AN ABSTRACT OF THE THESIS OF

CLINTON EARL MILLER   for the   MASTER OF SCIENCE
_____   _____
        (Name)   (Degree)

in Chemistry (Analytical) presented on   March 31, 1971
   _____   _____
        (Major)   (Date)

Title: OPTIMIZATION BY TRANSFER FUNCTION ESTIMATION
       _____

       OF THE GALVANQVOLTAMMETRIC DETERMINATION OF
       _____

       DISSOLVED CHLORINE IN A FLOWING STREAM
       _____

Abstract approved __*Redacted for Privacy*_____
                    ⁄ ⌣   Dr. Harry Freund

Optimization of the galvanovoltammetric determination of dis-

solved chlorine in a flowing stream was achieved through the use of

an analog computational device and improvements in the design of the

galvanovoltammetric cell and accompanying electronic circuitry. An

analysis system, applicable to industrial use over a range of flow

rates and dissolved chlorine concentrations, was constructed.

A Fortran program, SIMPLEX, was written to approximate

the transfer function of a galvanovoltammetric cell and its associated

sampling system. An analog computational device was built to rapidly

output the steady state value following a step change at the input of

the galvanovoltammetric detection system.

Optimization by Transfer Function Estimation
of the Galvanovoltammetric Determination of
Dissolved Chlorine in a Flowing Stream

by

Clinton Earl Miller

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1971

APPROVED:

Redacted for Privacy

Professor of Chemistry
in charge of major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

Date thesis is presented _____ March 31, 1971 _____

Typed by Muriel Davis for Clinton Earl Miller

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

OPTIMIZATION BY TRANSFER FUNCTION ESTIMATION OF THE GALVANOVOLTAMMETRIC DETERMINATION OF DISSOLVED CHLORINE IN A FLOWING STREAM

I. INTRODUCTION

Continuous analysis involves the measurement of a component in a flowing stream of the sample solution (3, vol. 5, p. 69). Many industrial chemical processes are continuous operations which make use of flowing streams as, for example, the bleaching of wood pulp by chlorine. It would be desirable to continuously follow the chlorine concentration so as to insure production of high grade pulp. In addition to process analysis, recent pressure by the general public on industry to lessen pollution of public waters, many of which are flowing bodies, has encouraged the use of continuous analyzers to monitor pollutants. One technique being adapted to continuous analysis is voltammetry.

Development of the Galvanovoltammetric Cell

Voltammetry involves the study of current-voltage relationships in an electrochemical cell operated under conditions of diffusion control. The current is directly proportional to the concentration of the electroactive species (7). When a small working electrode is placed in a quiescent solution, the diffusion-limited current is on the order of microamperes. However, if the same electrode is placed in a

flowing stream, the current is limited by both convection and diffusion, and is on the order of milliamperes.

McGee and Bleak of Beckmann Instruments developed a diffusion-convection controlled cell (5) which measures SO_2 in ambient air (Figure 1). The cell's anode, which is controlled by a constant electron current$\underline{1}/$ sink, generates I_2 from I^-. The I_2 solution is then allowed to mix with air being bubbled into the cell. After the air is mixed with the I_2 solution, the solution passes the cathode where I_2 is reduced back to I^-.

A third electrode of activated carbon, previously treated with oxygen, and called the bipolar electrode, is part of the cell and its potential is held at a "virtual" ground by an operational amplifier current-to-voltage (I-V) converter. Bleak and McGee say (5, p. 3) that the bipolar electrode serves as a "reference" to the anode and cathode, and "consequently registers any unbalance between the anodic . . . and cathodic . . . currents."

As long as there is no reductant in the sample air stream, to reduce the I_2 before it reaches the anode, then the current flowing into the cathode equals that flowing out the anode. If any SO_2 is in the air, then a corresponding amount of I_2 is reduced to I^- before it reaches the cathode. The electron flow into the cathode will then

_____

$\underline{1}/$ Unless otherwise noted, all references to current mean electron flow.
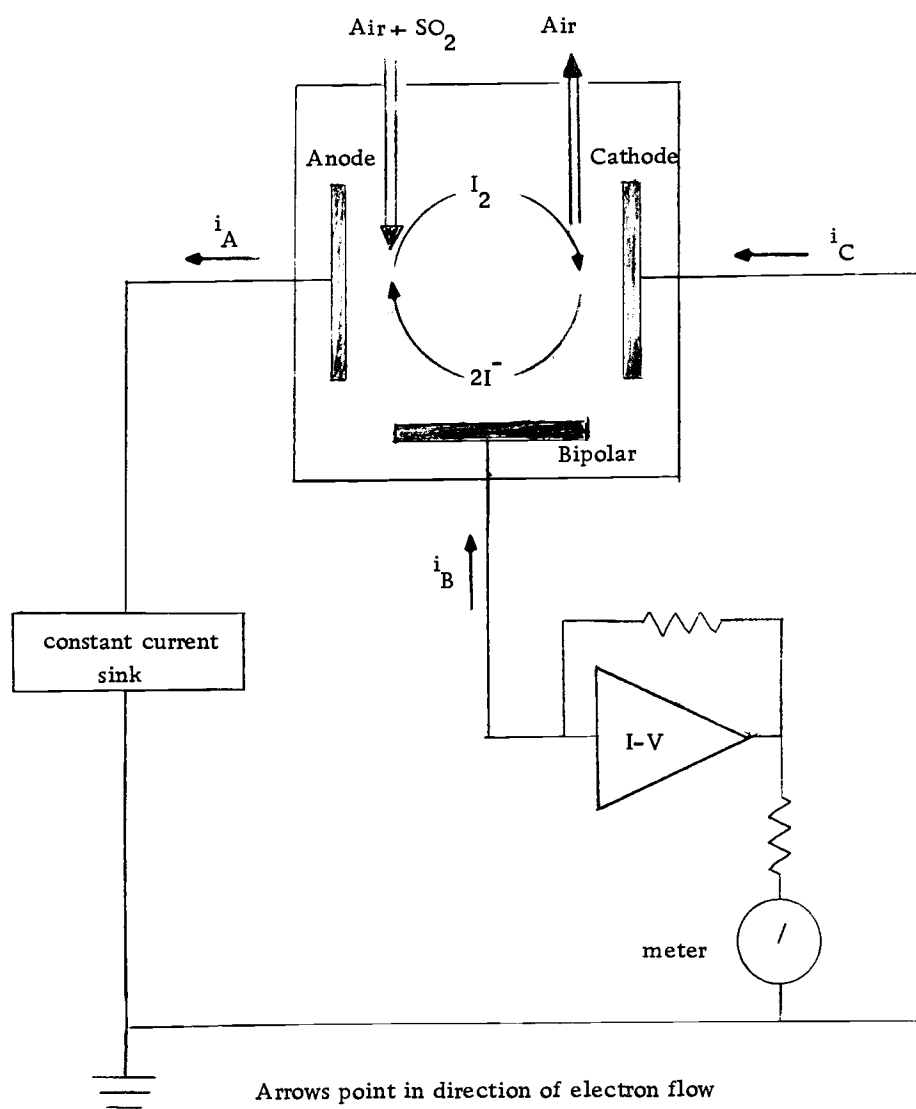
Figure 1. McGee-Bleak Schematic

be lower than that flowing out the anode. The bipolar reflects the imbalance by drawing current from the I-V converter.

Thus, the higher the SO_2 concentration in the air, the less I_2 there is to be reduced at the cathode, which in turn, increases the current drawn to the bipolar electrode. The current passing through bipolar electrode, then, is proportional to the SO_2 concentration in the air.

Based on the three-electrode approach used by McGee and Bleak, Kendall (12, p. 85-120) developed a continuous dissolved chlorine analyzer (Figure 2). The chlorine solution enters the cell and passes between the innermost and middle cylinders of three concentric cylinders. The middle cylinder is a tube of "thirsty glass" which acts as a salt bridge between the dissolved chlorine solution and the elctrolyte comprising part of the third electrode. The innermost cylinder is a glass spacer tube around which is wrapped a piece of platinum gauze, which acts as the cathode. The anode, another piece of platinum gauze, lies across the solution outlet of the cell. Between the thirsty glass and outermost cylinder, which is Lucite, lies a very large piece of platinum gauze immersed in an electrolytic solution. The large gauze is the third, or bipolar electrode and comprises part of a massive $Pt/Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ half cell.

The electrical circuitry (Figure 3) used by Kendall (12, p. 120-

Sample inlet
(12/2 Ball Joint)

bipolar lead

cathode lead

bipolar chamber
fill hole (4mm dia.)

bipolar chamber
vent hole

spacer tube
(4 cm long, 11mm O.D.)

lucite plate
(0.6 cm thick, 4 cm dia.)

bipolar chamber

tubing
(35 mm O.D., 6 cm long)

sample stream
chamber

"thirsty glass" tube
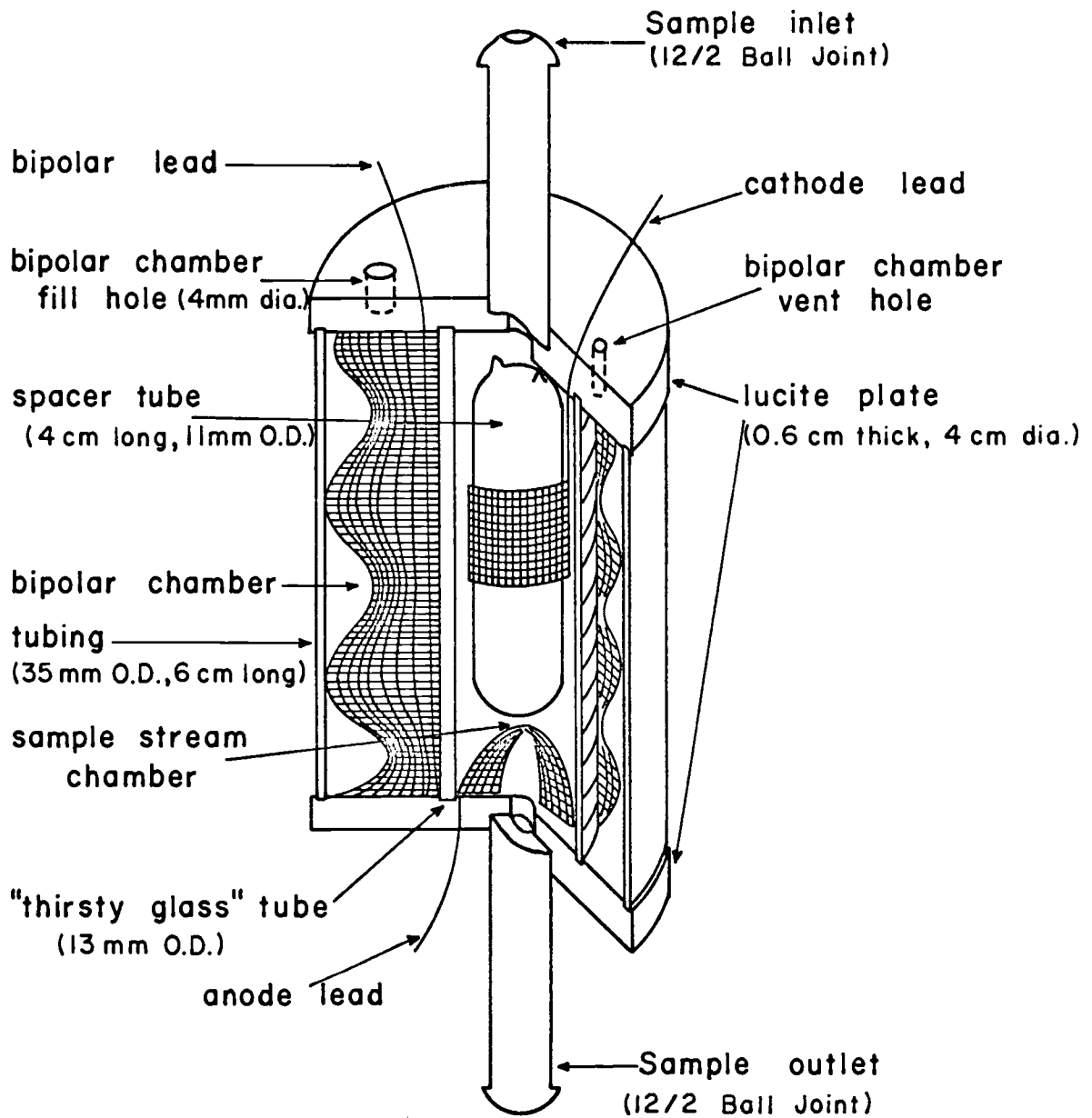(13 mm O.D.)

anode lead

Sample outlet
(12/2 Ball Joint)

Figure 2. Kendall Cell Cutaway
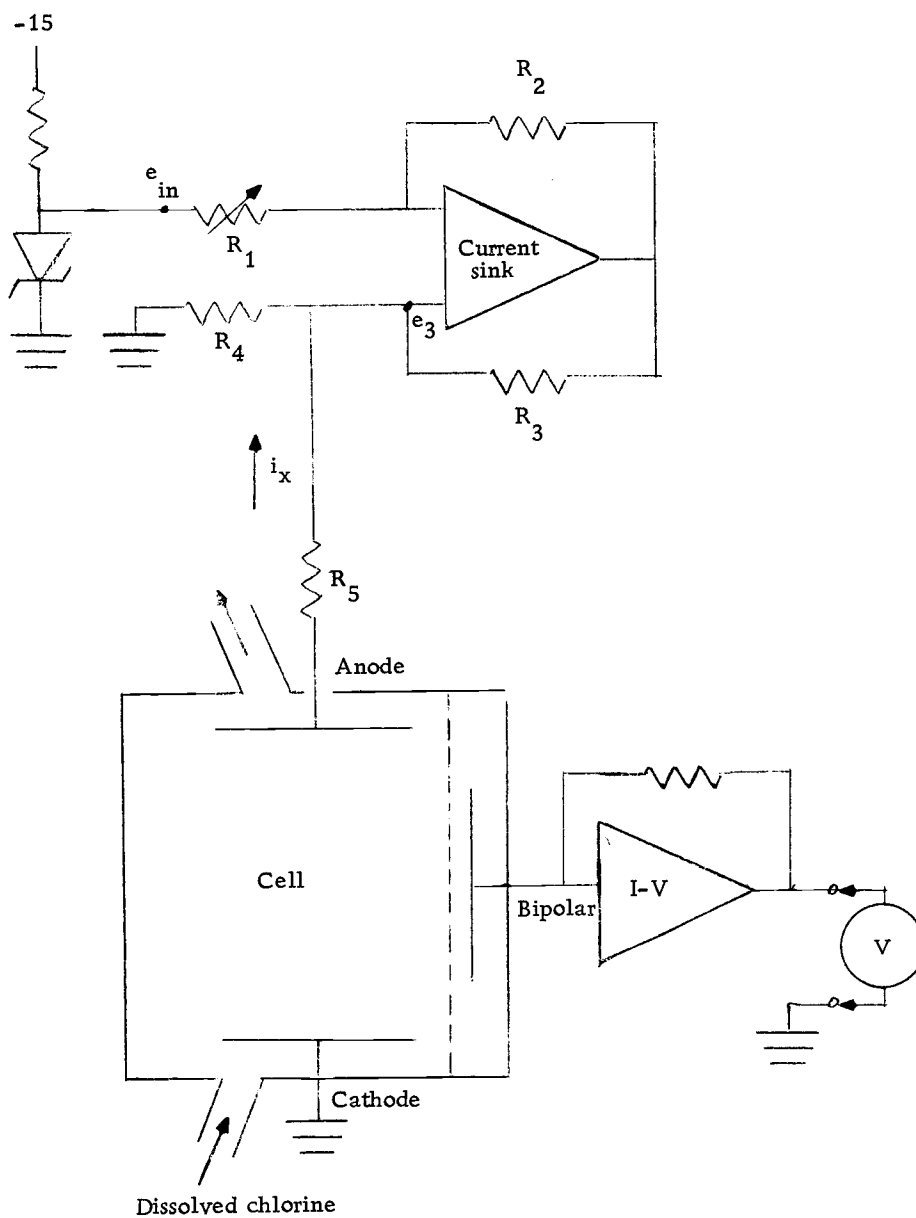
Figure 3. Schematic of Kendall's Cell

149) is similar to that used by McGee and Bleak. The cathode is wired to ground; the bipolar electrode is held at a "virtual" ground by an operational amplfier current-to-voltage converter, and an operational amplifier current sink is used at the anode. The current sink is constructed in such a manner that the current flowing from the anode, i_x, is related to the potentials e_3 and e_{in}, and resistors R_1 and R_4 by (see Appendix I):

$$i_x = -[e_{in}/R_1 + (1/R_4 - 1/R_1)e_3] \qquad (1)$$

Kendall set R_4 equal to the anticipated value of R_1, so that

$$i_x \cong -e_{in}/R_1 \qquad (2)$$

R_1 could then be varied over a short range to adjust the anode current.

As the dissolved chlorine passes the cathode, current can flow into the cathode controlled by the diffusion and convection of the dissolved chlorine toward the cathode. The contribution of current by convection is dependent upon the flow rate, cell geometry, and chlorine concentration; and the contribution of current by diffusion is dependent upon chlorine concentration and cell geometry. If the flow rate is held constant for a given cell (along with other parameters that affect the flow rate, such as solution temperature and density) then the cathode current is solely dependent upon the chlorine

concentration.

Kendall demonstrates (12, p. 33-46) that if the current level passed by the anode is higher than that which is passed by the cathode, then the difference in currents in levels flows from the I-V converter to the bipolar. If, in turn, the anode current is lower than that which the cathode passes, then current equal to the difference in levels flows from the bipolar electrode to the I-V converter. If the anode and cathode currents are the same, then no current is passed by the bipolar electrode. It can be seen, then, that the algebraic sum of the bipolar and cathodic currents is equal to the anodic current.

If the galvanovoltammetric cell is to measure the dissolved chlorine in a stream, whose chlorine level fluctuates around a certain concentration, called the set point, then the anodic current is set equal to the cathodic current at the set point. The bipolar current then would measure the deviations in dissolved chlorine from the set point concentration.

Galvanovoltammetry is defined by Kendall (12, p. 46-47) to be the measurement of current flowing to or from the bipolar electrode or to the working electrode in an electrochemical cell. It is necessary that the cell consist of working and counter electrodes, between which a constant current is applied, and a third or bipolar electrode which forms a galvanic cell with the working electrode and is also common to the counter electrode. Note that the current being

measured is proportional to the electroactive species.

Kendall chose the name galvanovoltammetry because of the galvanic cell formed by the bipolar and cathode and the voltammetric response of the cathode current (12, p. 46).

Response of a Continuous Analyzer

One of the problems of any continuous analyzer is that the output lags the input. For example, if a step change in concentration is presented to the input, the output will record no change for a period of time, t_{delay}, and will then respond by exponentially approaching a steady state value. This fixed period is called the transition time (Figure 4) (3, vol. 2, p. 72-74).

One can simulate the continuous analyzer with an electrical black box, where the input concentration corresponds to an input voltage, and the analyzer response corresponds to an output voltage. Roger Blaine and Harry Freund demonstrate that if one uses a capacitor charging through a resistor as a basic unit, called a resistor-capacitor (RC) network, (Figure 5a) then the black box during the transition time could correspond to n number of RC networks in series, assuming no "loading" between networks (4).

The output of a capacitor charging through a resistor is related to the input by
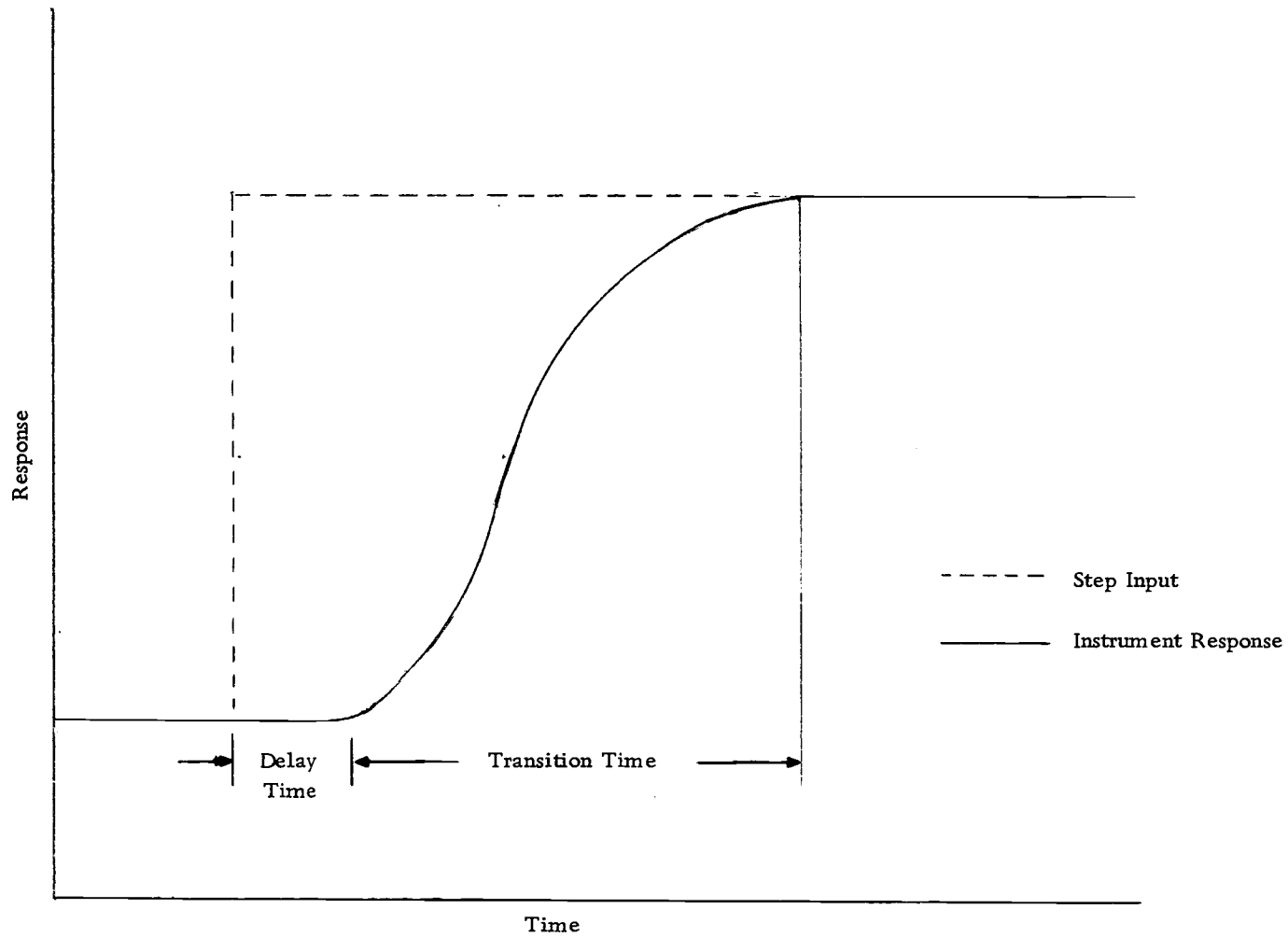
$$V_I - V_O - iR = 0 \qquad (3)$$

Figure 4. Typical Response of Continuous Analyzer Following Step Input Change

10
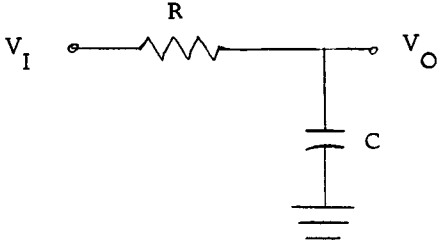
Figure 5a. An RC Network

$R_1 \cdot C_1 = T_1$

$R_2 \cdot C_2 = T_2$
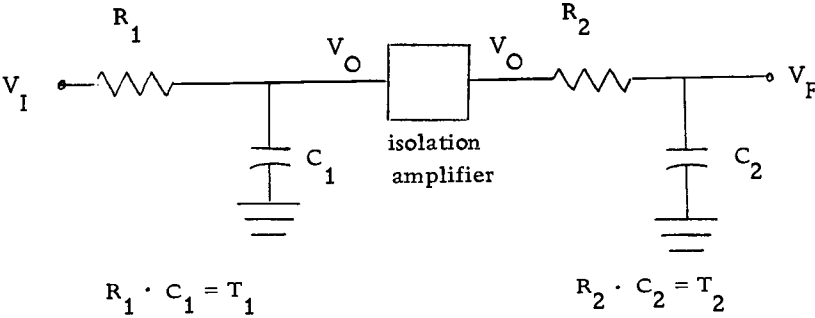
Figure 5b. Two RC Network Analog

where V_O is the output voltage, V_I is the input voltage and i is

the current flowing through the resistor of R ohms. From basic

electricity, i can be related to the capacitance C by

$$i = \frac{dV_O}{dt} C \tag{4}$$

so that

$$V_I - V_O - RC\frac{dV_O}{dt} = 0 \tag{5}$$

If an ideal isolation amplifier[2] is placed at V_O, a second RC

network is placed at the output of the isolation amplifier, and the

product of the resistance and capacitance or time constant in the first

network is set equal to T_1, and in the second, equal to T_2 (Figure

5b), then V_F, the output of the second RC network, is related to the

output of the first by

$$V_O - V_F - T_2\frac{dV_F}{dt} = 0 \tag{6}$$

Combining equations (5) and (6) gives

$$V_I = V_F + (T_1 + T_2)\frac{dV_F}{dt} + T_1 T_2 \frac{d^2 V_F}{dt^2} \tag{7}$$

For a step change in a continuous analyzer which has a two-RC

network analog, the input would correspond to V_I, and the

instrument response during the transition time corresponds to V_F.

---

[2] Note that the potential at the input and output of the isolation
amplifier are essentially equal at all times. The amplifier has an
infinite input impedance and no output impedance, so that all it serves
to do is to isolate the two RC networks to prevent loading.

By finding the constants T_1 and T_2 graphically, and using an analog computer, Blaine and Freund show that the steady state for a two-RC network could be found during the transition time by proper weighting of the instrument response and its first and second derivatives (4).

Purpose of This Research

It is the intent of this research to build a galvanovoltammetric cell for the wide-range continuous analysis of dissolved chlorine in a flowing stream, to find a mathematical expression for the transitions taking place in the galvanovoltammetric detection, and to build an electronic device that would find the steady state concentration of chlorine during the transition time following a step input.

II. DESIGN OF GALVANOVOLTAMMETRIC CELL
AND BASIC ELECTRONIC PACKAGE

The objective of the cell and electronic circuitry design is to make a device suitable for wide-range industrial use. Therefore, the galvanovoltammetric cell must be simple to clean and maintain, and be as rugged as possible. The electronic package must be able to give a wide span of anode currents.

Cell Design

Poly-vinyl chloride (PVC) was chosen as the basic construction material. Parts A, B, and C (Figure 6) were machined out of three-inch PVC rod. Part D is a piece of two-inch diameter PVC pipe (SCH 40) obtained from the Oregon State University Physical Plant plumbing shop. The electrode holder was machined out of one-inch PVC rod.

As in Kendall's cell, the three concentric-cylinder approach is used (see Figure 7). However, the stream containing dissolved chlorine enters the cell from the bottom and flows out of the top. The flow reversal is made because reactions taking place at the anode often liberate gases, and if the anode were below the cathode, the rising gas bubbles would interfere with the diffusion-convection processes, and would become trapped in the upper portion of the cell.

The innermost of the three cylinders is the electrode holder,

Figure 6. Exploded View of Cell

Connector to Electronic Package
for Anode and Cathode

Part A

Stream Outlet ⟶

Electrode
Holder

Electrolyte
Inlet
Plug

Part C

Bipolar
Connection

Bipolar
Electrode

Part D

Thirsty Glass

Electrolyte
Outlet
Plug

Part B

Stream Inlet
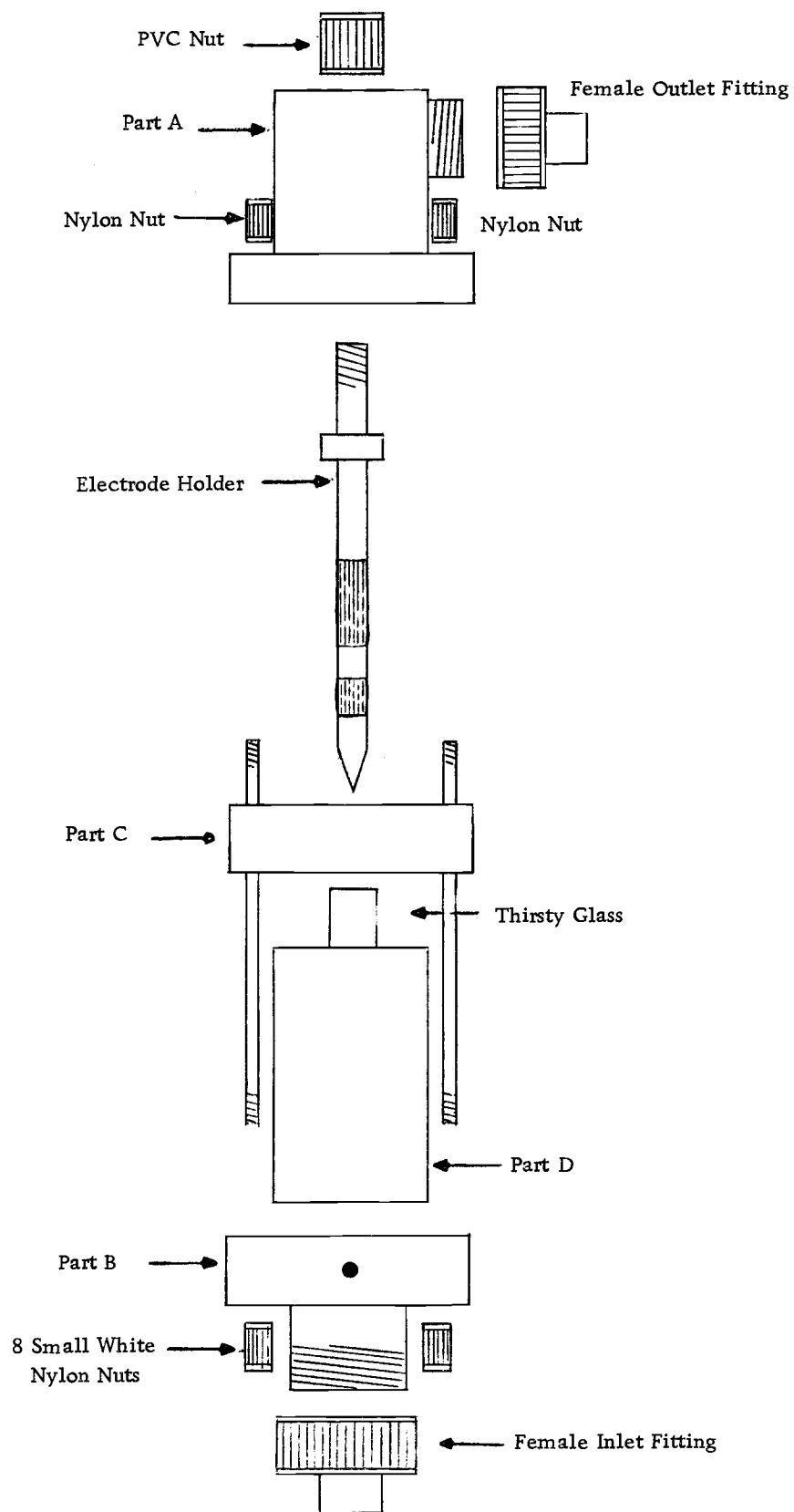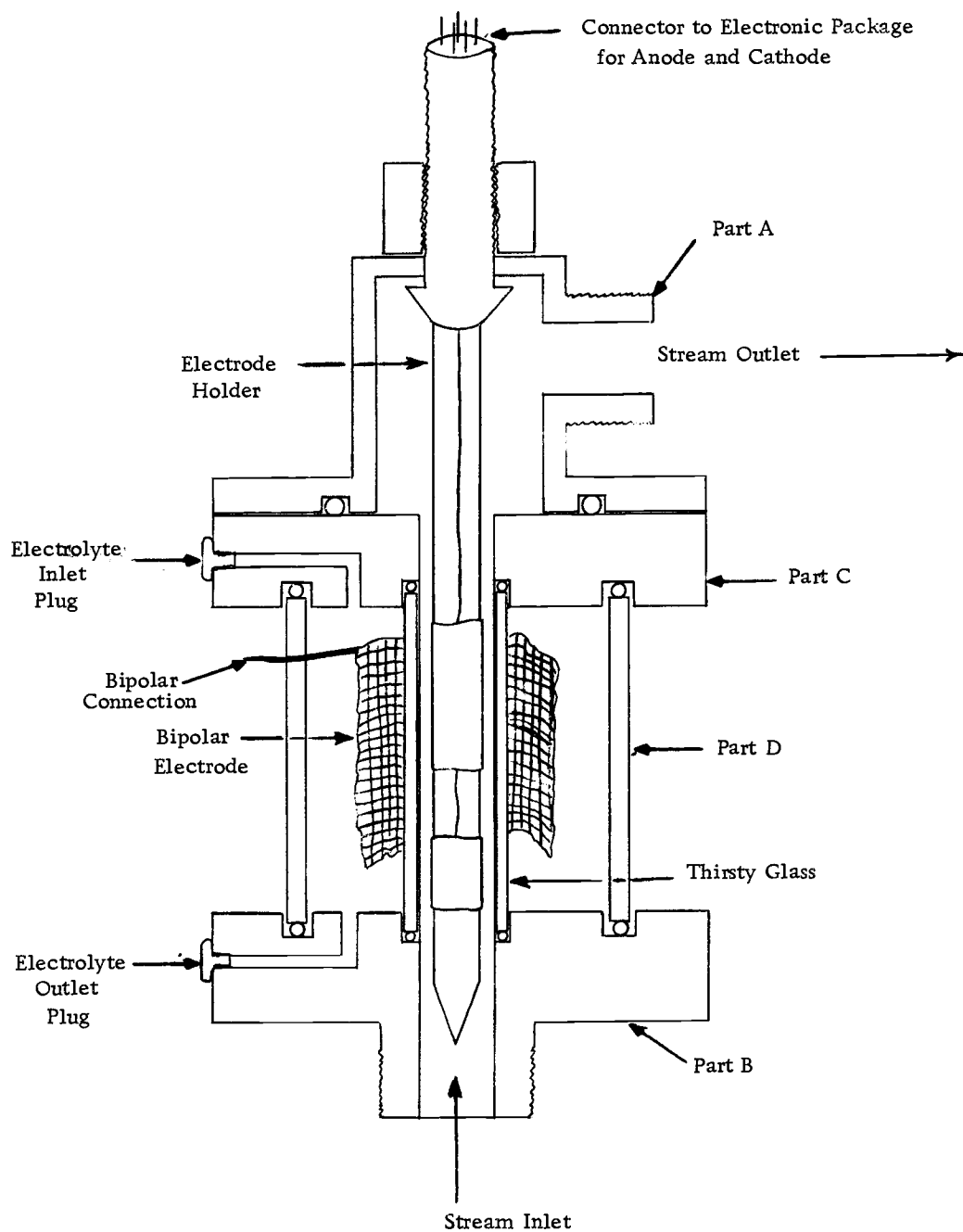
Figure 7. Cutaway View of Cell

upon which two pieces of heavy platinum foil, 1.25 cm by 0.50 cm,

and 1.25 cm by 1.50 cm, have been secured. The smaller piece is

placed below the larger one, and serves as the cathode. The larger

piece is the anode. Two insulated platinum wires that are spot welded

to the electrodes run inside of the electrode holder to an Amphenol

miniature hexagon plug (No. 126-216) that is glued to the top of the

electrode holder. Here, connection can be made by the corresponding

female receptacle for hookup to the electronic package. The electrode

holder is designed to be interchangeable with another electrode holder

having a cathode of differing size so that the range of the cell can be

rapidly changed.

The middle cylinder is a piece of 13 mm "thirsty glass" (unfired

Vycor, brand 7930 from Corning Glass Works). Even though the nor-

mal size is 13 mm, the actual size is closer to 15 mm, and as with

most glass tubing, the outside diameter is not uniform from piece to

piece. It is often necessary, therefore, to file down the outsides of

either end of the "thirsty glass" so that it will fit in Parts A and C.

If the "thirsty glass" is allowed to dry out with any bipolar

electrolyte inside it, then it becomes too brittle to be used again,

shattering with a slight touch. It is necessary then, to replace the

"thirsty glass," or to immerse it in water before it has a chance to

dry out, each time the cell is dismantled.

The outermost cylinder is Part D. Inside of it is a 3.0-cm by
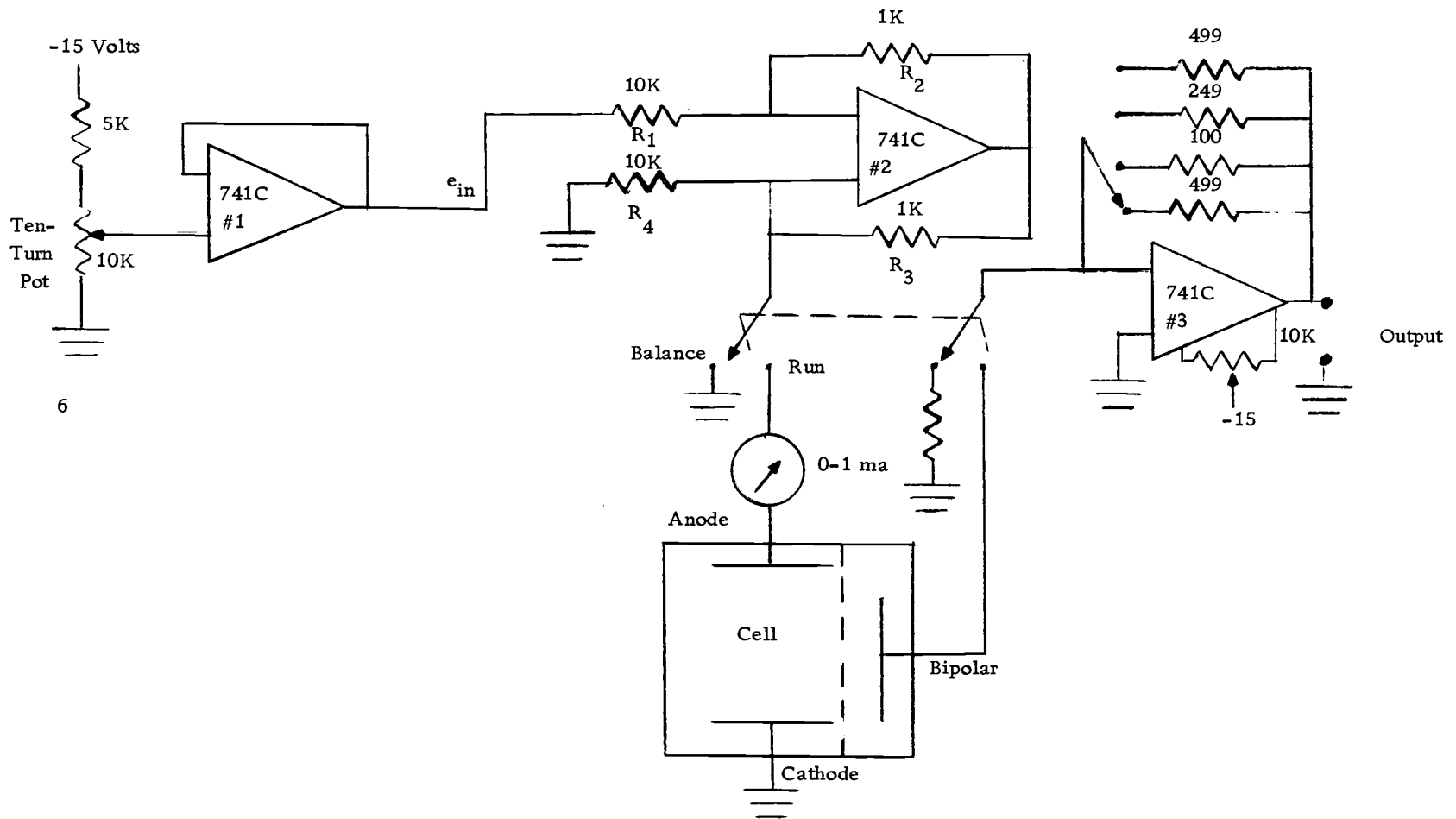
Figure 8. Electronic Schematic

6.0-cm rectangle of platinum gauze, which serves as the bipolar electrode. The gauze is secured to Part D by means of a piece of 20 gauge platinum wire which is spot welded to the gauze and passes through the wall of the PVC pipe to the outside. The wire, which is glued to the PVC pipe with epoxy cement, serves as a plug for connection to the electronic package.

Four monel rods, permanently fixed to Part C, hold Parts A, B, and C together with eight nylon nuts. The electrode holder fits through a hole in the top of Part A and is secured with a PVC nut. Butyl rubber O-rings between each piece establish a water-tight seal.

The bipolar electrolyte is the $Pt/Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ system. It is made by dissolving 53.1 grams of potassium ferricyanide (Hunt photographic grade), 71.2 grams of potassium ferrocyanide (Baker Reagent 3114), 50.4 grams of sodium chloride (Mallinkrodt 7581), and 0.4 grams of sodium hydroxide (Mallinkrodt 7708) in 320 ml of distilled water. The unused bipolar electrolyte is stored in a polyethylene wash bottle and added to the cell via one of two filler holes in Part C as needed.

Electronic Circuitry

Changes from Kendall's electronics were made in the accompanying electronic apparatus (Figure 8), in order to have a usable cell over a wide range. A 15-volt modular dual power supply (Analog

Devices Model 902) with a stability of $\pm$ 0.003 volts is used. An operational amplifier current sink is used, but the voltage at e_{in} is varied, instead of resistor R_1, to change the constant current of the anode.

The voltage of e_{in} is varied by using the voltage at the center tap of a ten-turn potentiometer that has a ten volt drop across it. An operational amplifier in a voltage-follower configuration is used to isolate the potentiometer from the current sink, preventing any significant current from flowing out of the center tap and destroying the linearity of the potentiometer. Thus, anode currents ranging linearly from zero to one milliamp are obtained. The anode current is read on a Knight 0-1 milliammeter.

The current to voltage (I-V) converter, which uses the bipolar current as its input, has four ranges. One percent feedback resistors of 49.9, 100, 249, and 499 ohms are used. The I-V converter is balanced by putting the range switch at the "500" position and the function switch at the "Balance" position. The 10,000-ohm Helipot trimpot, found through a small hole on the right side of the case, is adjusted with a screwdriver until the output of the I-V converter is zero (11).

The operational amplifiers used are three dual-in-line package Fairchild 741C's (Catalog No. U6E7741393) which are internally compensated (11). The electronic apparatus is housed in a Vector 10-inch by 4.5-inch by 4.65-inch aluminum case.

III. PARAMETER DETERMINATION AND CALIBRATION
OF GALVANOVOLTAMMETRIC CELL

One of the uses of a dissolved chlorine continuous analyzer

would be in the determination of the chlorine concentration near the

end of the wood pulp bleaching stage in the pulp and paper industry.

Rapson, as cited by Kendall (12, p. 88), says that the concentration of

dissolved chlorine in this situation is on the order of 1.0×10^{-3} N. In

this research, it was decided that the chlorine levels dealt with would

be on the order of that used in wood pulp bleaching.

Cell Parameters

One of the conditions necessary for proper operation of the gal-

vanovoltammetric cell is that the bipolar electrode should not be al-

lowed to polarize. To prevent polarization, the bipolar current should

not become too large, no more than one or two milliamperes (12, p.

94).

Recall at the set point concentration

$$i_c = i_a \qquad (8)$$

If the set point is in the middle of the expected operating range,

where the lower end of the range is zero concentration, then for the

expected operating range

$$0 \leq i_c \leq 2(i_a) \qquad (9)$$

Now for any galvanovoltammetric cell,

$$i_b = i_a - i_c \qquad (10)$$

so that the bipolar current, under the above conditions would be

bounded by

$$-i_a \leq i_b \leq i_a \qquad (11)$$

To prevent polarization, the bipolar current should be bounded by

$$-1.0 \text{ ma} \leq i_b \leq 1.0 \text{ ma} \qquad (12)$$

Therefore,

$$i_a = 1.0 \text{ ma} \qquad (13)$$

and at the set point concentration,

$$i_c = 1.0 \text{ ma} \qquad (14)$$

The cathode current in the galvanovoltammetric determination of

chlorine (12, p. 99) is related to cell geometry, flow rate, and chlor-

ine concentration by

$$i_c = 1240 \ FwD \ [\frac{fy}{\alpha v}]^{0.64} \ [\frac{v}{D}]^{0.56} \ N \qquad (15)$$

where   F = Faraday

w = electrode width in cm

D = diffusion constant of chlorine in cm^2/sec

f = flow rate in cm^3/sec

y = electrode length in cm

α = cross-sectional area of electrode chamber in cm^2

ν = kinematic viscosity in cm^2/sec

N = normality of chlorine in sample.

The values of D and ν at 25°C for chlorine generated in the manner described in the next section are 10^{-5} cm^2/sec and 1.23×10^{-2} cm^2/sec respectively (12, p. 99). For a 1.0×10^{-3} N chlorine solution to cause a one milliampere current to flow through the cathode, equation (15) reduces to

$$1.9 = w \left[\frac{fy}{\alpha}\right]^{0.64} \tag{16}$$

The flow rate was chosen to be 35 ml/min, or 0.584 cm^3/sec. The cross-sectional area of the chamber between the "thirsty glass" and the electrode holder is about 0.1 cm^2. One cathode size that would comply with equation (16), the flow rate, and cross-sectional area named above is a rectangle 0.50 cm by 1.25 cm which is the size of the cathode described in Section II.

Calibration of the Cell

Once the cell parameters were established, the cell was calibrated with different sample solutions of known chlorine concentrations. The chlorine was generated electrically at an anode from a brine solution according to

$$2 \text{ Cl}^- \rightarrow \text{Cl}_2 + 2e^- \tag{17}$$
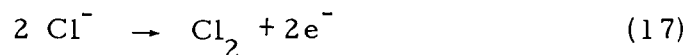
Kendall found (12, p. 93) that 3.0 M NaCl and 0.05 M HCl electrolyte could be used to generate a solution containing 2.0×10^{-3} N Cl_2, at a current efficiency of 99.9 percent.

To prepare a 3.0 M NaCl and 0.05 M HCl electrolyte, 1800 grams of technical grade sodium chloride and 40 milliliters of concentrated hydrochloric acid were added to a carboy containing five liters of distilled water. The carboy was shaken until the salt dissolved, then the solution was diluted to 10 liters by the addition of more distilled water.

The calibration flow system was set up in the following manner:

The carboy was elevated onto an inverted trash can and connected with 3/8-inch Tygon tubing to a chlorine generator cell (Figure 9). The chlorine generator was constructed like a polarographic H-cell with a neck in the bottom of the long side (Figure 10).

The short side of the chlorine generator cell contained a one-inch by one-inch piece of platinum gauze which served as a cathode. The frit separating the two sides of the cell allowed some of the brine to flow slowly from the long side to the short side of the cell to replenish the electrolyte around the cathode. Capillary tubing in the rubber stopper at the opening at the top of the short side allowed the hydrogen being evolved at the cathode to escape, as well as some of the electrolyte. A platinum wire woven into the cathode passed through the rubber stopper for connection with an alligator clip to a constant
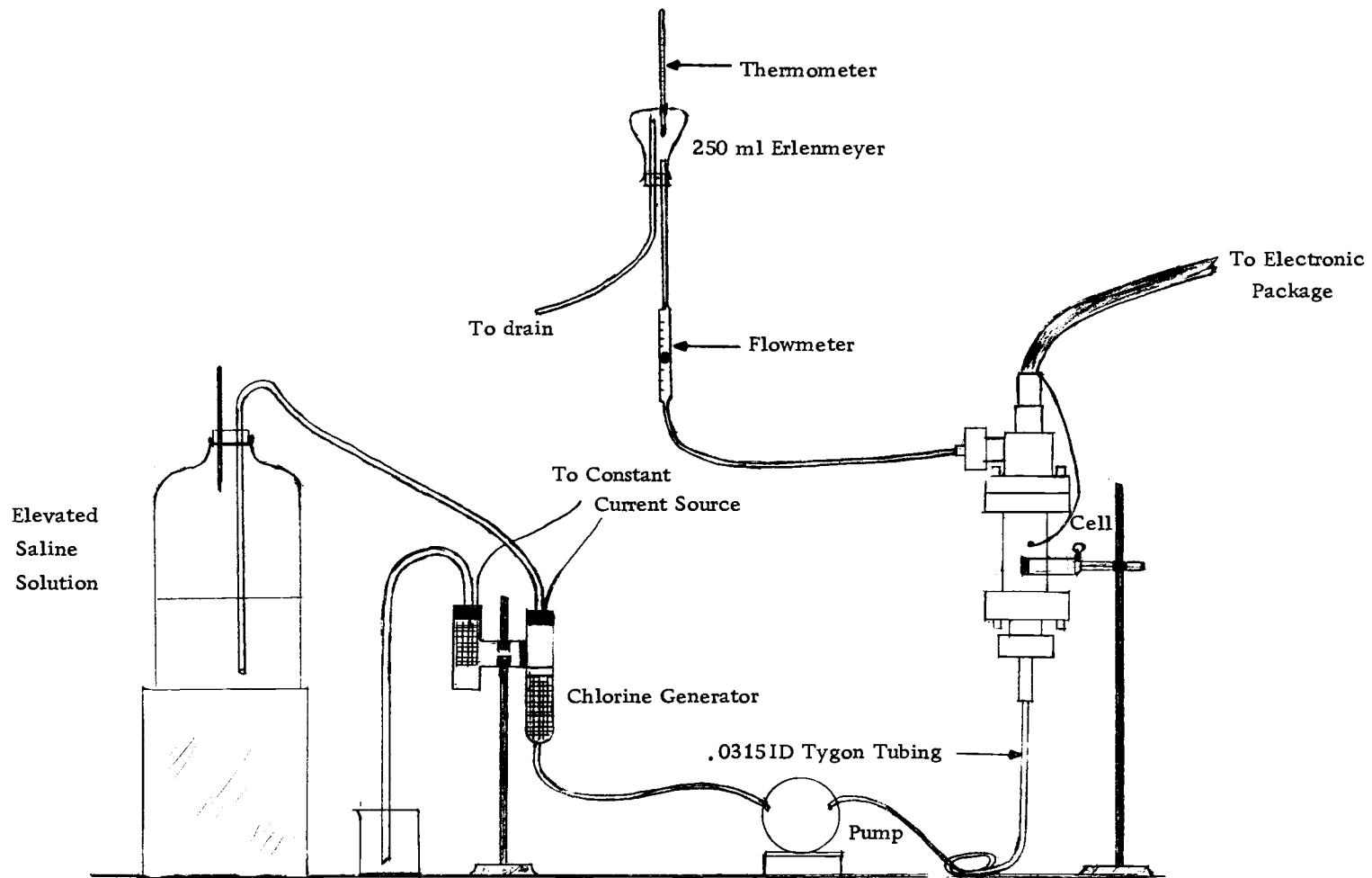
Figure 9. Diagram of Dissolved Chlorine Calibration System

Thermometer

250 ml Erlenmeyer

To Electronic Package

To drain

Flowmeter

To Constant Current Source

Elevated Saline Solution

Cell

Chlorine Generator

.0315 ID Tygon Tubing

Pump

To saline tank

To constant current
source

To constant
current source

To drain

Cathode

Glass spacer tube

Medium
frit

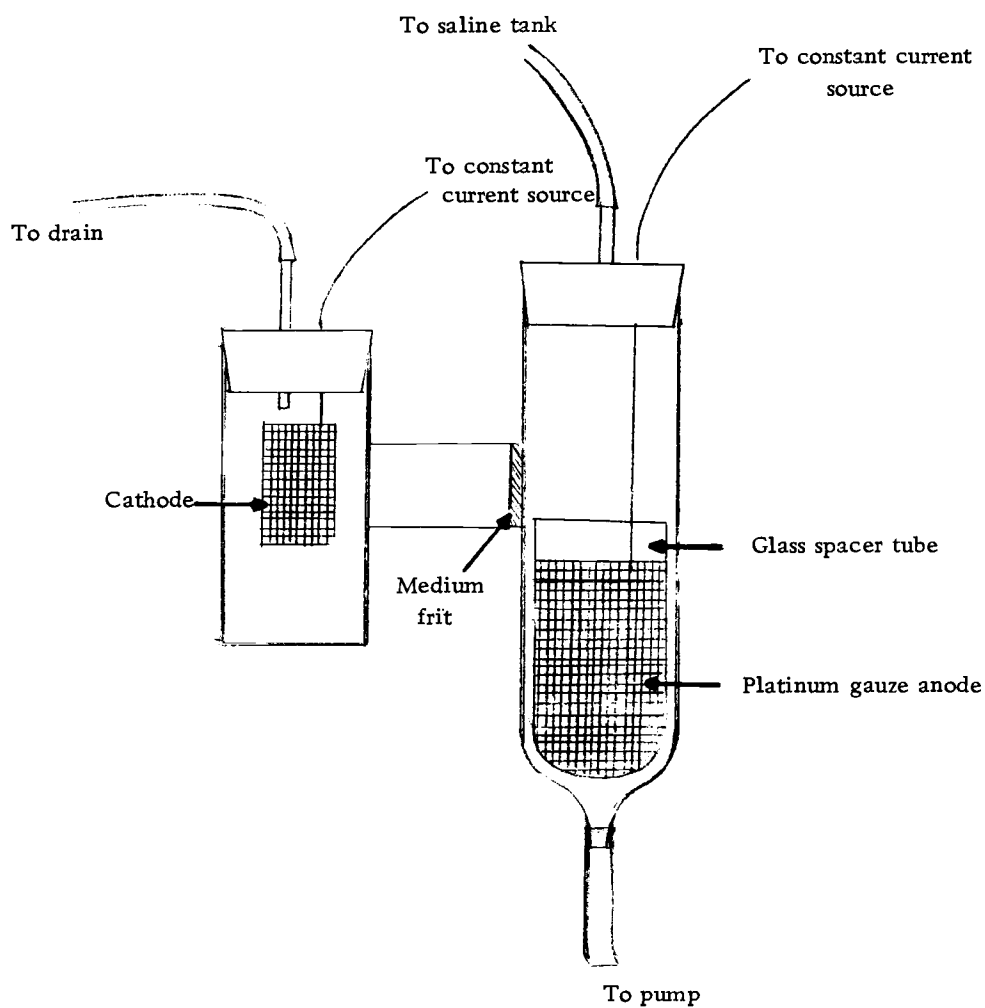Platinum gauze anode

To pump

Figure 10. Chlorine Generator

current source (see Appendix II).

Another one-inch by one-inch piece of platinum gauze, this one serving as the anode, was wrapped into a cylinder and wedged between the inside wall of the long side of the cell and a glass spacer tube. The spacer tube forced the electrolyte into as much contact with the anode as possible. An insulated platinum wire, which was woven into the anode, passed out the rubber stopper at the top of the long side, as the other connection to the constant current source. Also passing through the rubber stopper was glass tubing which was the connection to the Tygon tubing from the carboy. A ten-foot section of 0.0315-inch ID Tygon tubing ran from the neck at the bottom of the anode side of the cell through a Cole-Parmer Masterflex variable speed pump (Model 7020-13) to the galvanovoltammetric cell. The extra length of Tygon was necessary in case a constant temperature bath would be needed for sample temperature regulation. However, it was found that over a period of a few hours, the sample temperature at the inverted Erlenmeyer flask (below) was still the same, within $0.5^{\circ}C$.

Tygon tubing (3/8 inch) carried the sample from the cell to a Gilmont flowmeter (Model 3220-12) where the flow rate at the sample stream was monitored. The sample went from the flow meter up to an inverted 250 ml Erlenmeyer flask, which served as a reservoir for monitoring a sample temperature, and for giving the pump a more even flow rate. The sample solution was then sent to the drain.

For the actual calibration runs, the flow rate was set at 35.0 milliliters per minute, the I-V converter range switch was set at "500," and the anode current was set at 0.5 milliamperes. Four runs were made, with the results graphed in Figure 11.
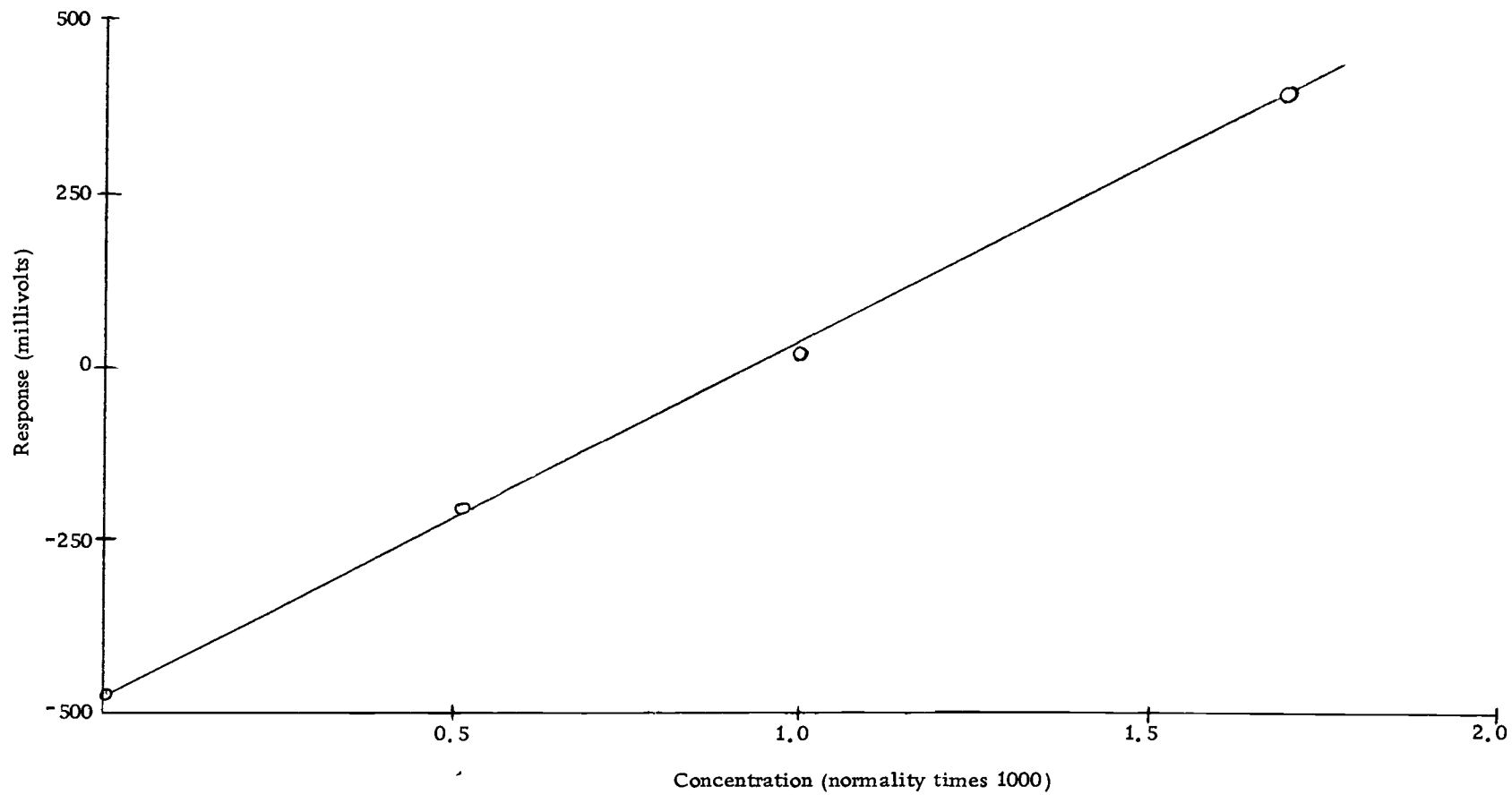
Figure 11. Calibration Curve

IV. TRANSFER FUNCTION ESTIMATION AND DESIGN OF THE STEADY STATE PREDICTOR

In the introduction, it was shown that the transfer function during the transition time could be approximated by two RC networks in series. Therefore, it was decided that two RC networks in series would be assumed as an electrical analog to the galvanovoltammetric cell detection system of this research.

Solution of Equation (7)

Recall for a two-RC network analog

$$V_I = V_F + (T_1 + T_2)\frac{dV_F}{dt} + (T_1 T_2)\frac{d^2 V_F}{dt^2} \qquad (7)$$

In order to use equation (7) to build a prediction device, it is necessary to find the values for T_1 and T_2 for the particular flow system. It is easy to measure V_F, that is the I-V converter output, as a function of time after a step change at the input. By solving equation (7) for V_F as an explicit function of time, then the solution could be used to calculate T_1 and T_2 from experimental results.

Recall that for the first RC network of a two-RC network analog

$$V_I = V_O + T_1 \frac{dV_O}{dt} \qquad (5)$$

and for the second RC network,

$$V_O = V_F + T_2 \frac{dV_F}{dt} \tag{6}$$

It can be shown (see Appendix III) that the solution of equation (5), in terms of V_O and time, is

$$V_O = V_I (1 - \exp(-t/T_1)) \tag{18}$$

Similarly, the solution for equation (6) is

$$V_F = V_O (1 - \exp(-t/T_2)) \tag{19}$$

Substituting equation (18) into (19) gives

$$V_F = V_I (1 - \exp(-t/T_1))(1 - \exp(-t/T_2)) \tag{20}$$

If the output of the two-RC network is initially at some potential B, then equation (20) is rewritten

$$V_F = V_I (1 - \exp(-t/T_1))(1 - \exp(-t/T_2)) + B \tag{21}$$

Equation (21) is the solution of the differential equation in (7) with respect to time.

Observe that if t equals zero, then

$$V_{F(t=O)} = B \tag{22}$$

and if t is large, then

$$V_{F(t=\infty)} = B + V_I \tag{23}$$

For a given set of data following a step change, B is the I-V converter output at time zero, and V_I is the difference between B and the I-V converter output after a long period of time.

Time Constant Estimation Using SIMPLEX

Blaine and Freund (4) give a graphical method for finding T_1 and T_2, providing that one time constant is relatively larger than the other. Graphical methods are tedious, and therefore, undesirable; and if T_1 and T_2 are about the same size, then some other way of time constant estimations must be found. An alternative is with the use of a digital computer.

By using approximations of T_1 and T_2 initially, the computer can be programmed to seek after successively better values for T_1 and T_2. A Fortran program, SIMPLEX, (see Appendix IV) was written to seek better and better approximations to the values T_1 and T_2 by minimizing the sum of the squares of the deviations between the experimentally obtained I-V converter output voltage at time t_i and the voltage expected from equation (21) for many values of t_1. The minimizing is done by sequential application of the regular simplex as outlined by Spendley, Hext, and Wimsworth (14).

The program performs (3) in the following manner:

A set of data with the I-V converter output versus time, where time equals zero at the beginning of the transition time, is input to the computer along with appropriate values for V_I and B. Estimations of the values of T_1 and T_2 and the degree of uncertainty is requested by the program. SIMPLEX then selects three pairs of T_1

and T_2 that would correspond to the vertices of an equilateral triangle, called a regular simplex, plotted$\underline{3}/$ on a graph whose axes are T_1 and T_2. Figure 12 shows a regular simplex with vertices of (b, f), (c, d), and (a, e) where a, b, and c correspond to particular values of T_1; and f, d, and e correspond to particular values of T_2.

For each vertex, the values of T_1 and T_2 are substituted into equation (21) and the sum of the squares of the deviations between the experimentally obtained I-V output and the theoretical output from equation (21) is computed over the set of data, which is usually 75 points. A new simplex is obtained by reflecting the vertex corresponding to the largest sum of the squares across the line joining the other two vertices. In Figure 12, the time constants corresponding to (a, e) give the largest sum of squares in the simplex so that the new simplex with vertices (g, h), (b, f), and (c, d) is obtained by reflecting (a, e) across the line between (b, f) and (c, d).

The sum of the squares is calculated for the new simplex. If the largest sum of the squares does not correspond to the most recently obtained vertex of the simplex, then another new simplex is obtained as above. If the largest sum of the squares does correspond to the most recently computed vertex, then a new simplex is obtained by

$\underline{3}/$ SIMPLEX does no actual plotting; only values corresponding to various positions on a graph are actually used in the computation. The use of graphs here is merely to give a visual representation of what the program does.
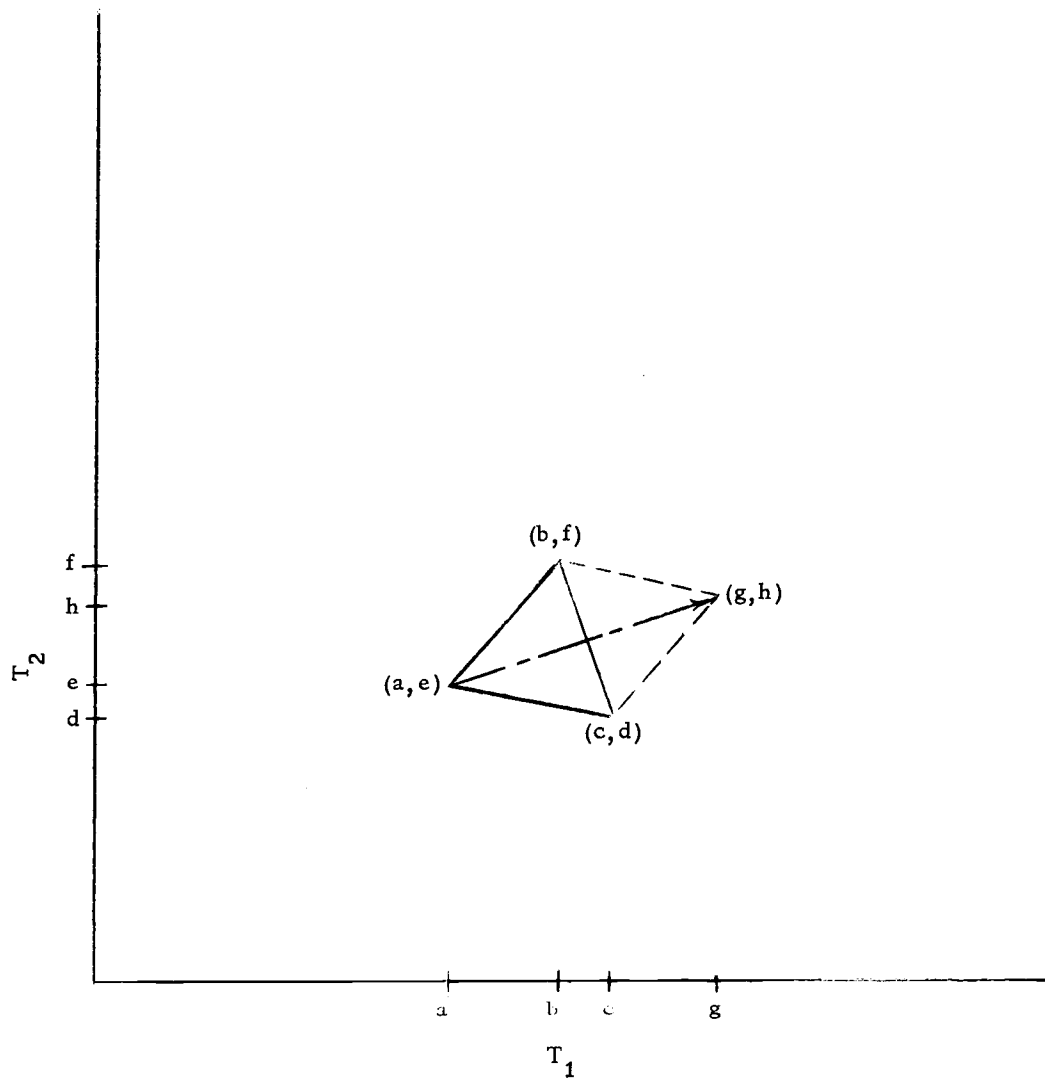
Figure 12. Formation of A New Simplex

reflecting the vertex corresponding to the second largest sum of squares, across the line joining the other two vertices. This is necessary so that the new simplex is not the same as the simplex used to obtain the current simplex. In Figure 13, the regular simplex that has the vertices (j, k), (g, h), and (l, m) was obtained by reflecting (b, f) across the line between (j, k) and (g, h). To form another simplex, normally one would reflect the vertex corresponding to the greatest sum of the squares. But here (l, m) corresponds to the greatest sum of the squares, so that the vertex corresponding to the second greatest sum of the squares, or (g, h), is reflected to obtain the simplex with vertices (j, k), (e, m), and (m, e).

It can be shown that the program takes the way of steepest descent in computing a new simplex as it migrates toward a least sum of the squares of deviation and that the program has a 99.3 percent chance of finding the best approximation to T_1 and T_2, whatever the initial estimations of T_1 and T_2 are (11). The program outputs each simplex as it is computed.

After many simplexes have been computed, a vertex corresponding to the least sum of the squares of deviations computed thus far in the program, will be surrounded by six simplexes. In Figure 13, the point (p, q) is surrounded by six regular simplexes and it corresponds to the least sum of squares for any vertex of any simplex computed thus far. At this point, the program gives the option to
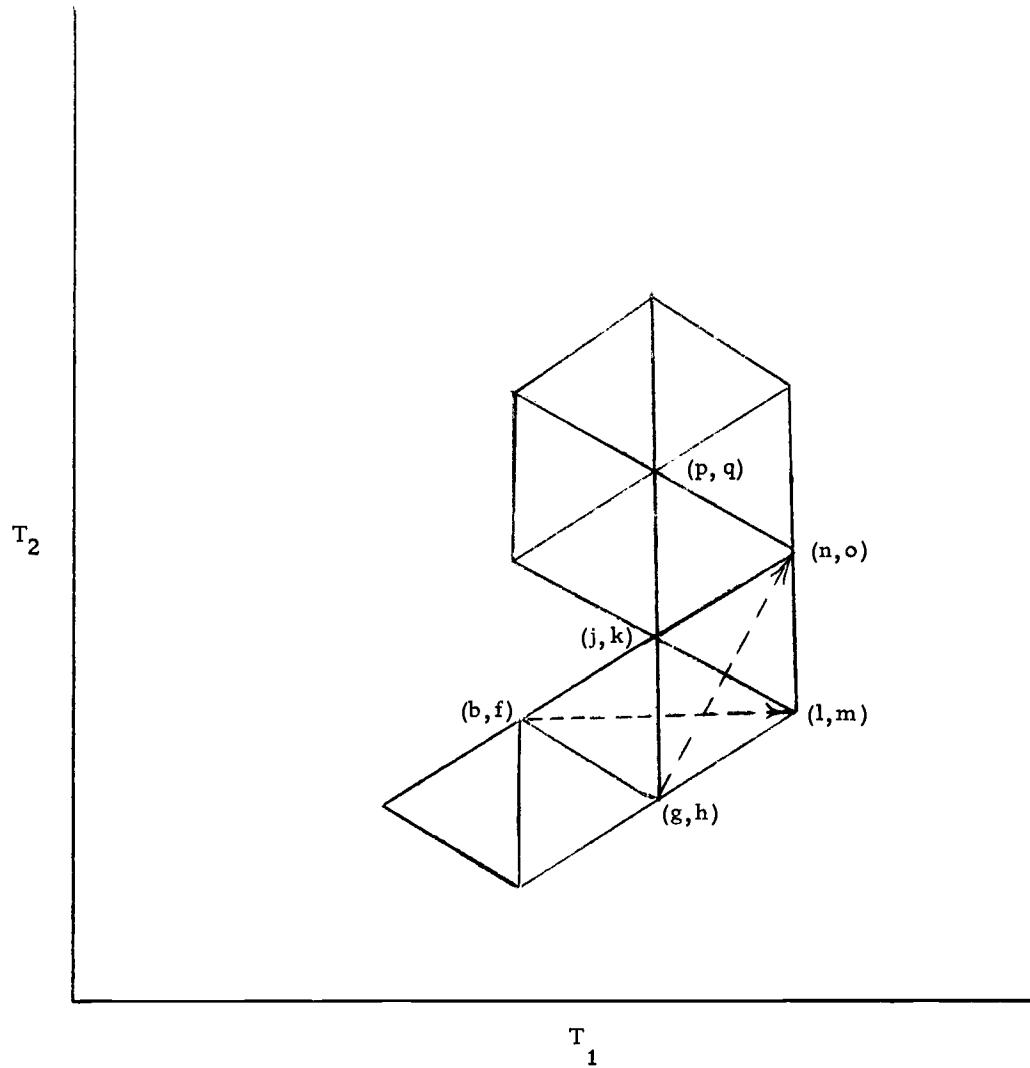
Figure 13. Progression of SIMPLEX Toward a Least Sum of Squares

discontinue execution or to cut the size of the simplex in half and start again with one vertex of the new simplex being the same point as is the one which was surrounded. Usually the simplex size is cut in half each time a point is surrounded, until the sum of the squares for each vertex of a given simplex varies by no greater than one percent from the sum of the squares corresponding to the other vertices.

The values for the vertex corresponding to the least sum of the squares of the deviations of the last simplex calculated are then used as the best approximations to T_1 and T_2 for a given flow system of a galvanovoltammetric cell.

Design of the Steady State Predictor

In order to use equation (7) for the prediction of the steady state, it is necessary to find the first and second derivatives of the output of the I-V converter. The ideal operational amplifier differentiator, shown in Figure 14a, can be shown (6) to give an output E_{out} where

$$E_{out} = -R_1 C_1 \frac{dE_{in}}{dt} \qquad (24)$$

However, input noise pulses which have a high rate of change would produce such high potentials at E_{out} as to obscure the derivative of the desired input signal. The Burr-Brown Research Corporation (6) shows that if the differentiator circuit is modified by putting a resistor, R_2, at the input and a capacitor, C_2, in the feedback loop,
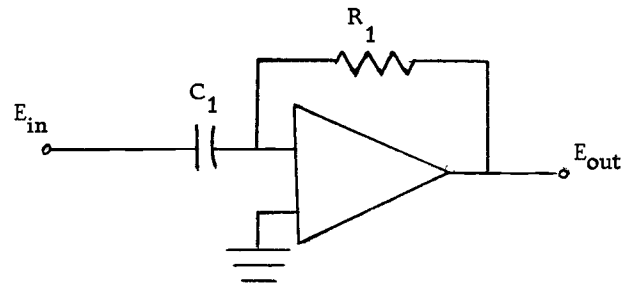
Figure 14a. Ideal Differentiator
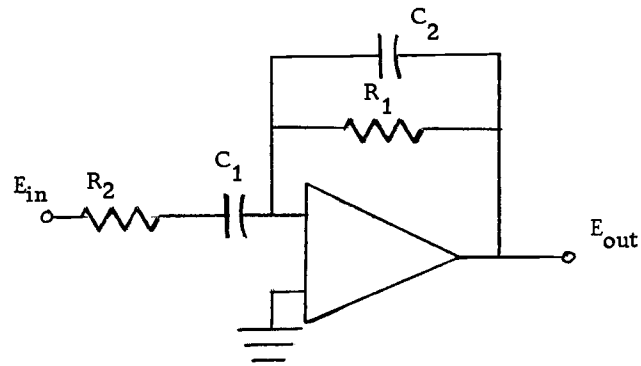
Figure 14b. Differentiator with R_2 and C_2 Added
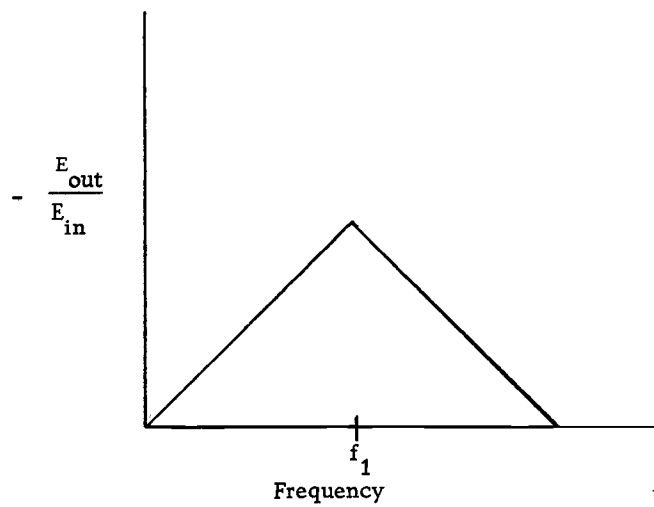
Figure 14c. Response of Modified Differentiator

as in Figure 14b, then for a signal E_{in}, whose frequency is greater

than f_1 and f_2 where

$$f_1 = \frac{1}{2\pi R_2 C_1} \tag{25}$$

and

$$f_2 = \frac{1}{2\pi R_1 C_2} \tag{26}$$

E_{out} will decrease with increasing frequency. For frequencies less

than f_1 and f_2, equation (24) still holds. Figure 14c shows the

qualitative response of the differentiator in Figure 14b to a changing

frequency where f_2 is equal to f_1.

It was found by substituting various values for R_2 and C_2

that if R_2 was set at 270,000 ohms and C_2 at 0.05 microfarads,

where R_1 equals 10,000 ohms and C_1 equals 5.0 microfarads, then

the differentiator circuits in the Steady State Predictor (below) gave

an output that had a noise level of plus or minus one millivolt, and

still was in accordance with equation (24) for measuring the rates of

change for the I-V converter output.

The Steady State Predictor was built as in Figure 15, and

housed in a Bud 8.0-inch by 6.0-inch by 3.5-inch minibox. An

Amphenol 5-pin connector (Catalog No. 126-216), found in the right

side of the basic electronic package, (Section II) furnishes access to

the dual power supply, the output of the I-V converter, and ground
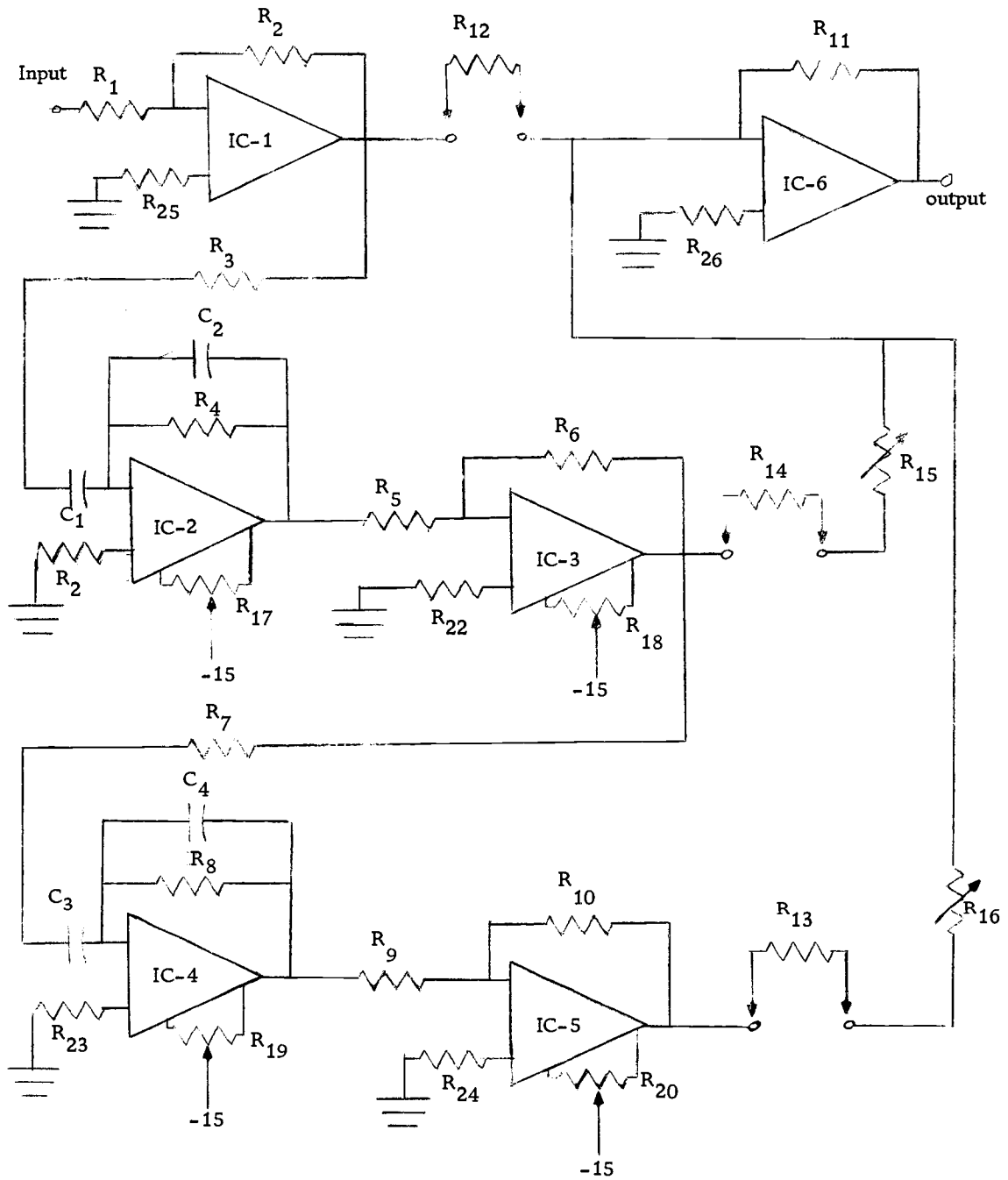
Figure 15. Circuit for Steady State Predictor

for the prediction device.

Integrated circuit operational amplifier 1 (IC-1) is a booster

amplifier for the I-V converter output to insure that the voltage used

in the Steady State Predictor are within the operating range of the in-

tegrated circuit operational amplifiers. IC-2 takes the first deriva-

tive of the amplified I-V converter output and IC-4 takes the second

derivative. IC-3 and IC-5 are invertors so that the derivatives are

of the proper sign. IC-6 sums the weighted outputs of IC-1, IC-3,

and IC-5. Resistors 17 through 20 are 10,000-ohm Helipot trimpots

used for balancing (11) the operational amplifiers which are Fairchild

741C's (Catalog No. U6E7741393).

Using equation (24) and the values for the components of the

Steady State Predictor as found in Appendix III, it can be seen that

the output of IC-3 is 5.1 times the derivative of the I-V converter out-

put and that the output of IC-5 is 27.0 times the second derivative of

the I-V converter output.

Three pairs of banana jacks are connected between the output

and input of IC-1 and IC-6, IC-3 and R_{15}, and IC-5 and R_{16}. Re-

sistors 12 to 14 are one percent resistors in three double banana plugs

that fit into the banana jacks. By substituting proper values for R_{12},

R_{13}, and R_{14}; and by adjusting R_{15} and R_{16}, which are Helipot

10-turn 10,000-ohm potentiometers, the correct weighting of the

amplified I-V converter output, and its first and second derivatives

in accordance with equation (7), can be obtained.

The prediction device is balanced by switching the I-V converter function switch to "Balance," varying R_{17} and R_{18} until the output of IC-3 is zero; then varying R_{19} and R_{20} until the output of IC-5 is zero. Holes in the underside of the Prediction Device provide access to R_{17}, R_{18}, R_{19}, and R_{20} for a screwdriver adjustment.

V. INSTRUMENT EVALUATION

To evaluate an analog computational device, the response of the device to step, ramp, and sinusoidal inputs is normally observed (4). For the galvanovoltammetric cell and its associated sampling system, the easiest of the above three to perform is the step change, because it is necessary only to provide the analyzer with two discrete chlorine concentrations, rather than the continuously varying concentrations that would be required for ramp or sinusoidal inputs. This research was limited to the evaluation of the instrument for the step change.

Estimation of T_1 and T_2 for Sampling Systems

To construct a system for a step change to take place, the same system as the calibration setup was used, except that the chlorine generator was replaced with a three-way stopcock to which two different three-gallon carboys were connected (Figure 16). One carboy contained the 3.0 M NaCl and 0.05 M HCl solutions used in the calibration step and the other contained the same solution that also had 6.2×10^{-4}N dissolved chlorine. The chlorine solution was obtained by collecting the solution coming from the pump during the calibration step. To provide sampling systems with differing time constants, a ten-foot and a two-foot length of the 0.0315-inch ID Tygon tubing (cf. Figure 9) were used.

Saline
Solution →

3 Way Stopcock

Cell

Saline Solution
with Generated
← Chlorine

2' or 10' piece →
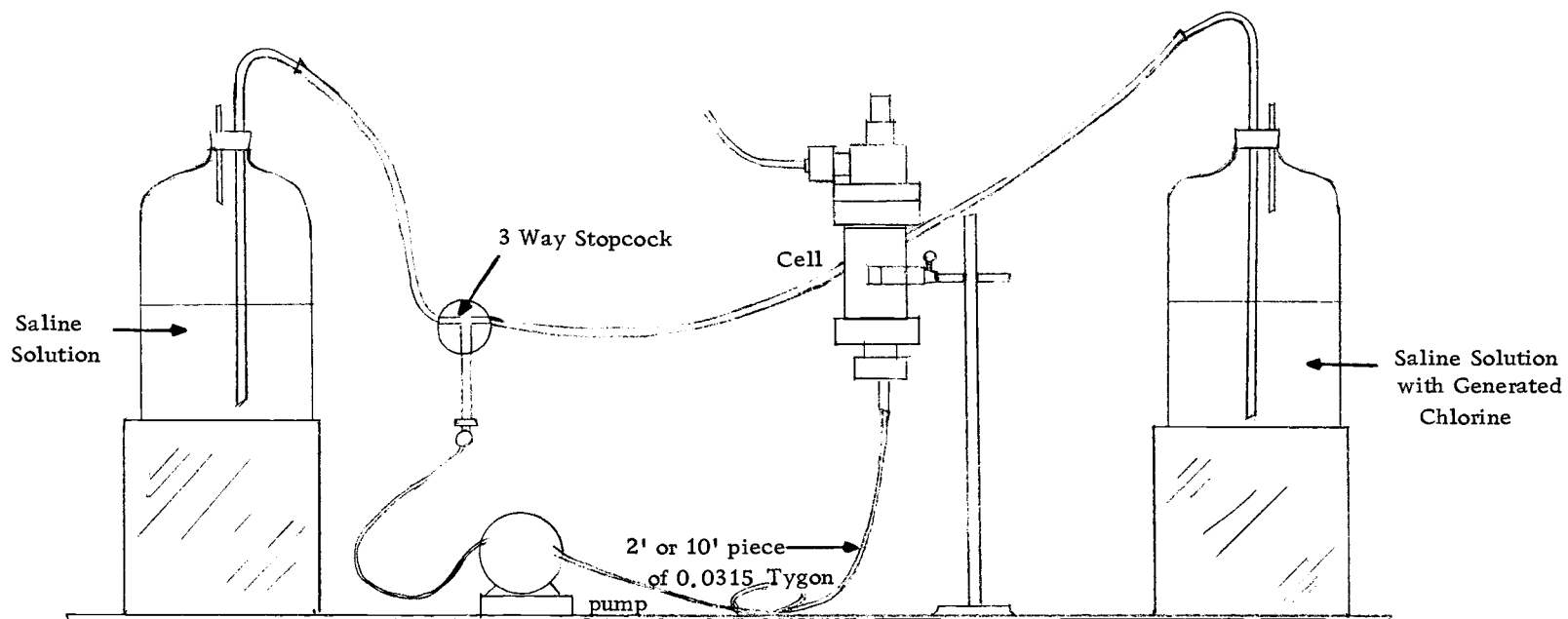of 0.0315 Tygon
pump

Figure 16.   Diagram of Step Input System

A twist of the valve provided a step change of 6.2×10^{-4} N

chlorine. It was found that solutions containing more dissolved chlor-

ine than 6×10^{-4} N lost the chlorine to the air upon standing for a short

time. Therefore, the level of 6.2×10^{-4} N was chosen so that large

quantities of dissolved chlorine could be prepared at one time.

The output voltage from the I-V converter was read by a spec-

ially modified Heath Universal Digital Instrument, Model EU804A

(10). It was modified so that a parallel-to-series (P-S) converter

built by Morteza Janghorbani and John Starkovich (12) could convert

the DVM readout to ASCII code, acceptable for readout by a teletype-

writer. The teletypewriter was used to punch a paper tape of the out-

put of the Digital Instrument, used in the digital voltmeter mode.

The output voltage was read every six seconds, starting from

time zero, the point at which a step change in concentration was made

by a twist of the three-way stopcock. The data was entered into the

Oregon State Open Shop Operating System (OS-3) computer (2) where a

Fortran program, POINTS, (see Appendix VI) plotted the output volt-

age versus time on the OS-3 computer plotter (1).

Figure 17 shows a plot of the I-V converter output versus time

for the flow system with the ten-foot length of 0.0315-inch ID Tygon

tubing where the step change was from 6.2×10^{-4} N chlorine to a

chlorine-free solution at time zero.

SIMPLEX calculated T_1 and T_2 for both sampling systems;
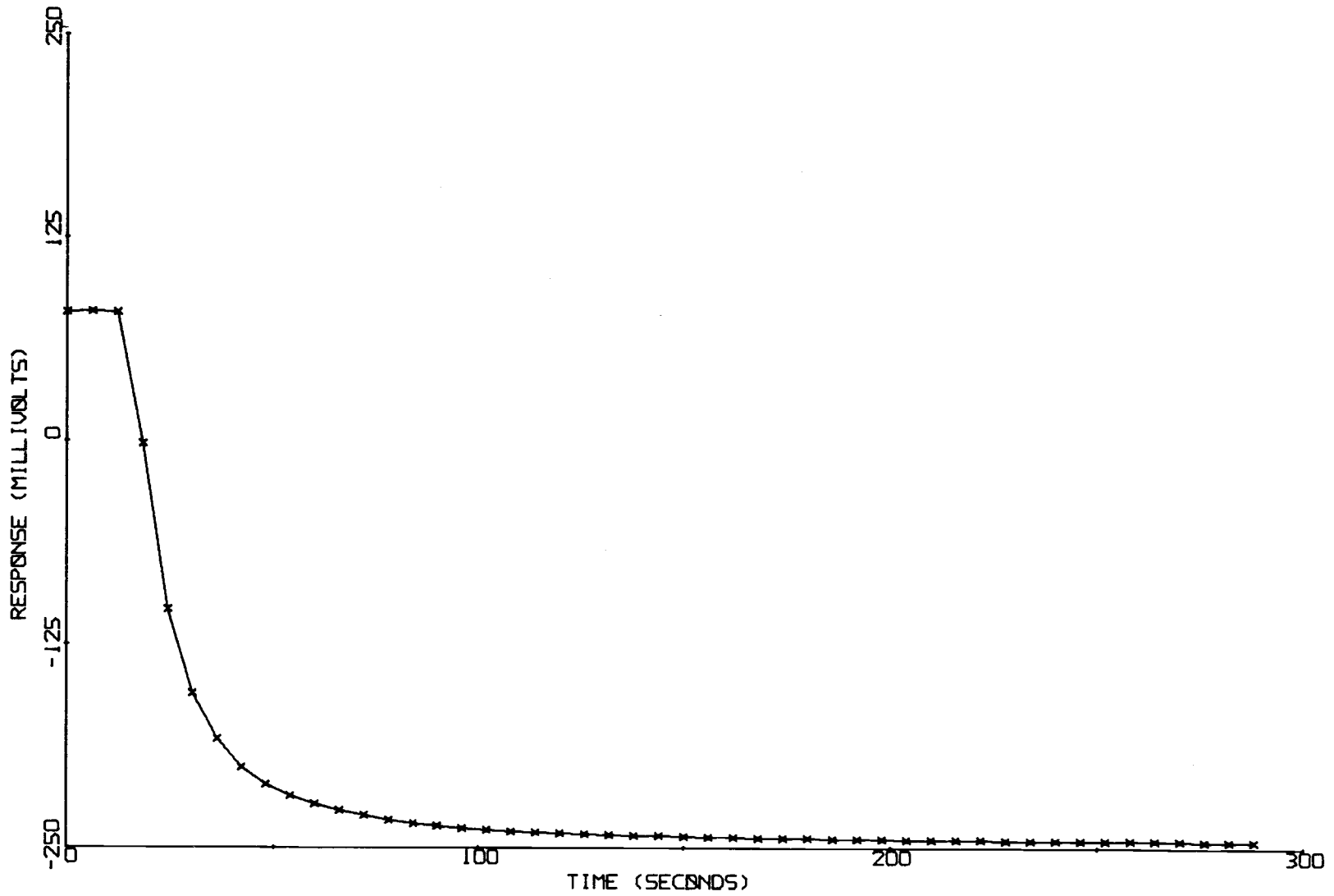
Figure 17. I-V Converter Output Following Step Change.

the results are shown in Table I. The standard deviation of the ex-
perimental values versus the values from equation (21) was calculated
for each sampling system over the first 75 points by using the sum
of the squares from SIMPLEX.

Table I. Time Constants for Sampling Systems

Length of Tygon tubing (0.0315-inch ID)	T_1	T_2	Standard Deviation	Percent of Deviation for Step Change
10.0 feet	4.3	15.6	4.9 mV	1.6
2.0 feet	2.1	12.6	4.7 mV	1.2

Steady State Predictor Evaluation

Using the time constants, T_1 and T_2, provided by SIMPLEX,
values were obtained for resistors 12 through 16 of the Steady State
Predictor. The Steady State Predictor was then used to compute the
equilibrium level of the I-V converter output following a step input
to the galvanovoltammetric cell and sampling system.

The Heath Universal Digital Instrument, set for a measurement
period of 1.0 second, was connected to the output of the Steady State
Predictor and the output was again read on the teletypewriter. In
addition, a Fairchild Digital Multimeter (Model 7050) was connected
to the I-V converter to measure its output.

A step change in concentration was made, and the output of the

Steady State Predictor was printed on the teletype every three seconds.
The Fairchild Digital Multimeter was read every six seconds and re-
corded manually. The results were entered into the OS-3 computer
and plotted using program POINTS.

For the sampling system where T_1 and T_2 equal 4.3 and 15.6
respectively, R_{12} was set at 10,000 ohms, R_{13} and R_{14} were set
at zero ohms (wires were used in the banana plugs instead of resistors)
R_{15} was set at 2,620 ohms, and R_{16} was set at 2,200 ohms. Figure
18 shows a plot of the Steady State Predictor and I-V converter outputs
versus time for the above sampling system was equal to zero at the
point when the chlorine concentration at the input changed from
6.2×10^{-4} N to 0.0 N. The Steady State Predictor as shown in Figure
18 gave values that were within 3.4 percent of the I-V converter out-
put at 200 to 300 seconds.

RESPONSE (MILLIVOLTS)

250

125

0

-125

-250

× STEADY STATE PREDICTION OUTPUT

ᵥ I-V CONVERTER OUTPUT

100   200   300
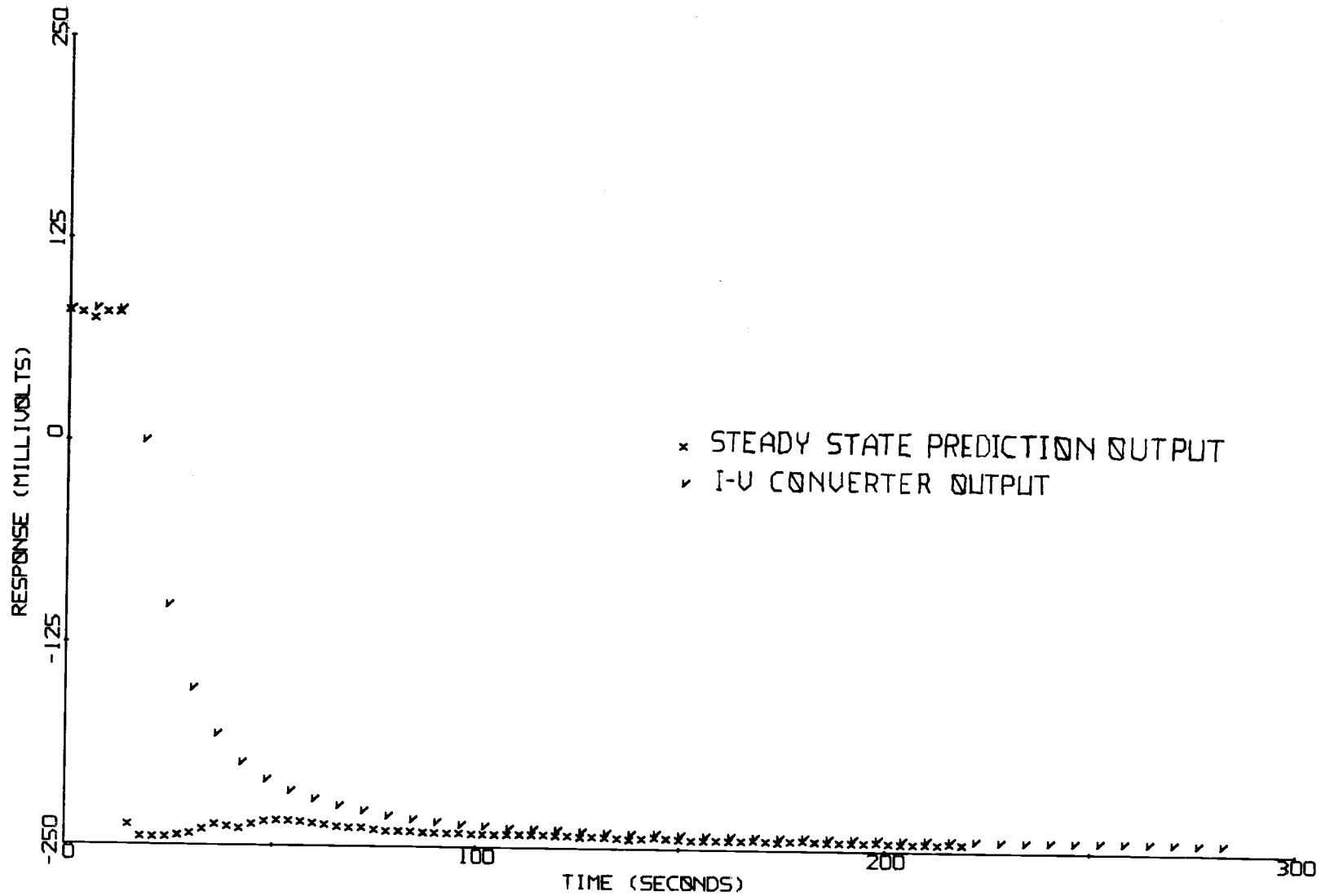
TIME (SECONDS)

Figure 18.   I-V Converter and Steady State Predictor   Outputs Following a Step Change.

VI. SUMMARY AND CONCLUSION

The interchangeability of electrode holders, and consequently,

cathode sizes, makes the galvanovoltammetric cell as described in

Section II usable over a wide range of concentrations and flow rates.

The cell is easily disassembled for cleaning, lending itself to indus-

trial use where the sampling stream may not be completely free of

particulates. The basic electronic package enhances the wide-range

use of the galvanovoltammetric cell because the anode current can be

varied from zero to one milliampere. Previous work by Kendall was

limited to a cell that could not be disassembled, whose cathode size

could not be changed easily, and whose anodic current range was

small.

The development of the Fortran program, SIMPLEX, offers a

novel method for determining the time constants for a flow sytem.

It is rapid and has a very high probability of eventually approaching

the best values for T_1 and T_2 even if the initial estimations of T_1

and T_2 are grossly in error.

It can be seen (Figure 18) that the output of the Steady State

Predictor exhibits a small oscillation following the initial step change.

The deviation can be attributed to the fact that the two-RC network

analog does not completely hold for the galvanovoltammetric cell

and its associated sampling system, and that the differentiator circuits

have a certain amount of noise in the output that cannot be completely eliminated.

It should be noted that this research only involved the use of the step change in the instrument evaluation. Theoretically, if the device can predict the steady state equilibrium according to equation (7) for a step change, then the device should also compute the input to the analyzer for a ramp or sinusoidal change. For a complete study however, any further research into the use of the Steady State Predictor as constructed should involve the observation of the instrument response during ramp and sinusoidal inputs to the galvanovoltammetric cell and sampling system.

It should also be noted that the Steady State Predictor has an upper limit to the size of the time constants, T_1 and T_2, for a sampling system. As T_1 and T_2 become larger, the first and second derivatives become smaller at any given point in time, but their contributions in equation (7) become larger. Eventually, the output noise of the differentiator circuits would overcome the desired output signal as T_1 and T_2 are increased.

Still, it can be seen from Figure 18 that the Steady State Predictor offers an improvement in the speed of the detection of dissolved chlorine in a flowing stream under the conditions stated above.

BIBLIOGRAPHY

1. Baughman, Jo Ann and C. Dean Pielstick. Using the plotter:
    Documentation and examples. Rev. ed. Corvallis, Oregon
    State University Computer Center, 1969. 77 p.

2. Baughman, Jo Ann, Mary Berryman and Dean Pielstick. OS-3:
    A user's manual with examples. Corvallis, Oregon State Uni-
    versity Computer Center, 1969. 68 p.

3. Blaedel, W. J. and R. H. Laessig. Automation of the analytical
    process through continuous analysis. In: Advances in analytical
    chemistry and instrumentation, ed. by C. N. Reilly and F. W.
    McLafferty, Vol. 5. New York Interscience, 1966. p. 66-168.

4. Blaine, Roger and Harry Freund. Use of transfer function for
    optimization of the continuous analysis process. Accepted for
    publication by Proceedings of the Industrial Waste Management
    Conference.

5. Bleak, Thomas M. and John J. McGee. Coulometric monitor
    for SO_2 in ambient air. Paper 66-109 read before the 1966
    National Conference of the Air Pollution Control Association,
    San Francisco, June 20, 1966.

6. Burr-Brown Research Corporation. Handbook of operational
    amplifier applications. Tuscon, Arizona, 1963. 87 p.

7. Delahay, Paul. New instrumental methods in electrochemistry.
    New York Interscience Publishers, Inc., 1954. 437 p.

8. Fairchild Semiconductor. The μA741C internally compensated
    operational amplifier. Mountain View, California, 1969. 6 p.

9. Heath Company. The Heath Universal Digital Instrument Model
    EU805A. Benton Harbor, Michigan, 1968. 86 p.

10. Janghorbani, Morteza. Optimization of response surfaces.
    Paper read before a seminar in analytical chemistry, Depart-
    ment of Chemistry, Oregon State University, Corvallis,
    Oregon, Oct. 15, 1970.

11. Janghorbani, Morteza, John Starkovich, and Harry Freund. A low cost parallel to serial converter for digital instrumentation. Analytical Chemistry 43:493-495. 1971.

12. Kendall, Donald. The theory and application of galvanovoltammetry. Design, construction and evaluation of a continuous liquid stream analyzer employing a galvannovoltammetric detector and low cost automatic digital concentration readout. Doctoral dissertation. Corvallis, Oregon State University, 1970. 177 numb. leaves.

13. Schwendiman, Carl J. FORTRAN: Entering, editing, and running from remote units under OS-3. Corvallis, Oregon State University Computer Center, 1969. 33 p.

14. Spendley, W., G. R. Hext, and F. R. Himsworth. Sequential application of simplex designs in optimisation and evolutionary operation. Technometrics 4:441-461. 1962.

APPENDICES

APPENDIX I

Derivation of Equation (1)

R_x is unknown variable
resistance of cell
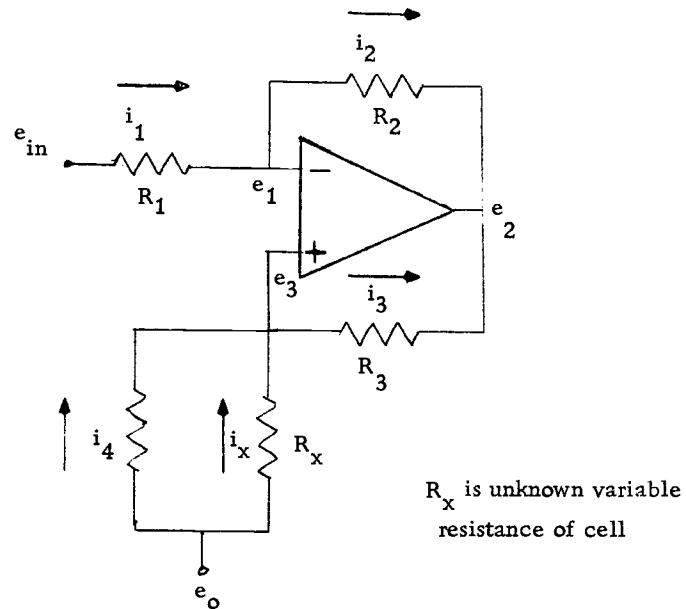
Assuming an ideal operational amplifier, no current flows into the inverting (-) or noninverting (+) inputs and $e_1 = e_2$. Also assume here current flows from positive to negative.

$$(e_1 - e_2) = (e_3 - e_2)$$

If $R_3 = R_2$, then

$$(e_1 - e_2)/R_2 = (e_3 - e_2)/R_3$$

$$i_2 = i_3$$

$$i_1 = i_2$$

$$\therefore \quad i_1 = i_3$$

$$i_3 = i_4 + i_x$$

$$\therefore \qquad i_1 = i_4 + i_x$$

$$i_1 = (e_{in} - e_1)/R_1$$

$$i_4 = (e_0 - e_3)/R_4$$

$$(e_{in} - e_1)/R_1 = (e_0 - e_3)/R_4 + i_x$$

$$e_1 = e_3$$

$$(e_{in} - e_3)/R_1 = (e_0 - e_3)/R_4 + i_x$$

if $e_0 = 0$ (ground)

$$(e_{in} - e_3)/R_1 + (e_3)/R_4 = i_x$$

$$(e_{in})/R_1 - (e_3)/R_1 + (e_3)/R_4 = i_x$$

$$(e_{in})/R_1 + (1/R_4 - 1/R_1)e_3 = i_x$$

or for electron flow,

$$-[e_{in}/R_1 + (1/R_4 - 1/R_1)e_3] = i_x$$

APPENDIX II

Constant Current Source
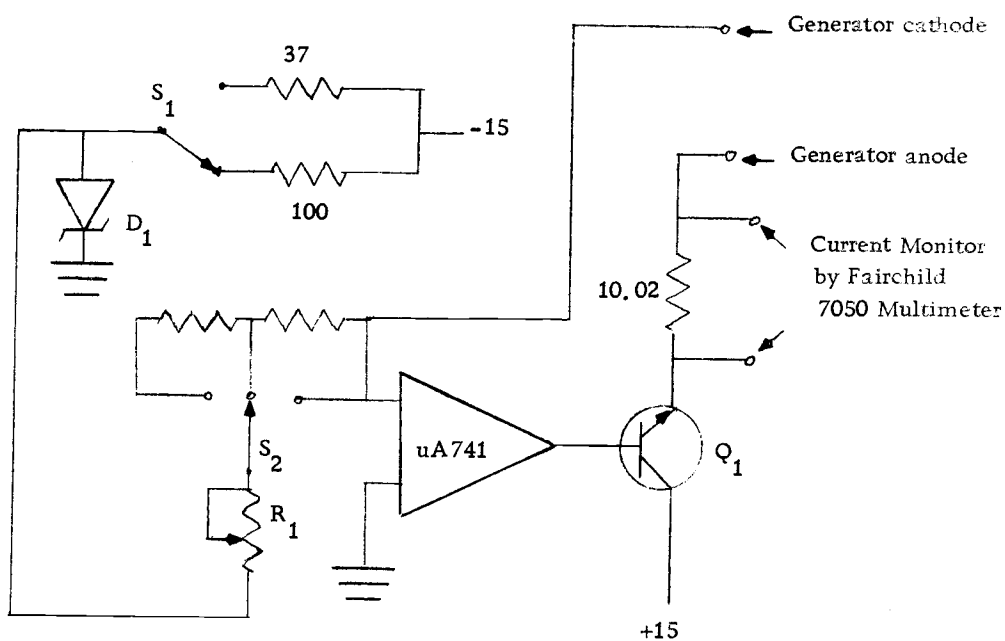
D$_1$ 3.3 V zener diode

Q$_1$ T1P47 power transistor

R$_1$ 100-ohm, 10-turn potentiometer

Constant current source above was built by Kendall (12, p. 183-184). A Spar Electronics dual power supply (Model 1500) set at 15 volts was used to supply the necessary power. By using S$_1$ and S$_2$ and varying R$_1$, appropriate currents are obtained.

APPENDIX III

Solution of Equation (5):

$$V_I = V_O + T_1 \frac{dV_O}{dt}$$

$$\frac{dV_O}{dt} + \frac{V_O}{T_1} = \frac{V_I}{T_1}$$

multiply each term by $\exp(t/T_1)$

$$\frac{dV_O}{dt} \exp(t/T_1) + \frac{V_O}{T_1} \exp(t/T_1) = \frac{V_I}{T_1} \exp(t/T_1)$$

$$\frac{dV_O}{dt} \exp(t/T_1) + \frac{V_O}{T} \exp(t/T_1) = \frac{d}{dt}[V_O \exp(t/T_1)]$$

$$\therefore \quad \frac{d}{dt}[V_O \exp(t/T_1)] = \frac{V_I}{T_1} \exp(t/T_1)$$

integrating both sides

$$V_O \exp(t/T_1) = V_I \exp(t/T_1) + C$$

where C is an arbitrary constant,

$$V_O = V_I + C \exp(-t/T_1)$$

To evaluate C, when $t = 0$, $V_O = 0$

$$\therefore \qquad C = -V_I$$

$$V_O = V_I - V_I \exp(-t/T_1)$$

$$V_O = V_I (1 - \exp(-t/T_1))$$

which is equation (18).

APPENDIX IV

Program SIMPLEX

```
      PROGRAM SIMPLEX
      DIMENSION X(100),Y(100),A(3,4),C(3,4)
  200 FORMAT (' RC1,RC2,AND VARY')
  201 FORMAT (' HOW MANY POINTS')
  202 FORMAT (' V AND B')
C  INITIAL SIMPLEX IS CALCULATED FROM INPUT INFORMATION
C  AND PLACED IN ARRAY A
      PRINT 200
      RC1=FFIN(60)
      RC2=FFIN(60)
      VARY=FFIN(60)
      A(1,1)=RC1
      A(2,1)=RC1
      A(3,2)=RC2
      A(2,2)=RC2-VARY
      A(1,2)=RC2+VARY
      A(3,1)=RC1+1.73205*VARY
      PRINT 201
      NUM=FFIN(60)
      PRINT 202
      V=FFIN(60)
      B=FFIN(60)
      DO 300 J=1,NUM
      X(J)=FFIN(1)
  300 Y(J)=FFIN(1)
   10 CALL LSTSQ(A,3,X,Y,V,B,NUM,C)
      C(3,4)=C(3,4)+1.
C  NEW POINT OF SIMPLEX IS CALCULATED
   12 DO 13 K=1,2
   13 A(1,K)=(C(2,K)+C(3,K))-C(1,K)
      DO 16 K=2,3
      DO 15 L=1,4
   15 A(K,L)=C(K,L)
   16 CONTINUE
      CALL LSTSQ(A,1,X,Y,V,B,NUM,C)
      IF (C(3,4)-6.) 18,18,23
   18 C(3,4)=C(3,4)+1.
C  CHECK TO SEE IF NEW POINT WILL CAUSE REFLECTION
C  BACK TO PREVIOUS SIMPLEX.  IF SO NEW SIMPLEX IS
C  CALCULATED USING SECOND LARGEST SUM OF SQUARES
      IF (A(1,3)-A(2,3))12,19,19
   19 DO 20 L=1,2
   20 A(1,L)=(C(1,L)+C(3,L))-C(2,L)
      DO 21 L=1,4
      A(2,L)=C(1,L)
   21 A(3,L)=C(3,L)
      GO TO 16
C  WHEN LOWEST SUM OF SQUARES IS SURROUNDED BY SIMPLEXES
C  OPTION IS GIVEN TO CUT SIMPLEX SIZE IN HALF AND
C  START AGAIN OR TO END EXECUTION
    4 FORMAT (' QUIT=1,REFIG=0.')
   23 PRINT 4
      NQ=FFIN(60)
      IF (NQ)24,24,25
   24 DO 110 I=1,2
  110 A(3,I)=C(3,I)
      DO 210 I=1,2
      DO 210 J=1,2
  210 A(I,J)=(A(3,J)+C(I,J))/2.
      GO TO 10
   25 CONTINUE
      END


      SUBROUTINE LSTSQ (A,ML,X,Y,V,B,NUM,C)
      DIMENSION A(3,4),X(100),Y(100)
      DIMENSION C(3,4), F(3,4)
C SUM OF THE SQUARES OF DEVIATIONS FROM
C THE EXPERIMENTAL VALUES IS CALCULATED
      DO 10 J=1,ML
      A(J,3)=0.
      A(J,4)=1.
      DO 10 I=1,NUM
      W=V*(1.-EXP(-X(I)/A(J,1)))*(1.-EXP(-X(I)/A(J,2)))+B
      SQ=(Y(I)-W)**2
   10 A(J,3)=A(J,3)+SQ
C VALUES IN ARRAY A ARE PLACED IN ARRAY C IN DESCENDING
C ORDER OF SUM OF SQUARES OF DEVIATION
      DO 9 I=1,3
      DO 9 J=1,4
    9 F(I,J)=A(I,J)
      N=3
      DO 50 I=1,3
      IQ=1
      C(I,3)=0.
      DO 20 J=1,N
      IF (C(I,3)-F(J,3))15,15,20
   15 DO 16 K=1,4
   16 C(I,K)=F(J,K)
      M=J
   20 CONTINUE
      DO 30 J=1,N
      IF (J-M) 25,30,25
   25 DO 26 K=1,4
   26 F(IQ,K)=F(J,K)
      IQ=IQ+1
   30 CONTINUE
   50 N=N-1
C ARRAY C IS OUTPUT
    1 FORMAT (3(X,F10.4),X,F4.0)
    2 FORMAT (3(/), 8X, 'RC1',8X,'RC2',6X,'SUMSQ')
      PRINT 2
      DO 3 L=1,3
    3 WRITE (61,1) (C(L,K), K=1,4)
      RETURN
      END
```

APPENDIX V

Values of Components for Steady State Device

Component	Value	Remarks
R_1	100 ohms	1% resistor
R_2	1,000 ohms	1% resistor
R_3, R_7	270,000 ohms	
R_5, R_9	100 ohms	1% resistor
R_4, R_8	10,000 ohms	1% resistor
R_6, R_{10}	10,000 ohms	1% resistor
R_{11}	1,000 ohms	1% resistor
R_{15}, R_{16}	10,000 ohms	10-turn potentiometer
R_{17}, R_{18}, R_{19}, R_{20}	10,000 ohms	trimming potentiometer
R_{21}, R_{23}	10,000 ohms	
R_{22}, R_{24}	100 ohms	
R_{25}	10 ohms	
R_{26}	100 ohms	
C_1	5.1 microfarads	measured capacitance
C_3	5.3 microfarads	measured capacitance
C_2, C_4	0.05 microfarads	

APPENDIX VI

Program POINTS

```
      PROGRAM POINTS
      DIMENSION IA(10)
C POINTS WAS WRITTEN BY C.E. MILLER TO
C PLOT ONE OR TWO SETS OF DATA ON A GRAPH 10X15
C INCHES.  Y AXIS GOES FROM -250 TO 250.  X
C AXIS GOES FROM 0 TO 300.  LABELING OPTION
C AVAILABLE.  SUBROUTINES AXISXY, PLOTXY
C AND LABEL ARE PECULIAR TO OS-3 FORTRAN
C COMPILER.  SEE OS-3 PLOTTER MANUAL
C LUN 1 IS OUTPUT TO PLOTTER
C LUN 3 IS FILE FOR LABELING INFORMATION
C LUN 5 IS FILE FOR DATA TO BE PLOTTED
C LUN 7 IS FILE FOR ADDITIONAL DATA TO BE PLOTTED
    1 FORMAT (' WHAT ARE THE NUMBER OF POINTS')
    2 FORMAT (' PEN MARK')
    3 FORMAT (' PEN POSITION BETWEEN POINTS 1=DOWN0=UP')
    4 FORMAT (' LABELING? 0=NO  1=YES')
    5 FORMAT (2F6.1,I3,2I2,10A4)
C AXES ARE SET
      IF (AXISXY(1,15,10,50.,300.,500.,0.,-250.,0.,-250.,125.,0))10,35
C FIRST SET OF DATA TO BE PLOTTED
   10 PRINT 1
      J=FFIN(60)
      IF (J)29,29,11
   11 PRINT 2
      IPEN =FFIN(60)
      PRINT 3
      IPOS=FFIN(60)
      DO 15 I=1,J
      X=FFIN(5)
      Y=FFIN(5)
   15 CALL PLOTXY(X,Y,IPOS,IPEN)
      CALL PLOTXY(0.,0.,0,0)
C SECOND SET OF DATA OPTION
      PRINT 1
      J=FFIN(60)
      IF(J)29,29,142
  142 PRINT 2
      IPEN=FFIN(60)
      PRINT 3
      IPOS=FFIN(60)
      DO 143 I=1,J
      X=FFIN(7)
      Y=FFIN(7)
  143 CALL PLOTXY(X,Y,IPOS,IPEN)
C LABELING OPTION
   29 PRINT 4
      IW=FFIN(60)
      IF(IW)20,35
   20 J=FFIN(3)
      DO 200 I=1,J
      READ(3,5)X,Y,INUM,ISIZE,IDIR,(IA(K),K=1,10)
      CALL PLOTXY(X,Y,0,0)
  200 CALL LABEL (INUM,ISIZE,IDIR,IA)
   35 IF(AXISXY(0,0,0,0,0,0,0,0,0,0,0,0))45,45
   45 CONTINUE
      END


      INFORMATION IN LUN 3
11
 296.0-260.0   4 2 0300
 196.0-260.0   4 2 0200
  96.0-260.0   4 2 0100
     0-260.0   4 2 00
  -2.0-265.0   4 2 3-250
  -2.0-140.0   4 2 3-125
  -2.0 -15.0   4 2 3  0
  -2.0 110.0   4 2 3 125
  -2.0 235.0   4 2 3 250
 -10.0-110.0  21 2 3RESPONSE (MILLIVOLTS)
 122.0-275.0  14 2 0TIME (SECONDS)
```