$(36)=DATAFILES @ DAT$(37)=FIGUREFILES
5930 DAT$(38)=VAL$ (DATADRIVE) @ DAT$(39)=VAL$ (FIGUREDRIVE)
5940 DAT$(40)=DATASTORES @ DAT$(41)=FIGSTORES @ DAT$(42)=VAL$ (DRIVE)
5950 DAT$(43),DAT$(44)="" @ DAT$(45)=PLOTFIGS
5960 DAT$(46)=VAL$ (YMIN)&", \\
5970 \\
5980 DAT$(47)=ZPRINTS
5990 DAT$(48)=SKIPFLAGS @ DAT$(49),DAT$(50)=""
6000 DAT$(51)=VAL$ (E2) @ DAT$(52)=VAL$ (E10) @ DAT$(53)=VAL$ (E11)
6010 DAT$(54)=VAL$ (E3) @ DAT$(55)=VAL$ (E13) @ DAT$(56)=VAL$ (E14)
6020 DAT$(57)=VAL$ (T2) @ DAT$(58)=VAL$ (T23) @ DAT$(59) (T24)
6030 DAT$(60)="" @ DAT$(61)=RINSE$
6040 RETURN
6050 IF ERRN =50 THEN LOADBIN "UTIL/1" @ GOTO 6100
6060 IF ERRN =67 OR ERRN =66 THEN 6100
6070 IF ERRN =55 THEN OUTPUT 723 ;"CC 2,3,4T" @ I=0 @ GOTO 500
6080 IF ERRN =11 THEN menu
6090 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
6100 DISP ERN ,ERRL @ WAIT 2000
6110 RETURN
! Display results on 'printer.is' default
PRINT CHR$(12) @ FOR K=1 TO 60 @ PRINT CHR$(64+K)&CHR$(41)&PERIOD$(1,4)&AS$(K)&PERIOD$(1,45-LEN(AS$(K)))&" "&DAT$(K) @ NEXT K @ PRINT CHR$(12) @ RETURN
END

! Single variable: ! Single variable check
CLEAR @ DISP "Calculating"
SINGLEFLAG,T,N,A,B,C,T0=0
IF El<>E5 THEN T0=1 @ GOTO 6270
IF T1<>T4 THEN T0=2 @ GOTO 6270
IF T3<>T10 THEN T0=3 @ GOTO 6270
IF E2<>ElO THEN T0=4 @ GOTO 6270
IF E3<>E13 THEN T0=5 @ GOTO 6270
IF T2<>T23 THEN T0=6 @ GOTO 6270
IF ROTMIN<ROTMAX THEN T0=7 @ GOTO 6270
IF FIAFLAG$="YES" THEN N=1 @ GOTO experiment3 ELSE menu
ON TO GOSUB 6280,6310,6320,6290,6300,6330,6340 @
N=ABS(INT((B-A)/C))+1 @ GOTO 6350
A=E1 @ B=E5 @ C=INCPOT @ RETURN
A=E2 @ B=E10 @ C=E11 @ RETURN
A=E3 @ B=E13 @ C=E14 @ RETURN
A=T1 @ B=T4 @ C=T5 @ RETURN
A=T3 @ B=T10 @ C=T11 @ RETURN
A=T2 @ B=T23 @ C=T24 @ RETURN
A=ROTMIN @ B=ROTMAX @ C=1 @ RETURN
FOR I=0 TO N-1 @ X(I+1)=A+C*I @ NEXT I
SINGLEFLAG=1
GOTO experiment3
!
ROT=ROT+1 @ IF ROT>ROTMAX THEN ROT=ROTMIN
GOSUB 20 @ N1=8+ROT(ROT) @ N2=32768+ROT(ROT) @ N3=16384+32768+ROT(ROT) @ RETURN
decode:
ON ERROR GOTO error3 @ error=0 @ FOR I=1 TO 20 @ CODE(I)=0 @ NEXT I
FOR I=1 TO LEN(CODE$) @ IF CODES[1,1]=CHR$(32) THEN CODES=CODES[2,LEN(CODE$)] @ GOTO 6440
IF CODES[1,1]<>"" THEN 6470
FOR I=1 TO 100 @ CODE(I)=1 @ NEXT I @ GOTO 6580
TS="1"
FOR I=0 TO 9 @ IF CODES[1,1]=VAL$(I) THEN TS="-1"
NEXT I @ IF TS <> VAL$(-1) THEN CODES=CODES[2,LEN(CODE$)] ELSE 6510
IF LEN(CODE$)=0 THEN error3 ELSE 6480
T=VAL$(CODE$) @ IF T<0 OR T>99 THEN error2 ELSE CODE(T)=1
IF LEN(VALS(T))=LEN(CODES) THEN 6580
CODES=CODES[1+LEN(VALS(T)),LEN(CODES)] @ IF LEN(CODES)=0 THEN CODE(T)=1 @ GOTO 6580
6540  T$=CODES[1,1] @ CODES=CODES[2,LEN (CODES)] @ IF T$="" OR T$="-" THEN 6550 ELSE error1
6550  t1=VAL (CODES) @ IF t1<0 OR t1>99 THEN T=t1 @ GOTO error2
6560  IF T$="" 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 @ FIAFLAGS$="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+0I;"T OP 7 ";E6;" 12 100T OP 13 ";N2+0I;"T OP 7 ";E12;" 12 ";T25;"T"
7055 ! 625 !
7060 ! 630 OUTPUT 723 ;"OP 7 ";E6;" 12 ";T9;"T OP 14 .03 13 ";N3+0I;" 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 @ TO=T25/20
7140 ! 620 N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12 ";T12;" 13 ";N1+0I;"T OP 7 ";E6;" 12 1T OP 13 ";N2+0I;"T"
7150 ! 625 FOR K=1 TO 20 @ OUTPUT 723 ;"OP 7 ";E0;" 12 ";TO;"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+0I;" 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+0I;"T OP 7 ";E30;"T OP 13 ";N2+0I;"T OP 7 ";E6;" 12 ";T27;"T OP 12 ";T9;"T"
7255 ! 625 !
7260 ! 630 OUTPUT 723 ;"OP 14 .03 12 18 13 ";N3+0I;"T OP 11 .02T OP 7 ";E12;" 12 ";T25;"T" @ DISP E6,I @ RET=2 @ I=I+1 @ GOTO 620
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 1
7340 ! 440 1
7345 ! 590 1
7350 ! 620 N=I @ X(I)=I*T @ RET=1 @ OUTPUT 723 ;"OP 7 ";E15;" 12 ";";
7355 ! 630 OUTPUT 723 ;"OP 7 ";E6;" 12 ";";
7360 ! 630 OUTPUT 723 ;"OP 7 ";E6;" 12 ";";
7370 ! 4640 WFM=4
7380 !
8000 END