A micro computer controlled high speed high resolution cyclic voltammeter
by Russell Allen Bonsteel

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

Abstract:
In cyclic voltammetry, the technique of applying known voltages to an electrochemical cell and recordings the response waveform on an x-y recorder is a area of significant growth. In its infancy, the voltages applied to the cell were delivered by manual control through a network of vacuum tubes, resistors, and capacitors. The waveform response curves were both crude in accuracy and precision. The next generation of electronics brought about the operational amplifier. While this increased the accuracy of the waveforms, reproducibility was still lagging because of the manual timing application of the input voltages, especially for multiple run sequences.

It is proposed that by using state of the art integrated circuits and computer control that the manual application of the voltages can be eliminated and thereby increase both the precision and the reproducibility of the voltammetric waveform.

With the implementation of the integrated circuits and computer control new schematic designs had to be employed. Solid state analog switches were used to route precise currents or voltages to carefully matched operational amplifiers. Timing routines were generated to maximize the amount of data to be collected and stored in computer memory. A sophisticated language called FORTH was ascertained to be the best vehicle to communicate between the computer and the cyclic voltammetric interface.

The results were excellent on the implementation of the voltages to the electrodes in the chemical cell. With the computer control, precision up to +- 7 parts per one thousand was achieved using a ten volt reference. By being able to store the analog data as a digital number, computer enhancement of the cyclic waveforms i.e. background elimination of supporting electrolytes are now also obtainable.

With the newly constructed cyclic voltammeter an investigation of the reduction of Lindane, a chlorinated pesticide, at sweep rates up to fifty times faster then previously accomplished was carried out. This data allowed extrapolation back to soil redox potential levels and may allow estimating the life span of the pesticide in the reductive environment.

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APPROVAL

of a thesis submitted by

Russell Allen Bonsteel

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date

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September 10, 1986
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Graduate Dean

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ABSTRACT

In cyclic voltammetry, the technique of applying known voltages to an electrochemical cell and recording the response waveform on an x-y recorder is a area of significant growth. In its infancy, the voltages applied to the cell were delivered by manual control through a network of vacuum tubes, resistors, and capacitors. The waveform response curves were both crude in accuracy and precision. The next generation of electronics brought about the operational amplifier. While this increased the accuracy of the waveforms, reproducibility was still lagging because of the manual timing application of the input voltages, especially for multiple run sequences.

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INTRODUCTION

The Electrode Processes

Two types of electrical processes occur at electrodes. One involves the transfer of electrons across the metal-solution interface. This process causes oxidation or reduction to occur. Since these reactions are governed by Faraday's law (i.e. the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called Faradaic processes. Electrodes at which Faradaic processes occur are sometimes called charge transfer electrodes. Under some conditions a given electrode-solution interface will show a range of potentials where no Faradaic reactions occur because such reactions are thermodynamically or kinetically unfavorable. However other processes, involving the electrode interface structures can occur such as adsorption and desorption with changing potential or solution composition. These processes are called nonfaradaic processes.[1]

Nonfaradaic currents arise from the formation of an electrical double layer at the electrode-solution interface. When a potential is applied to a metallic electrode immersed in an electrolyte, a momentary surge of current creates an excess (or a deficiency) of negative

charge at the surface of the metal. Because of ionic
mobility, the layer of solution immediately adjacent to the
electrode acquires an opposing charge due to excess counter
ions (see Figure 1a). According to the G-C-S theory
(Gary-Chapman-Stern)[2] the charged layer consists of two
parts: (1) a compact inner layer, in which the potential
decreases linearly with distance from the electrode
surface; and (2) a more diffuse layer, in which the
decrease is approximately exponential (Figure 1b). This
arrangement of negative and positive ions is termed the
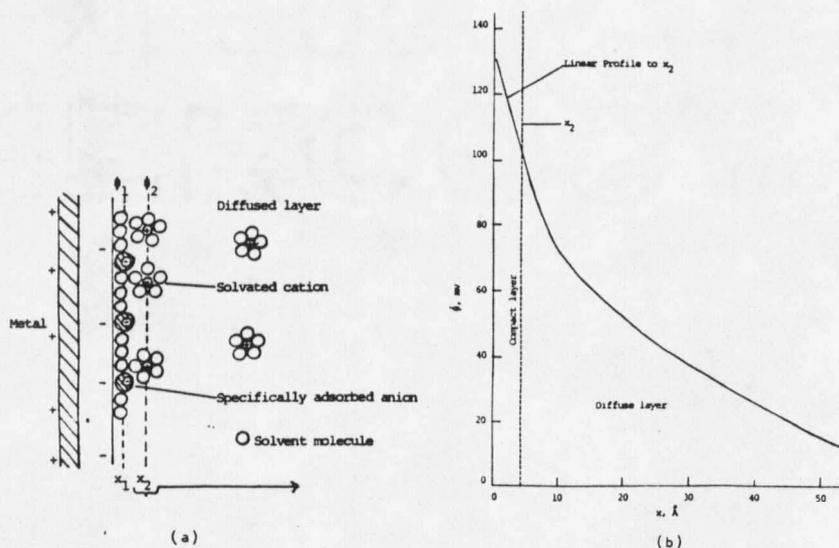electrical double layer.

Figure 1. (a) Proposed model of the
electrode-solution, double layer region.
(b) Potential profile through the solution
side of the double layer.

The double layer formed by an applied DC potential involves the development of a momentary current which then drops to zero as the electrode becomes polarized, no further current flows unless some faradaic process occurs. When an alternating potential is applied to the electrodes an alternating current flows in conjunction with the reversal of the charge relationship occurring with each half-cycle, as first negative and then positive ions are attracted to the electrode surface. A modest amount of electrical energy is consumed and converted to frictional heat from this ionic movement. Thus, each electrode surface behaves as a capacitor, the capacitance of which may be quite large (on the order of ten to a hundred microfarads per square centimeter).[3] The capacitive current increases with both increasing frequency and increasing electrode size. By controlling these variables, it is possible to arrange conditions so that essentially all of the electricity flowing through the cell is carried across the electrode interface by this nonfaradaic process.

Voltammetry

Information concerning chemical reactions (i.e. Faradaic) can be gained from an electrochemical cell by sweeping thru a known potential region with time and recording the i-e curve directly. The potential is usually varied (ramped with sweep rates ranging from 0.04