

AN ABSTRACT OF THE THESIS OF

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Title: A COMPUTER CONTROLLED ROBOT ANALYZER FOR  
IN SITU WATER QUALITY MONITORING

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A new, computer oriented system for automatic, in situ monitoring of water quality is proposed which makes full and effective use of modern computer technology. The main objective of this thesis work was the development of the concept for in situ computer controlled experimenting as a reasonable and effective means of automatically observing the wide range of aquatic parameters needed.

The established capability in the teleprocessing industry is assumed as starting point and an optimal design is sought for a sensing head which would meet current expression of requirements for automated water quality monitors while exploiting the advantages of both hardware and software in a total system context. A working model of such a sensing head was constructed and operationally tested using an EAI 690 hybrid computer to simulate the central

computer and telecommunications facility. This sensing head consisted of a peristaltic pump, a servo positioned valve, an array of six electrodes (2 glass pH, 3 silver-silver chloride and 1 gold micro-electrode) and a thermistor, along with buffer amplifiers and motor controllers to service these devices. A main feature is its design as a remote, computer peripheral, like a teletype, which understands up to 64 different commands and which returns coded responses. A second feature is its in situ design making the entire sensor head submersible and operable in depths to 100 meters.

A repertoire of programmed experiments was developed for the working model system to show how, for example, it could monitor the water quality parameters; temperature, pH, conductivity, dissolved oxygen, chloride ion, total carbon dioxide, total alkalinity, and a factor called "other ions". The last three in the list being derived from a novel titrametric method, that could be implemented in the particular set of devices in the model sensing head. Concepts of autoverification and autocalibration are introduced and applied with some success. Examples of data (taken at 1/2 meter or 100 meter submergence) for known test solutions and local river water are presented and discussed.

It is concluded that the proposed concept is both practical and feasible, having an almost open ended potential to monitor parameters for which sensors per se are not now available, and to do this with high levels of confirmed data return.

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In Situ Water Quality Monitoring

by

Kenneth Norman Birch

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## TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
I. INTRODUCTION	1
II. BACKGROUND	4
Water Quality Monitoring	4
The Robot Quality Monitor	5
Problems and New Approaches	7
III. AN <u>IN SITU</u> WATER QUALITY MONITORING SYSTEM	10
The Basic System Configuration	10
The Robot Sensing Head	15
The RØBØT ØPERATØR Program	22
The INTERPRETER Program	25
IV. THE MEASUREMENT OF WATER QUALITY PARAMETERS, THEORY AND PRACTICE	30
Temperature	30
pH	32
Chloride	37
Conductivity	40
Dissolved Oxygen	46
Total Carbon Dioxide and Alkalinity	47
V. SYSTEM DESIGN CONSIDERATIONS	54
The Readout Network - High Impedance Buffered, Differential Switching Network For <u>In Situ</u> Potentiometry	54
Floating Controlled Current/Voltage Driver For Working Electrode	66
The Command Structure and the Logical Control of the Switching	72
The <u>In Situ</u> Design	80
The Liquid Junction	88
The Titration Interpreter Program	92

<u>Chapter</u>	<u>Page</u>
VI. SIMULATION OF A WORKING MONITOR STATION AND RESULTS	103
Apparatus Configuration	103
Calibration	105
Operation and Results	111
Discussion of Performance	117
VII. CONCLUSIONS	122
BIBLIOGRAPHY	126
APPENDIX A Discussion on a Linearizing Circuit for a Thermistor	129
APPENDIX B Summary of Subroutines in RØBØT ØPERATØR	133
APPENDIX C A Discussion of Volumetric Independence In the Chloride Tag Method	136
APPENDIX D An INTERPRETER Program (FØRTRAN Listing)	141
APPENDIX E Example Data and Program Printout From INTERPRETER	160
APPENDIX F Preparation of Solutions and Electrodes	164
APPENDIX G Temperature Adjustment of Coefficients	168

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Block diagram of proposed robot experimenter monitoring system.	11
2. The robot sensing head,-- (schematic).	17
3. An active, linearizing thermistor bridge.	31
4. Diagram of conductivity cell.	42
5. Direct coupled, differential scanner configuration (schematic).	55
6. Buffered, differential scanner configuration (schematic).	55
7. Instrument amplifier configuration.	62
8. Electrode -- buffer -- scanner responses in distilled water.	65
9. Working electrode module (constant current configuration).	67
10. Working electrode module (controlled potential configuration).	67
11. Logic and timing diagram for generalized control flip-flop.	76
12. Electrode assemblies, pH and chloride (photograph).	81
13. Electrode array portion of robot sensing head (photograph).	83
14. Pump and valve mechanism (photograph).	86
15. Flow chart of INTERPRETER Program.	102



<u>Figure</u>	<u>Page</u>
16. Apparatus configuration for working model simulation.	104
17. Calibration response of pH configuration.	108
18. Calibration response of chloride ion configuration.	110
19. <u>In situ</u> titration of 0.002 N sodium carbonate.	113
20. <u>In situ</u> titration of 0.001 N sodium carbonate.	114
21. <u>In situ</u> titration of 0.0005 N sodium carbonate.	115
22. <u>In situ</u> titration of 0.002 N sodium carbonate at 150 psig.	116

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Table of robot commands with octal and ASCII coding.	79
2. List of transfer functions used in INTERPRETER program.	94
3. Summary of titration experiment results.	118

## LIST OF APPENDIX TABLES

<u>Table</u>	<u>Page</u>
1. Equilibrium coefficients and their temperature compensation.	170

# A COMPUTER CONTROLLED ROBOT ANALYZER FOR IN SITU WATER QUALITY MONITORING

## I. INTRODUCTION

The understanding and wise management of our fresh-water natural resources requires qualitative knowledge of the individual lakes and rivers. Agencies charged with the responsibility for monitoring the quality and quantity of water are anxious to use the technology of automation to aid them in their collection of basic data and to maintain a vigilance over endangered bodies of water. As a result of this need, a generation of robot water quality monitors have been developed. Their acceptance as useful tools for water quality management is witnessed by the some 800, or so, automated stations in operation throughout the world. In many places, it has been the practice to employ as many as ten remote stations on a given water basin, integrating them into a water quality network. Such integration almost always involves a computer at a central office with data being telemetered into this office from the remote stations.

It is the view of this writer that, as useful as these present monitoring networks may be, they fall far short of the performance and capability that could be realized if the powers of the modern digital computer were exploited to their fullest. Several recent reports, Suffet et al (1970), Maylath (1969) and Klein et al (1968) have

commented that more utilization of computers will be necessary if significant advances are to be made in this field. Unfortunately, the basic design of present generation robot monitors does not lend itself to effective operation with computers. This stems largely from the isolation of the central computer from the analytical and measurement processes in the sensors. The analyzer modules in each robot monitor form the first stage of isolation because they, not only test the water, but also interpret the results of these tests with simple electronic circuits. More isolation is injected by the data acquisition subsystem since it is generally restricted to sending only selected sets of the processed data to the central computer at fixed time intervals. Consequently, a computer at central office is relegated to simple filing and summarizing tasks, unable to interact in the primary measurement processes or assist in their interpretation.

This thesis proposes a computer controlled monitoring system using a relatively simple sensing head capable of performing a repertoire of analytical experiments, in situ. It is the contention that such an approach to the design of robot monitors is, first of all, practical and, secondly, provides the desired system concept which permits exploitation of a computer's full capability. This new approach is demonstrated by the operation of a working model system with one robot station. A prototype sensing head for this robot station was constructed to explore some of the design problems

and hardware-software trade-offs that result from following through this concept. In order to limit the scope of the prototype construction project it was decided to limit the experiment repertoire to electrochemical techniques only. The hardware built was sufficient to demonstrate the feasibility of the in situ apparatus required. An E.A.I. 690 hybrid computer facility was configured to simulate the rest of working model, monitoring system and a special chamber was used to generate the environmental conditions equivalent to 100 meters submergence in water.

## II. BACKGROUND

### Water Quality Monitoring

It is not enough to simply say that a lake or stream may be polluted. When it comes to formulating and enforcing management programs which are to be effective, realistic and economical, then more specific information is required. For example, it should be known what specific compounds or elements are in the water and from where they come. Furthermore, the effects of these components at their various concentrations must be understood and their rates of accumulation, dispersion or conversion to other forms must be realistically estimated. Since each water body is unique in its ability to support the industry and ecosystem which surround it, the information must be collected and applied for each water body on its own.

It is the role of water quality monitoring to provide quantitative data that can be used to answer these questions. Frequently, the monitoring role is expanded to include the first stage of quality control and pollution policing.

The conventional approach to this task is to manually take water samples at representative points within the water body, and at regular intervals of time. Normally these bottled samples are

transported to a centralized laboratory where they are analyzed following standard methods or by automated analytical instruments. The Environmental Protection Agency, the federal government agency charged with a responsibility for water quality monitoring, have some 100 different parameters they can routinely measure for any survey. Actually these parameters are the values that are produced by specified analytical procedures and are not necessarily parameters in the strict sense of the word.

Not all of these parameters can be adequately monitored by the conventional method because of the variability of some of them with time and/or their dependence upon their immediate environment. For example, parameters such as dissolved oxygen and pH are known to vary significantly in the space of an hour, while others, like certain nutrient forms, ( $\text{NH}_3$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ), gradually change form after the sample is taken. The need to include such parameters as these in water quality monitoring has spurred the development of automated sampling stations and on site automated analytical instruments.

### The Robot Quality Monitor

The Robot Water Quality Monitor is one of the more popular types of integrated sampling and analytical instruments used in the United States and Canada. Its development and current status

has been discussed by many publications (Klein, Dunsmore and Horton, 1968; Suffet, Radziul and Goff, 1970; Mentink, 1970).

The typical robot monitor has three main functions: to sample the water, to analyze it, and to record the results of the analysis. Sampling is generally done by a submersible pump placed in the water body being studied. The water is continuously pumped to the analyzer instruments, housed on shore, where the sample stream is divided among several analyzer modules. Each analyzer module is designed to measure the value of one water quality parameter and generates an output voltage signal proportional to that value. Probes and other sensing devices within each module produce electrical signals for an electronic circuit, resembling a simple analog computer, which interprets them and generates the output signal.

The analyzer modules used in these robot monitors are of two basic types. The more common, sensor type is mechanically passive and can be thought of as a "chemical transducer". The term sensor is applied to convey the high degrees of selectivity and sensitivity which are normally orders of magnitude greater than are found in transducers commonly used in other areas of instrumentation.

The other type of analyzer is referred to as the wet chemical analyzer. The essential difference between this and a sensor is that a proportional pump volumetrically mixes a reagent with the stream



of sample water and then the characteristics of this mixture are continuously sensed.

### Problems and New Approaches

Already there are requirements being expressed for a whole new generation of water quality monitoring instruments. This new generation must provide a capability to monitor a much greater range of parameters than is currently possible. Furthermore, it should do this with greater reliability and less manual supervision. There is also the requirement for some of these monitors to be capable of operating completely in situ so that off shore areas in lakes can be monitored, and so that monitoring could be continuous through periods of ice cover or floods.

The lack of sensors for nutrients, oxygen demand, toxic substances (like heavy metals and pesticides), biological activity indices (like chlorophyll a and  $\text{pCO}_2$ ), is a severe limitation on the present monitoring systems. Even the established sensors for temperature, pH, conductivity, dissolved oxygen, and turbidity are somewhat short of the long term reliability and accuracy requirements desired. The prospectus for the creation of more and better sensors is not good because of the extreme sensitivity and selectivity which such sensors must possess. Considering that a modern precision temperature sensor (e. g. a quartz crystal) obtains precision in the order of

0.005°C or 1 part in 1,500,000 (at 300°K.), and that one requires a phosphate sensor with a full scale range of 1.5 ppm (parts per million) and precision in the order of 0.01 ppm or better, then it is not surprising that new water quality sensors are not appearing which fill the need.

There are, however, many new sensing devices, such as selective ion electrodes and solid state photo detectors and light sources, plus many powerful, instrumental analytical techniques, like stripping voltammetry. All these show sensitivities in low ppm ranges. Unfortunately, the interferences are significant and the conventional techniques developed for handling these problems in the laboratory complicate the methodology and the interpretation to the point where it is unreasonable to incorporate them into sensor designs.

It is the theme of this thesis that one can take very practical advantage of many of the new sensing devices and established analytical techniques as well as the existing sensor technology. The approach is to redesign water quality monitoring networks based on an in situ, analytical experiment philosophy. It stems from the basic concept of an experiment which is defined by the Oxford Dictionary as;

an act or operation carried out under conditions determined by the experimenter (as in a laboratory) in order to discover some unknown principle or effect...

The proposed system can be described, paraphrasing this definition as follows:

- a) a convenient, reliable means for establishing the conditions is made possible within the confines of a robot sensor head, which
- b) reproducibly executes a sequence of events under the direct, supervisory control of a computer program, and which
- c) reports observations made by an array of sensing devices, through a multiplexed encoder (A/D converter), directly to a computer which
- d) analyzes this data by following interpreting algorithms.

The following chapters describe this proposed system in greater detail and give many specific examples of experiments with their interpreting algorithms.

### III. AN IN SITU WATER QUALITY MONITORING SYSTEM

#### The Basic System Configuration

Figure 1 is a block diagram of a complete water quality monitoring system based on the in situ, analytical experiment approach. In essence, it consists of a remote station, called a robot sensing head, and a shore based minicomputer facility. A full duplex telemetry system communicates commands from the computer to the sensing head and returns encoded responses back to the computer. In this configuration the sensing head becomes a remote terminal to the minicomputer such that the computer can be located at a convenient office on shore while the sensing head can be sited in the field. Only one remote station is shown for simplicity, however, the computer could be time shared among several other remote stations. The detail of the remote station depicts the specific case of a robot sensing head with a multi-electrode sensing array, as constructed for this thesis project.

The robot sensing head is the active portion of the remote station. It includes all the electronic and mechanical hardware to decode and execute the commands from the computer. It is composed of four types of functional modules:

- a) system service modules -- to handle internal signals or

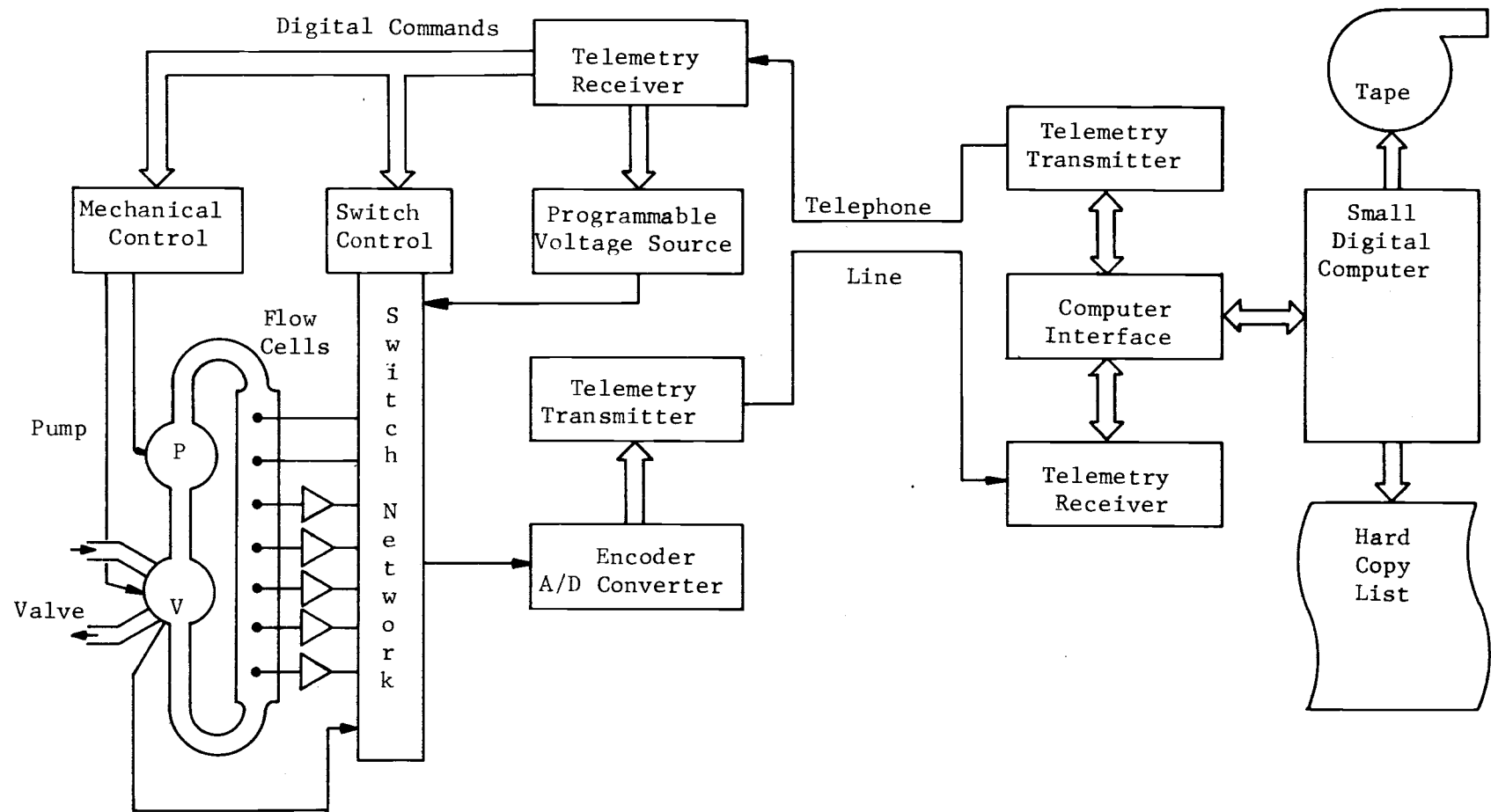


Figure 1. Block Diagram of Proposed Robot Experimenter Monitoring System

controls between the active modules and the rest of the system, e. g. A/D converters, D/A converters, power supplies, telemetry modems, etc.,

- b) motor modules -- to effect mechanical action (includes control circuits) e. g. sampling pumps, valves, heaters, etc.,
- c) sensory modules -- to sense and measure factors in the water under test (includes special buffer or driver amplifiers),
- d) passive modules -- to provide other elements that do not interact with the computer, i. e. flow cells, reagent reservoirs, ion exchange columns, etc.

The computer is the heart of the proposed system. As the master control element, it initiates all action at the remote stations and specifies the detailed steps of each action. It also interprets the raw data from the sensing devices in the robot and extracts the familiar water quality parameters. In addition, the computer displays, on its output device, the information gleaned from the robot monitors for basin management purposes and for maintenance of the network. Computer compatible data files can be produced, containing summarized, historic data.

Using the computer as the master control element is a new idea in water quality monitoring and an important aspect of the proposed

system. Its primary function, one very easily realized in a computer, is generating the detailed sequences of instructions for the in situ experiments, and issuing them with precise timing. These instruction sequences, are arranged into proven, machine language, micro-programs which can be called by an operator program to compose the various experiment routines. Previously acquired data and inputs from the human operator can be used to modify the order of events and the timing so as to optimize information content and accuracy. Where reasonable to do so, confirmation control schemes are employed so that before the computer proceeds with an instruction sequence, the robot sensing head can be interrogated to determine if the correct conditions prevail. This implies that the motor modules in the robot sensing head have feedback transducers. The computer can also be part of servo control loops to exercise precise, programmable control over functions such as pump speed, valve positioning, pressure regulation and water temperature.

The system monitors water quality by conducting experiments with a sample of water taken into the robot sensing head and then interpreting the results in terms of useful indices of water quality. Such experiments may be simple electrode potentiometric measurements from which some useful factors, like pH, red-ox potentials and certain ion activities, can be deduced directly. However, the experiments can be much more complex; involving many detailed

steps, requiring the addition of reagents or the execution of sophisticated electrochemical analytical techniques. Each experiment is defined by a routine or a sequence of instructions which can be executed repeatedly by the computer any time the operator of the system wishes. The measurements made by the robot sensing head during the course of an experiment are telemetered to the computer in the raw forms produced by the electrometric sensing devices (e.g. the potential between a specified pair of electrodes or the collector current of a phototransistor). In the computer, they are interpreted by fitting them to the best mathematical model of the experiment (often time variant and very nonlinear). The water quality parameters are thus assigned values which result in the best agreement with the observed experiment. Information gained during previous experiments is available to optimize and supplement later experiments. The term multivariable is applied to this system to convey the ability to use all available data in the interpretation of any one particular experiment. This permits exact compensation methods, estimation of confidence limits, rejection of spurious or questionable observations, and extraction of more than one water quality parameter from a given experiment.

Outwardly, this proposed system looks very similar to present robot water quality monitoring networks, employing similar hardware, (computers, telemetry, in situ sensing devices) and producing



similar data (a time series of parameter values for a given station). The fundamental difference is that it operates on a batch basis in which a sequence of analytical experiments are conducted in situ under the direct control of the computer. The signals derived from the sensing head carry values of primary, observable quantities, like resistance, potential or current, not quasi-processed values of parameters as produced by the analyzer or sensor modules of conventional monitoring systems. The basic differences in configuration between this proposed robot experimenter system and the conventional monitoring system can be seen to be:

- a) shifting interpretation functions from the simple analog circuits of individual analyzer modules to a digital computer,
- b) integration of the primary sensing elements into a single multi-purposed test cell, and
- c) substitution of a series of computer controlled analytical experiments, performed at regular intervals, for continuous analysis by banks of analyzer modules, operating in parallel.

### The Robot Sensing Head

The robot sensing head is housed in pressure cases suitable to permit emplacement in the water body at the desired depth for

observation. Justification for this in situ design comes from the advantages gained from a stable thermal environment and better sample handling. Effective thermal compensation of electrochemical cells demands that one be able to assume thermal homogeneity throughout the cell. There is also benefit from relaxed mechanical and electronic design since an operating temperature range from 0° to 35° C could be expected, lying well within the commercial class specification. By placing all the water handling and test apparatus below the surface, at the in situ depth, one can realize a water sampling system which avoids contamination by contact with the atmosphere, passage through long lengths of pipe, or subjection to violent pressure changes. The contamination problem is most acute when one wishes to accurately monitor water with volatile components which are far from their atmospheric equilibrium conditions. The additional engineering necessary to achieve this in situ capability is felt to be relatively minor compared to these benefits and the avoidance of much of the plumbing and civil engineering costs encountered for installation of each present day monitoring station. The prototype sensing head was designed to operate down to a depth of 100 meters, a point where in situ design begins to get more involved and where all but a few applications can be satisfied.

Figure 2 is a simplified composite schematic for the complete robot sensing head as constructed for this project. For simplicity,

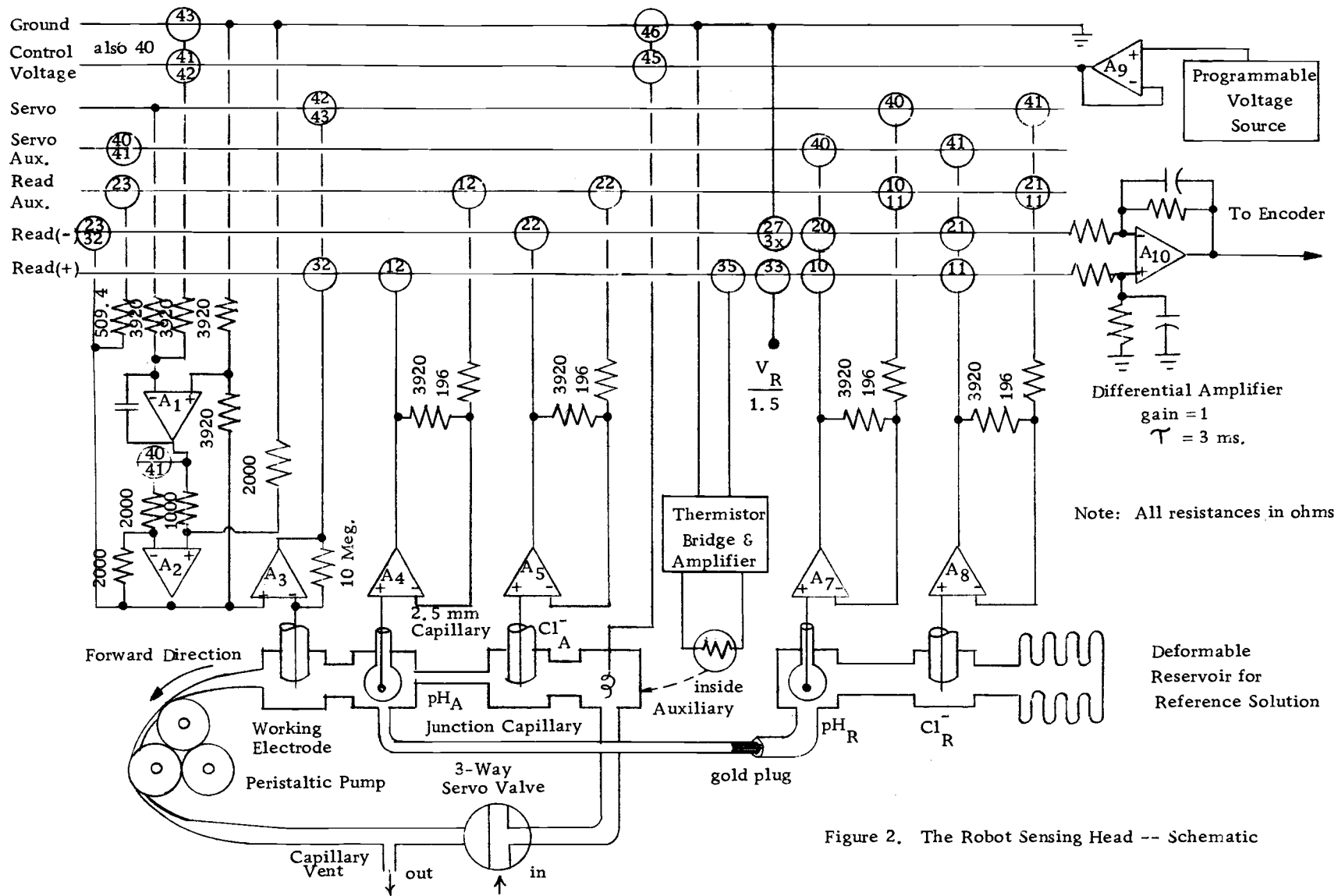


Figure 2. The Robot Sensing Head -- Schematic

only those components which are directly involved in the electrochemical experiments are shown. The logical control circuitry is discussed in Chapter V, but its presence is inferred by the small circles at some junction points in the diagram. Each circle represents a single pole, normally open, relay contact driven by solid-state latches controlled from the computer. The numbers inside the circles denote the octal code of the instructions which cause closure of that switch. By issuing a set of instructions, the computer program, can close appropriate relays to configure the circuits in the robot sensing head so that a specific electrochemical experiment can be performed. It is important to note that these relays, once switched onto the buses, remain on until some following command is given which requires use of the same bus. In other words, the command set is so arranged that conflicting use of the buses does not occur and that commands to undo previous commands are not needed.

All inputs to the robot sensing head are logical and derived through the telemetry interface. The programmable voltage source module generates a voltage level in the range +10 to -10 volts in response to a sequence of commands. The programmed voltage is placed on the "drive" bus and is used as the control or input signal for several experiments. For the working model system, this programmed voltage source was simulated on the E.A.I. 690 system

by utilizing one digital to analog channel with a service program which made it function as if it were receiving instructions over a telemetry link.

There is only one output from the robot sensing head, the encoded output voltage of the differential amplifier. The potential between any two available points within the sensing head can be transmitted to the computer by arranging for these potentials to be applied to the inputs of the differential amplifier. The "read(+)" and "read(-)" buses are directly connected to the respective differential inputs. These two buses and the relays, which can connect to them, form a programmable, differential scanner. The auxiliary bus is connected in conjunction with these "read(+)" and "read(-)" relays so that the two modules, involved in a differential measurement, are placed at the same common mode potential. Ground referenced potentials are accommodated by grounding the "read(-)" bus.

Once again the E. A. I. 690 system was used to simulate the return path to the computer. One analog-to-digital channel with sample and hold amplifier was used to simulate the encoder stage. The final working version of the system also included a single pole, low pass filter with a time constant of 0.003 seconds or 1 second, selected by the service program. The servo bus forms the primary feedback path for a number of closed loop controls. In this particular

sensing head, the servo bus is used when the working electrode is driven under controlled current or controlled voltage conditions. The auxiliary bus is used to connect the common mode levels of active modules.

The test cell is shown schematically in the lower portion of Figure 2. Basically, it is a closed loop of water contained by flow cells, around the individual electrodes, and by the interconnecting tubing. A more detailed description of the construction is given later in Chapter V.

The pump is a rotary, peristaltic type which can exchange the entire volume of water in the test cell (about fourteen millilitres) in approximately six seconds. The valve is a rotary "T" valve made of Teflon and glass. When the valve is in the position shown ("open"), the counter-clockwise rotation of the pump rollers will draw water from the input, through the test cell and expel it to waste. When the valve is rotated 90 degrees counter-clockwise to the "closed" position, the rotation of the pump circulates and mixes the water which is thus trapped in the test cell loop. The entire test cell, including the pump rotor and the "T" valve, are located outside the pressure case in the very water which is being analyzed. The pump motor and the valve servo mechanism are on the inside of the pressure case. Special torque feedthroughs were devised to couple the driving forces through the pressure case bulkhead.

The actual sensing part of the robot sensing head is an array of six electrodes. Four of these are designated "active" because they are the electrodes which make contact with the water being analyzed, (i. e. the water in the test cell). The other two are designated as "reference electrodes" because they are exposed to a reference solution and have constant potentials. A liquid junction, made through capillary tubing, provides the electrical connection between the reference solution and the water in the test cell. Micro-circuit operational amplifiers are used to buffer the high impedances presented by the glass pH electrodes and the silver/silver chloride electrodes. The working electrode is a gold button (0.78 sq. mm. in area) buffered by an operational amplifier, configured as a current-to-voltage follower. Associated with this working electrode is a network of amplifiers and relays which form a flexible control circuit. By closing appropriate relays, the working electrode can be controlled so that one of the three following conditions prevail;

- a) The potential of the working electrode, relative to any specified reference electrode, is forced to be a linear function of the "drive" voltage.
- b) The current through the working electrode is forced to be a linear function of the "drive" voltage.
- c) The current through the working electrode is kept at a near zero value (approximately 0.2 nanoamperes or less).

For most of the experiments, the working electrode is maintained in the zero current control mode so that no current flows through the water to complicate the potentials of the other electrodes.

### The RØBØT ØPERATØR Program

One of the keys to practical implementation of this fairly complex in situ analytical experiment concept is design of the robot sensing head as a computer peripheral. In order to reach the objective of demonstrating the practicality and potential of the proposed system, it was necessary to adopt some existing teleprocessing system as a reasonable starting point. Since there is an established teleprocessing industry employing voice grade telephone lines to transmit standard ASCII code at 10 cps, full duplex, then this capability was assumed. This meant that the robot sensing head could be regarded from the computer's point of view as a remote teletype terminal, accepting and understanding a set of 64 different instructions and returning standard ASCII coded responses.

The RØBØT ØPERATØR is the name of the program which resides in the central computer to operate the robot sensing head, directing it through its analytical routines and assimilating the resulting data. For the simulation phase of this project, a RØBØT



OPERATOR program was developed using HOI<sup>1/</sup>. This language facilitates stacking and nesting of subprograms (a property found to be very useful), however, its compact, numerical notation makes it difficult to comprehend. Since the ordering and timing of events is important in describing the analytical experiments, then the essential detail of the ROBOT OPERATOR will be presented, but in a pseudo symbolic form.<sup>2/</sup> The ROBOT OPERATOR is treated as a main program having access to subroutines which can be nested in three levels. Level, "0", subroutines are essentially machine language routines that allow special access to the system input/output devices (in this case the robot monitor). Level "1" subroutines are commonly used combinations of Level "0" subroutines and regular FORTRAN statements, such as simple experiment routines, (e.g. SUBROUTINE READPH or SUBROUTINE RUNPUMP).

The significance of the nesting number is to group these subprograms in such a way that their functions cannot conflict. In other words, a subroutine can only call routines with a lower nesting

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<sup>1/</sup> Hybrid Operator Interpreter is an E.A.I. systems program which has many characteristics of BASIC and comes with a set convenient of subroutines to interface with the analog computer portion of the 690 system.

<sup>2/</sup> This pseudo symbolic language is essentially, incomplete FORTRAN where all variables are assigned common storage, i.e. no variables passed in subprogram calling, no declarative statement but conventional assignment of I, J, K, L, M, and N to integers.

number to assure orderly nesting and avoid conflicting use of the test cell configuration in the robot sensing head. All the subroutines developed to operate the robot sensing head are summarized in Appendix B, but some examples are presented at appropriate points in the following chapters.

It is convenient to introduce some subroutines here, as they are frequently called and pertain to the robot sensing head generally.

The three nest level "0" routines are:

SUBROUTINE WAIT - a machine language routine that causes a delay in the progression of the program of W seconds. ( $100 > W > 0.1$ )

SUBROUTINE ENCODE - a machine language routine that initiates an A/D conversion at the remote station and assigns the encoded value received to the variable, E, (in Volts), after first adjusting it for any gain and zero offset errors in the conversion process, ( $+10.000 > E > -10.000$ ),

SUBROUTINE EXECUTE - a machine language routine that takes the first eight bits from the variable I and transmits them to the robot sensing head as an instruction.

Two of the nest level "1" routines are:

SUBROUTINE VALUE

I = 63 <sub>8</sub>	(This program sets $\tau = 1$ on
CALL EXECUTE	(input to A/D amplifier and
W = 2.0	(then waits 2 seconds to
CALL WAIT	(average the voltage value
CALL ENCODE	(before encoding it; $\tau = 0.003$
I = 64 <sub>8</sub>	(is set back before returning.
EXECUTE	(E is now the average over
RETURN	(2 seconds.
END	

SUBROUTINE VOLTSET - This program issues a series of instructions to the robot sensing head that cause the programmable voltage source to generate a voltage,  $V$ , where  $-10.0 < V < +10.0$  volts. This was actually a dummy program since the programmable voltage source was simulated, (i. e. the program waited 300 milliseconds and then set the D/A channel on the 690 system to the voltage  $V$ ).

Whenever the program encountered an error it aborted at that error point and returned to the executive level of H.O.I. This was acceptable for this working model stage but recovery points must be established and by-passing schemes developed before this program would approach the level of sophistication for true unattended operation.

### The INTERPRETER Program

The INTERPRETER is a computer program which takes the output files produced by the ROBOT OPERATOR program, extracts information about the water quality, and expresses this as values for the familiar water quality parameters. For each experiment routine in the ROBOT OPERATOR, a corresponding routine is needed in the INTERPRETER. Although the detailed techniques for analyzing and extracting parametric values from each experiment will be peculiar to that experiment, there are some general characteristics of the INTERPRETER which produce important advantages for a monitoring system based on this experimenter approach.

Before proceeding with the discussion of the INTERPRETER program, itself, it is fundamental to recognize the nature of the data table that results from conducting an experiment with this system. Each data point in such a table represent conditions at a specific point of time in an experiment. The conditions may be those forced by the experimenter routine or quantitative observations made by detectors and electrodes. For example, a titration experiment might result in a table of "reagent added" values with corresponding potentiometric electrode readings, covering a range beyond the usual "end point". Another example would be a time series of voltage and current readings during a chronoamperometric experiment. In other words, the data table produced by an experiment describes the experiment directly, but contains information on water quality parameters indirectly. It is the job of the interpreter routine to analyze such data tables and extract the parametric factors. Since the data is presented to the central computer in very raw form, the variety and the power of the techniques for performing this interpretation can be enormous.

The front line interpreting process would, in general, be the application of the best known transfer functions to extract familiar water quality parameters. Previously processed data would be available to compensate the transfer function for physical factors (e. g., temperature, pressure, flow rate) or for known interferences.

This kind of interpreting process is analogous to that done in the "signal processing" units found in present day water quality monitors. The difference and advantage is that the experimenter approach needs much less hardware in the field and the compensation can be much more sophisticated and accurate.

However, not every analytical experiment can be adequately described by a simple transfer function. For these it is necessary to fall back to more elaborate mathematical models of the experiment and include the pertinent aspects of the water chemistry. Computer modeling techniques for many of the basic forms of experiment have already been developed by spectroscopists, kineticists and process control engineers who have found advantage in using computer methods in their own fields. Parameter estimation by nonlinear regression analysis, perturbation analysis, and Grann extrapolation techniques have been applied to extract parametric information from inexact or noisy data (Dyresson, 1968).

One of the novel features of the INTERPRETER program is the use made of factors called "autovarification indices". In simple terms, an autovarification index is a measure of the degree to which the data table from an experiment conforms to the theoretical experiment characteristics. For example, one should be able to express the character of an experiment as a complex function of the significant water quality parameters (i. e. the parameters which the

experiment derives. plus the interfering factors known from other experiments) and the driving factors (i. e. the conditions forced by the experiment routine). If a theoretical set of entries could be calculated from this mathematical model, then the mean square deviation between the theoretical and observed dependent variables would be a good autovarification index. When such an index is low, one would have confidence that the parameter values derived from the experiment were true. However, when the autovarification index is large, the observer would know to treat the derived parameter values with caution. Furthermore, a large index value would suggest that either; the robot station was encountering water having characteristics which invalidated some assumption made in the theory of the experiment, or the robot station was suffering some malfunction or drift in calibration. In any event, the human observer of the monitor system is alerted so he can take action. It is perhaps not too far out of line to suggest that the autovarification index is a non-specific pollution detector and, therefore, a potential tool for the pollution policing role of monitoring.

The concept of the autovarification index can have useful application in the actual interpretation process of complex experiments through a technique called "parameter estimation by nonlinear regression analysis". In this method one begins with good guess values for the parameter values that are to be determined from the

experiment data. An autovarification index for the experiment using these guess values is computed along with a correction factor for each parameter. After improving the guess values by applying the correction factors, another autovarification index is computed and compared with the previous one. The method is iterative, continuing until no significant changes are being made in the parameters and the autovarification index is a minimum. The power of this technique is most apparent when the experiment is complex and there is difficulty in writing a concise mathematical statement to model it.

Another extension of the regression analysis technique is called autocalibration. It is the effect of letting one or more of the calibration factors for a sensor device become one of the "parameters" selected by the regression analysis. This can only be done if one takes care to observe that the statistical properties of the experiment and the data set will permit a reasonable estimate for these added factors. In other words, the experimenter monitoring system should be very capable of calibrating itself in the course of routine operation and thereby achieve extended unattended service in the field.

#### IV. THE MEASUREMENT OF WATER QUALITY PARAMETERS, THEORY AND PRACTICE

##### Temperature

Temperature, an intensive, physical parameter of the water, is one of the most important water quality parameters. It affects everything from the kinds of aquatic life in the water, to the weather of the surrounding area. It is one of the key variables in determining a water's ability to tolerate organic waste. In terms of this monitoring system, temperature is a significant factor involved in all the analytical methods used for other parameters.

In this system, temperature is sensed by a Y. S. I. #45000 precision thermistor which is exposed, in a thin walled, Teflon tube, to the water in the test cell. Figure 3 shows the active bridge network which produces an output voltage having a near linear relation with temperature over the range 0° to 30° C. Detail on the circuit function is given in appendix A.

The following is a pseudo listing of the subroutine, READT, which obtains a reading of temperature from the robot sensing head and assigns the variable T to it.



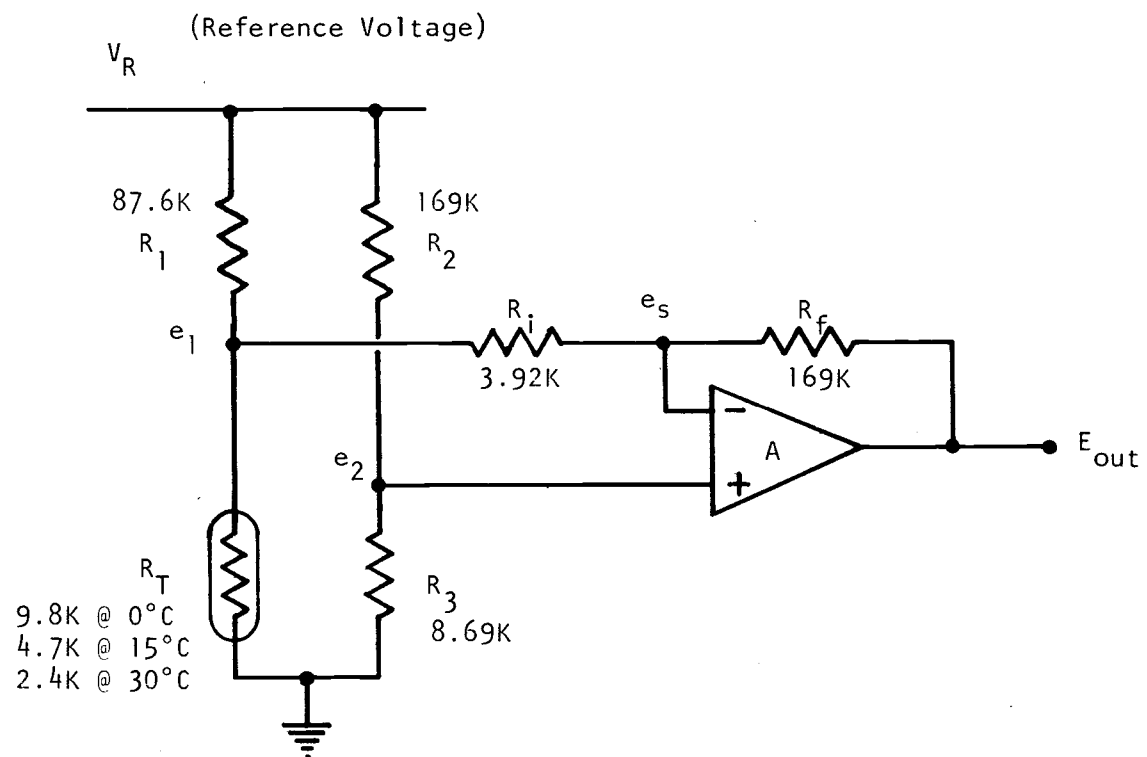


Figure 3. An Active Linearizing Thermistor Bridge

## SUBROUTINE READT

```

I = 358                (Close
CALL EXECUTE            (relay 35 and
CALL ENCØDE             (read output of bridge.
T = 15.                 (Compute value of T
T = T + 0.1501 * E      (in degrees Centigrade
T = T + 0.00076.4 * E **3 (using encoded reading, E,

```

pH

pH is an important parameter in aquatic chemical and biological systems. It plays a very significant role in the CO<sub>2</sub> carbonate system. As a result of the photosynthetic and respiration processes of living organisms in the water, pH can be an interesting way of observing these processes. It also is a factor in determining the effective toxicity of some trace metallic ions. pH is a highly variable parameter as a natural result of its involvement in the physical and biological processes such that it makes most sense to observe the parameter as a function of time, in situ.

Most analytical methods require careful control over pH or accurate knowledge of its value. In this system, the sensing of pH is done as a parametric measurement in itself, and also as an observable variable in other analytical experiments to measure other parameters.

The pH of a solution can be determined by the well known potentiometric method using the "glass" electrode which acts as a

selective ion electrode responsive to hydrogen ions. The glass electrode develops a potential, relative to a reference electrode, which is generally expressed by the relation,

$$E = E'_o - K_{pH} \cdot (pH)$$

where,  $E'_o$  = effective reference voltage, and

$K_{pH}$  = apparent electrode sensitivity factor for glass electrode.

The electrode sensitivity factor and the effective reference voltage are determined from a calibration in which the potential of the cell,  $E$ , is measured in two or more pH buffer solutions, having standard pH values.  $K_{pH}$  is approximately the Nernst factor,

$$K_{pH} = 2.303 \times \frac{RT}{F}$$

where  $R$  = gas constant,

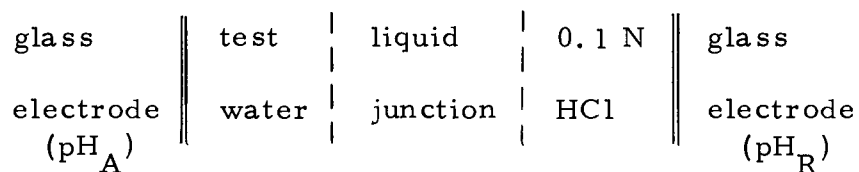
$T$  = temperature in degrees Kelvin,

$F$  = faraday.

The theory of glass electrodes and their practical construction is well covered by Ives and Janz (1961) and Bates (1964). Others like Ben-Yaakov and Kaplan (1968), and Ellis and Kiehl (1935) have discussed some of the practical facets of the use of glass electrodes as sensors for pH in natural water systems. The scheme used for pH

measurement in this working system is a direct application of these established principles with some novel adaptation for realizing a reference electrode within the multi-use concept for the sensing head. The pH measurement cell is configured within the sensing head by connecting the "read (+)" bus to the buffered output from the  $\text{pH}_A$  (active) electrode, and connecting the "read (-)" bus to the buffered output of the  $\text{pH}_R$  (reference) electrode. The  $\text{pH}_R$  electrode is a pH glass electrode, identical to the  $\text{pH}_A$  electrode but has a constant potential, since it is exposed to the reference solution of 0.1 N HCl. The measurement cell is completed by the liquid junction capillary which permits the test water to make electrical contact with the reference solution, but does not contaminate the test water, or vice versa.

Thus, the cell described below is created,



An expression for the resulting cell potential can be written:

$$E = E'_{OA} - K_A \cdot (\text{pH}_A) - E'_{OR} + K_R \cdot (\text{pH}_R) + E_J$$

where subscripts A and R denote active (test water) and reference electrodes, and where  $E_J$  is the junction potential at the interface of

the reference solution with the water in the test cell (discussion in chapter V).

An inherent advantage of this differential electrode method is that it provides a reasonable means for eliminating the unknown quantities,  $E'_{0A}$  and  $E'_{0R}$ , by assuming that they are the same for both reference and active electrodes and can, therefore, cancel each other in a differential measurement. The electrodes used for this sensing head were a matched set, taken from the same glass melt and filled with the same solution. It is assumed that since the electrodes are matched and exposed to the same environmental conditions (temperature and pressure) then their  $E'_0$  potentials should track each other sufficiently well that  $E'_0$  potentials can be dropped from the expression for the output potential,  $E$ . In practice, it is necessary to introduce a term,  $E_{PZ}$  to account for small asymmetry potentials and the zero offset of the differential amplifier. Furthermore, one can assume the electrode sensitivities will be the same, except for a small error term that can be included in  $E_{PZ}$ . The simplified expression for the cell can be written as

$$E_{pH} = K_{pH} \cdot [pH_R - pH_A] + E_{PZ} + E_J$$

where the subscript, pH, has been introduced to distinguish these terms from similar ones, to be defined later for other electrodes.

The term  $\text{pH}_R$  can be estimated since it is the pH of 0.1 N HCl for which it is known<sup>3/</sup> that the mean ionic activity of HCl is 0.798 at 25°C. hence,

$$\text{pH}_R \text{ } 25^\circ \text{C} = -\log_{10} [0.1 \times 0.798] = 1.098$$

The subroutine, READEPH, is called when a reading of pH is needed by the system. The pseudo listing for this subroutine follows:

#### SUBROUTINE READEPH

I = 12 <sub>8</sub>	(Clear (+) bus and
CALL EXECUTE	(then close relay 12;
I = 20 <sub>8</sub>	(clear (-) bus and
CALL EXECUTE	(close relay 20.
W = 2.0	(Wait 2.0 seconds
CALL WAIT	( to equilibrate, then
CALL VALUE	(read a 2 second average
EPH = E/21	(value for E, Set EPH
RETURN	(after correcting for amplifier gain.

This routine takes 4.5 seconds, and results in a new value assigned to EPH. The computation of  $\text{pH}_A$  is done by the INTERPRETER program which uses calibration factors,  $K_{\text{pH}}$  and  $E_{\text{PZ}}$  (corrected to the in situ temperature) and a computed value of  $E_J$ .

---

<sup>3/</sup> Gladstone and Lewis (1960), from Table 51.1, page 509.

### Chloride

Chlorides are present in widely varying concentrations in different bodies of natural water. Unlike temperature, pH, CO<sub>2</sub>, or O<sub>2</sub>, chlorides generally do not vary significantly over short periods and are often taken to be characteristic of the source and history of the water at a particular point. In this monitoring system, the chloride ion concentration is used in the titration experiment as a measure of the quantity of HCl titrant added.

The activity of the chloride ion can be determined by the well-known silver/silver chloride electrode which acts like a selective ion electrode to Cl<sup>-</sup> ions. The potential of this electrode is given by

$$E = E^{\circ}_{\text{Ag, AgCl}} - \frac{RT}{F} \ln \left\{ a_{\text{Cl}^{-}} \right\}$$

where:  $E^{\circ}_{\text{Ag, AgCl}}$  is the standard potential for silver/silver chloride,

$a_{\text{Cl}^{-}}$  is the activity of the chloride ion in the water.

This relation is good for relatively large concentrations of chloride ion, greater than about 10<sup>-3</sup> M. At concentrations less than this, there is reduced sensitivity due to dissolution of silver chloride from the electrode into the surface layer of water

surrounding the electrode. Consequently, the activity observed by the electrode, as reflected by the equilibrium potential it assumes, is made up of two components:

$$a_{\text{Cl}_t^-} = a_{\text{Cl}_w^-} + a_{\text{Cl}_e^-}$$

where the subscripts t, w, and e, denote the total observed, the component from the original water, and the component from the dissolving electrode, respectively. The electrode component of the observed chloride activity is a function of the solubility product,  $K_{\text{SP}}$ , for silver/silver chloride,

$$a_{\text{Cl}_e^-} = \frac{K_{\text{SP}}}{a_{\text{Ag}_e^+}}$$

Since each ion pair of AgCl that dissolves produces one  $\text{Cl}_e^-$  ion and one  $\text{Ag}_e^+$  ion, then the observed chloride activity can be written as a function of the original activity and the solubility product,

$$a_{\text{Cl}_t^-} = \frac{1}{2} \left\{ a_{\text{Cl}_w^-} + \sqrt{a_{\text{Cl}_w^-}^2 + 4 K_{\text{SP}}} \right\}$$

When  $a_{\text{Cl}_t^-}$  is substituted for  $a_{\text{Cl}^-}$  in the simple potential equation for the silver chloride electrode, then the relation holds reasonably well down to concentrations when  $a_{\text{Cl}_w^-}$  is the same order as the square root of the solubility product.



When chloride ion activity is to be measured, the sensing head is configured as a high impedance differential amplifier that looks at the potential between the active "chloride" electrode,  $\text{Cl}_A^-$ , and the reference "chloride" electrode,  $\text{Cl}_R^-$ . Thus, the potentiometric method for determining chloride ion activity is analogous to the method described for pH. By using the definition

$$\text{pCl} = -\log \left\{ a_{\text{Cl}_t^-} \right\}$$

and the same assumptions as for the pH method, the differential output voltage from this cell can be written

$$E_{\text{Cl}} = K_{\text{Cl}} \cdot \left\{ \text{pCl}_A^- - \text{pCl}_R^- \right\} + E_{\text{CZ}} + E_{\text{J}}$$

where:  $K_{\text{Cl}}$  is the sensitivity of the active silver/silver-chloride electrode,

$E_{\text{CZ}}$  is a composite offset term, and

$E_{\text{J}}$  is the junction potential.

The term  $\text{pCl}_R^-$  can be estimated from the mean ionic activity of HCl as was done for pH, and assuming  $a_{\text{Cl}^-} \simeq a_{\text{H}^+}$ , so that

$$\text{pCl}_{\text{R}25^\circ\text{C}}^- = 1.098 \text{ also.}$$

The subroutine, READECL, is called to set up this chloride measurement experiment. The pseudo listing for this program follows:

## SUBROUTINE READECL

I = 11 <sub>8</sub>	(Clear (+) bus and
CALL EXECUTE	(close relay 11;
I = 22 <sub>8</sub>	(clear (-) bus and
CALL EXECUTE	(close relay 22.
W = 2.0	(Wait 2 seconds to
CALL WAIT	(equilibrate, then
CALL VALUE	(encode a 2 second average E.
ECL = -E	(Assign ECL after correcting for
RETURN	(amplifier gain. Return

This routine measures only the voltage ECL, leaving the calculation of  $[Cl^-]$  for the INTERPRETER program.

### Conductivity

Conductivity is a measure of the waters ability to conduct electric current and represents the aggregate effect of all ions in the water. The significance of this parameter in water quality studies depends upon the precision to which the conductivity can be determined and the degree to which the ionic composition of the water is known. In this system, the measurement of conductivity has two specific purposes:

1. to provide a means for self standardizing the pH and  $Cl^-$  measuring methods, and
2. to provide an alternate method for estimating the elements of the carbonate system.

The scheme for determining conductivity is an adaptation of the

four electrode, direct current method described by Elias and Schiff (1956). A simplified diagram of the test cell is shown in Figure 4. A known, constant current,  $I$ , is forced between the two exciting electrodes,  $E_1$  and  $E_2$ . A portion of the potential drop through the solution is sensed between the potentiometric electrodes  $E_{p1}$  and  $E_{p2}$ . If  $R_w$  is the effective resistance of the water volume between the two potentiometric electrodes, then the difference voltage sensed by these electrodes is simply

$$E_{\text{diff}} = E_{p1} - E_{p2} = I R_w + E^*$$

where  $E^*$  is the residual value of  $E$  when no current flows. By making two measurements, using different values of current,  $I_1$  and  $I_2$ , and assuming  $E^*$  stays constant during their measurement, then  $R_w$  can be calculated as

$$R_w = \frac{E_{\text{diff}(1)} - E_{\text{diff}(2)}}{I_1 - I_2} = \frac{\Delta E}{\Delta I}$$

Since the dimensions of the volume are known, the conductivity of the water is thus:

$$K = K_{\text{cell}} \cdot \frac{1}{R_w}$$

where  $K_{\text{cell}}$  is determined with water solutions of known conductance.  $K_{\text{cell}}$  is theoretically equal to the length,  $l$ , divided

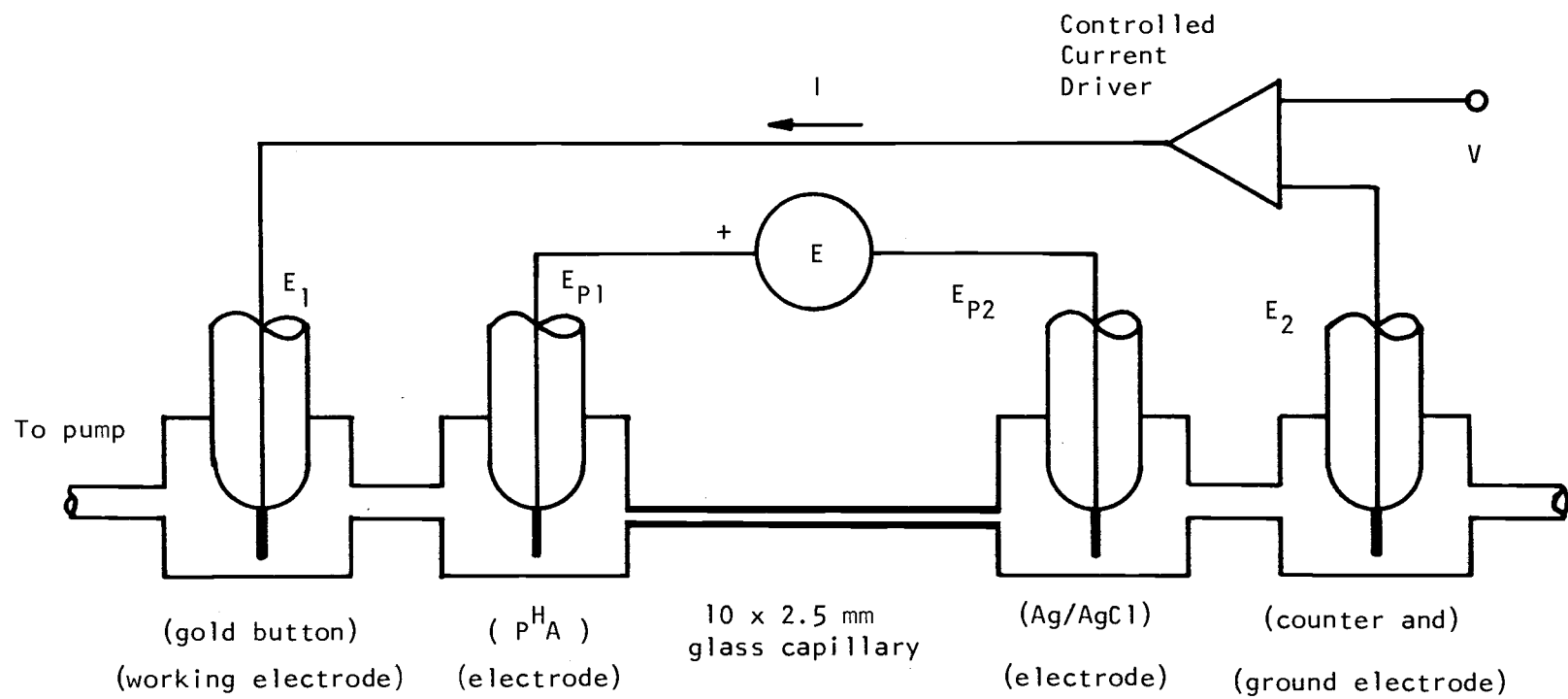


Figure 4. Diagram of Conductivity Cell

by the cross sectional area,  $A$ , of the cylindrical volume between the two electrodes  $E_{p1}$  and  $E_{p2}$ .

From inspection of the relation for  $R_w$ , it is obvious that the precision of the method is tied to the precision of the current and voltage measurement, and to the magnitude of the difference between the two sets of values. In other words, if the precision of current measurement is  $\delta E$ , then the precision of the conductance measurement is,

$$\frac{\delta E}{\Delta E} + \frac{\delta I}{\Delta I}$$

assuming  $\delta E$  and  $\delta I$  are much smaller than  $(E_1 - \Delta E)$  and  $(I_1 - \Delta I)$  respectively. A consequence of this is that for a fixed range of  $I$  and  $E$  there is only one value of conductance at which maximum resolution can be realized.

The robot sensing head (Figure 2) was designed so that the four electrode conductivity cell (Figure 4) could be realized without the necessity of building such a cell strictly for measuring conductivity. The working electrode, set in its controlled current mode, forces a current through the water in the test cell to ground at the auxiliary electrode. The only path available for this current is past the active pH and chloride electrodes and through the glass capillary tube. The peristaltic pump constricts the Tygon tubing so tightly that it

prevents the flow of current through the pump which would otherwise be a parallel path to ground.

The active pH electrode becomes the potential sensing electrode,  $E_{p1}$ , and the active chloride electrode becomes  $E_{p2}$ . Relays (12<sub>8</sub> and 22<sub>8</sub>) are closed to form a high impedance, differential amplifier (gain of 21) with the output,

$$E = 21 \left\{ E_{pH_A} - E_{Cl_A} \right\}$$

Conductivity is calculated from the following equation:

$$K = K_{Cell} \left\{ \frac{I_{(1)} - I_{(2)}}{E_{(1)} - E_{(2)}} \right\} \div 21$$

where:

$K_{cell}$  - is the cell constant

$I_1$  and  $I_2$  - are the values of the current driven through the cell for cases 1 and 2, respectively, and

$E_{(1)}$  and  $E_{(2)}$  - are the measured values of  $E$ , the amplified, difference voltages for cases 1 and 2 respectively.

The computer program subroutine which supervised the measurement of conductivity is called READCØND:

SUBROUTINE READCØND	
DATA CURLIM/5., -5. /	(Initialized at + and - 5 $\mu$ amps.
I = 428	(Put working electrode in
CALL EXECUTE	(programmed current mode,
I = 128	(connect pH <sub>A</sub> electrode to
CALL EXECUTE	( (+ read) bus, and
I = 228	(connect Cl <sub>A</sub> electrode to
CALL EXECUTE	( (- read) bus.
DØ 2 J = 1, 2	(This loop optimizes drive cur-
	rent;
1 V = CURLIM(J)	(Set the drive current (I <sub>1</sub> or I <sub>2</sub>
CALL VOLTSET	(depending upon value of J) to <sup>2</sup>
W = .1	(guess value stored in
	CURLIM(J),
CALL WAIT	(Then wait 100 ms
CALL ENCØDE	(and encode the value of E.
IF (ABS(E). GT. 9. 5), V = V*. 9	(If E high, reduce drive;
IF (ABS(E). LT. 8. 5), V = V*1. 1+. 02	(If E low, increase drive;
IF (ABS(V). GT. 9. 5), V = 9. 5	(if drive high, set at 9. 5 $\mu$ a;
IF (V. EQ. CURLIM(J)), GØ TØ 2	(if drive optimized, continue;
CURLIM(J) = V	(otherwise try new value
GØ TØ 1	(of V = CURLIM(J).
2 CØNTINUE	(This next loop is the measure-
	ment.
DØ 3 J = 1, 2	(Proceed to drive
V = CURLIM(J)	(currents CURLIM (1) and (2)
CALL VØLTSET	(through cell and
W = .1	(measure E1 and E2
CALL WAIT	(as averaged values
CALL VALUE	(over 2 seconds,
3 EDIF(J) = E/21	(backing out gain of buffer
	amplifiers.
CØND = CURLIM(1) - CURLIM(2)	(Compute CØND
CØND = CØND/ (EDIF(1) - EDIF(2))	(having units of mhos.
I = 438	(Restore working electrode
CALL EXECUTE	(to potentiometric mode.
RETURN	(Return.

This program includes an algorithm to find a rough optimum value for the current driven through the cell. The residual value  $E^*$  can be quite large and biased to one side of the range of the differential amplifier, hence, the practical optimum drive current is

one which is as large as possible without over ranging the amplifiers in the system. Since the optimum values of forward and reverse drive currents are remembered from one time to the next, the subroutine starts with current drive values which are probably very close to the optimum and few iterations are needed in general.

The application of the calibration factor  $K_{\text{cell}}$  to obtain conductivity in micromhos/cm is done by the INTERPRETER program. Since  $C\text{OND}$  is computed from units of  $\mu\text{a/mv}$ , then it will have units of  $\text{ohms}^{-1} \times 10^{-3}$ .

### Dissolved Oxygen

Dissolved Oxygen is the amount of oxygen apparently dissolved in the water as a molecular gas following Henry's Law. In natural waters, oxygen enters mainly through exchange with the atmosphere and photosynthesis of green aquatic flora. Oxygen is consumed by most aquatic life and by various stages of decomposition of organic matter. At 25°C, in relatively pure water, the equilibrium concentration of dissolved oxygen is typically 8 mg/l and at 0°C it is 14.7 mg/l. It is a highly variable parameter in natural water systems and its measurement is a vital index of water quality.

The conventional instrumental method for monitoring dissolved oxygen is the membrane diffusion limiting polarographic probe. Hoar (1968) gives a review of this conventional technique plus some

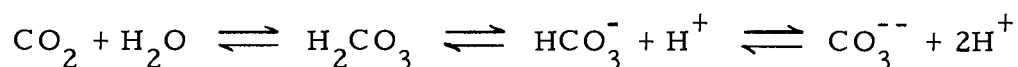


of the many variations that have been tried. Since it was desired to limit the scope of this working model project, the proving of apparatus to measure dissolved oxygen was not completed. Nevertheless, the working electrode was designed to form the cathode in a conventional Clark Cell as well as the driving electrode in the conductivity cell.

### Total Carbon Dioxide and Alkalinity

The monitoring of total carbon dioxide in natural waters, particularly eutrophic lakes, can be used to observe effects of net biological activity. Combined with simultaneous measurements of dissolved oxygen this parameter can indicate primary production (Teal and Kanwisher, 1966). Alkalinity is a measure of the buffering capacity in natural water systems and determines the ability of a water to absorb  $\text{CO}_2$  and cause changes in the pH.

These two parameters are essentially two different ways of reporting the status of the carbon dioxide - carbonate system and will, therefore, be discussed together as a chemical system. Inorganic carbon is found in natural waters in three basic forms which are equilibrium with each other according to:



The formation constants<sup>4/</sup> for this system are usually given as:

$$\beta_1 = \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{--}] [\text{H}^+]} \quad \beta_2 = \frac{[\text{H}_2\text{CO}_3]^*}{[\text{CO}_3^{--}] [\text{H}^+]^2}$$

where  $[\text{H}_2\text{CO}_3]^* \simeq [\text{H}_2\text{CO}_3] + [\text{CO}_2]$  and implies that

$\beta_2$  includes the dissociation of carbonic acid.

Total carbon dioxide is defined as the sum of the three forms:

$$C_{\text{Tot.}} = [\text{H}_2\text{CO}_3]^* + [\text{HCO}_3^-] + [\text{CO}_3^{--}]$$

The quantity, total alkalinity, is a measure of the equivalent concentration of all cations associated with the alkalinity producing anions except the hydrogen ion. In effect then,

$$\text{Total Alkalinity} \simeq [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{OH}^-] - [\text{H}^+]$$

where it is assumed that other concentrations, such as  $\text{PO}_4^{--}$

and  $\text{SO}_4^{--}$ , are negligibly small.

The above relationships can be combined with the ionization product of water,

$$[\text{H}^+] [\text{OH}^-] = K_w$$

---

<sup>4/</sup> Actually,  $\beta_1$  and  $\beta_2$  are functions of temperature, pressure and the general chemical composition of the sample water, i. e. they are apparent formation constants.

The INTERPRETER program (Chapter V) attempts to account for temperature and ionic strength effects.

to produce four equations giving all the components of the carbonate system as a function of  $[H^+]$  and  $C_{Tot}$ .

$$[CO_3^{--}] = C_{Tot} / (1 + \beta_1[H^+] + \beta_2[H^+]^2)$$

$$[HCO_3^-] = [CO_3^{--}] \beta_1[H^+]$$

$$[H_2CO_3]^* = [CO_3^{--}] \beta_2[H^+]^2$$

$$A = \frac{C_{Tot} (2 + \beta_1[H^+])}{1 + \beta_1[H^+] + \beta_2[H^+]^2} + \frac{K_w}{[H^+]} - [H^+]$$

The conventional method for determining total alkalinity is a potentiometric titration with 0.02 N acid. There are two inflection points on the titration curve: one about pH 8.3, corresponding to the equivalence point for the conversion from carbonate to bicarbonate; the other about pH 4.5, corresponding to the equivalence point for the conversion from bicarbonate to carbonic acid.

The conventional potentiometric titration method for alkalinity has not been used for in situ monitoring for two main reasons. Firstly, it has been difficult to construct apparatus which will function underwater and achieve reasonable precision in the volumetric measurements of sample and reagent. Secondly, the output is a series of volume measurements and pH readings, a form which cannot be meaningfully displayed or recorded until computations have been performed to pick out the equivalence points.

The chloride tag method was devised to demonstrate the feasibility of in situ titration using a multivariable approach. In this method the concentration of hydrochloric acid added is determined by a direct measurement of the chloride ion concentration with a selective ion electrode. Since every  $H^+$  ion introduced to the test solution will be accompanied by a  $Cl^-$  ion then the increase in  $Cl^-$  ion concentration is directly related to the total  $H^+$  ions added. The main advantage of the method in in situ titration is that volumetric measurements are not needed, hence, the automated apparatus can be relatively simple. Appendix C provides a discussion to show the method is theoretically independent of any volumetric factors. Apart from this tag method for measuring acid added, the procedure is very similar to the conventional potentiometric titration method. A series of readings of pH and pCl are made, each set of readings being taken after some small amount of HCl has been added. The series of pCl readings are converted to chloride ion concentrations which are then taken to be equivalent to  $H^+$  added. A plot of pH vs  $[Cl^-]$  results in a curve which is essentially the same as obtained by the conventional method. From this plot, one can determine the equivalence points and pick off the concentration of acid added, which is the alkalinity. Chapter V describes the computer method used to perform the conversion from ECL to  $[Cl^-]$  and to also extract values for total alkalinity and total carbon dioxide.

Conductivity also changes with the addition of an acid titrant to water containing alkalinity, a fact that has led to the suggestion (K. Park and H. Freund, 1964) of a conductimetric titration method for alkalinity. Since the working model could easily make conductivity readings at the same time it made the pCl and pH readings, then it was decided to try this conductimetric method as well. The interpreting program made good use of this simultaneous conductivity data.

The titration experiment calls for the addition of small amounts of HCl, each followed by mixing and the measurement of temperature, pH, pCl and conductivity. The process continues until the pH of the test solution is lowered below a pH of 3. A sequence of pump operations was devised to pull small amounts of the standard acid reagent into the test cell. With the pump running "fast forward", a reduced pressure exists in the test cell which slowly draws acid through the junction capillary. Running the pump in "fast reverse", pushes a core of mixed test solution into the junction capillary, both sealing off the test cell and again establishing a "liquid junction" for the potentiometric measurements. The time period spent going "fast forward" was roughly related to the size of the acid addition. Readings of temperature, pH, pCl and conductivity were made using the subroutines outlined previously. Thus, the titration subroutine

could adjust the size of acid additions to give reasonable distribution with pH and pCl.

The following is a pseudo listing of the titration subroutine used in this working model. Before it is called, it is assumed that FLUSH and FILL have been just previously executed such that the test cell is filled with a fresh sample ready to be analyzed.

SUBROUTINE TITRATE	
P = .168	(Set valve to circulate
CALL VALVSET	(water in closed loop.
DØ K = 1, 20	(Prepare to take 20 reading
	sets.
S = + 1	(Run pump,
CALL PUMPØN	(slowly forward, while
CALL READT	(measuring water tempera-
	ture and
CALL READEPH	(measuring EPH.
S = 0	(Stop
CALL PUMPØN	(pump,
IF (EPH. GT. -. 04Ø)GØ TØ 2	(Quit if pH under 3.
W = 2	(Wait
CALL WAIT	(2 seconds.
CALL READECL	(Measure ECL and
CALL READCØND	(conductivity.
S = + 2	(Run pump fast forward
CALL PUMPØN	(to draw HCl into test
W = K + 5	(cell. Let run for
CALL WAIT	(K + 5 seconds, then
S = -2	(run pump full
CALL PUMPØN	(speed, reverse
W = 5	(for 5 seconds to
CALL WAIT	(reset liquid junction.
WRITE ( - - )T, EPH, ECL, CØND	(File in Data Table.
1 CØNTINUE	(Make more measurements.
2 RETURN	

This program has the temperature and pH measurements made

while the pump is slowly circulating the water in the test cell, thereby minimizing self-heating and the so called, alkaline leaching errors encountered with glass electrodes in low buffered waters.

## V. SYSTEM DESIGN CONSIDERATIONS

### The Readout Network - High Impedance Buffered, Differential Switching Network For In Situ Potentiometry

The readout network is a major subsystem within the sensing head. It is responsible for selecting any of the desired potentials within the sensing head and transferring them to the telemetry link for transmission to the computer. It was conceived that the most direct approach to the design of this subsystem would be to use a reed relay multiplexer followed by a general purpose buffer amplifier that fed directly to the telemetry link. Such a configuration is depicted in Figure 5. The desired potential points are represented as Thevinin sources. The relay network represents the general case where provision is made to measure any one potential relative to any other. However, after taking a closer look at the characteristics of the sources, it was found that a configuration having dedicated buffer amplifiers would result in a more practical system. The favoured configuration is depicted in Figure 6. Some of the more important considerations that went into the design of this subsystem are described in the following.

Before evaluating the characteristics of electrodes as voltage sources, it is necessary to examine the environment in which they



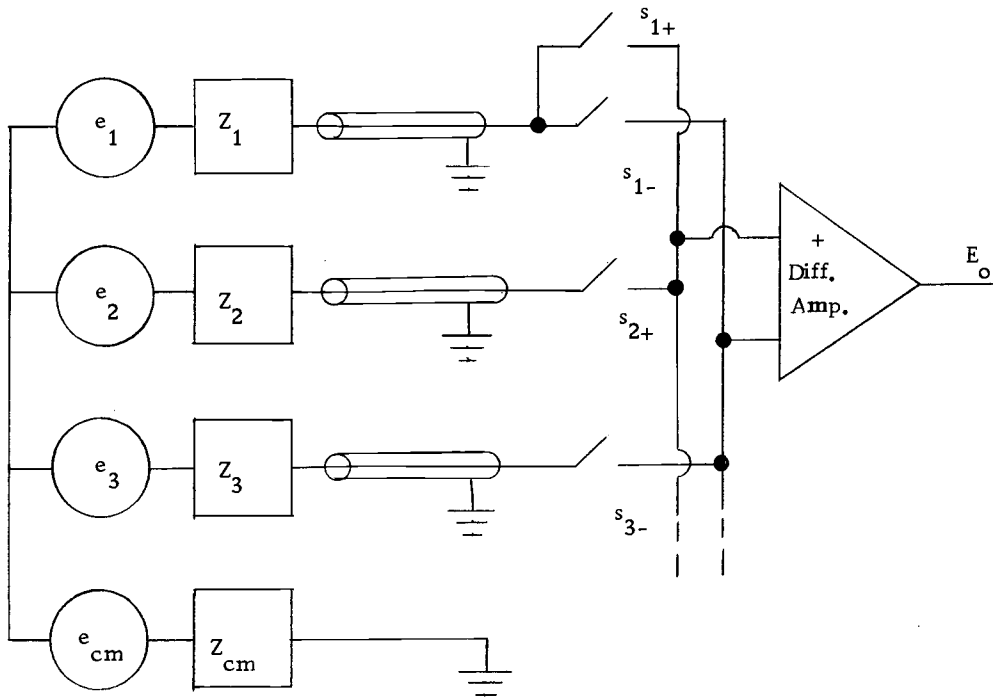


Figure 5. Direct Coupled, Differential Scanner Configuration

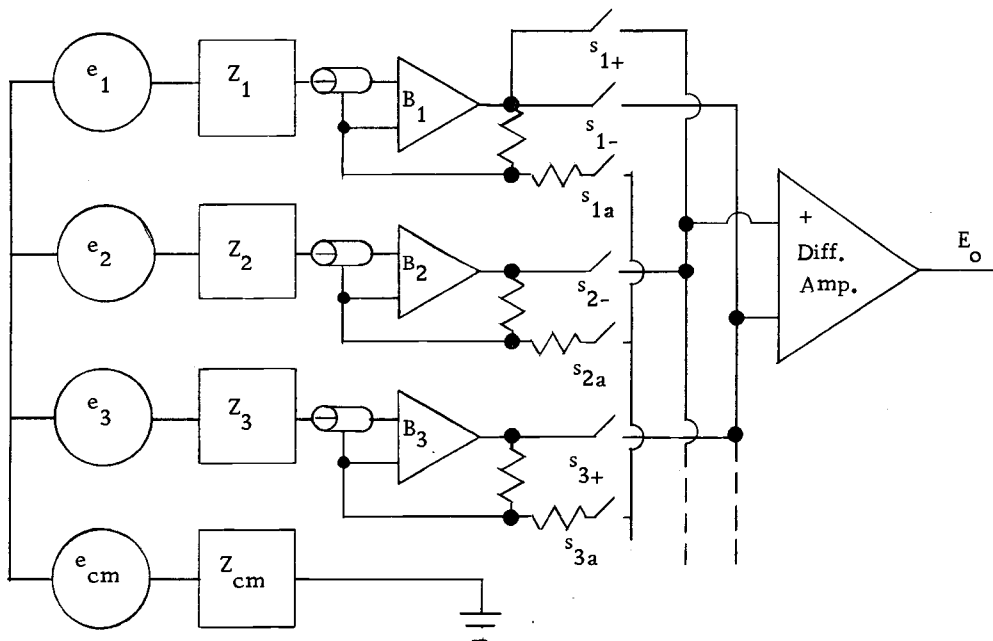


Figure 6. Buffered, Differential Scanner Configuration

must operate. This environment is natural water which could be anything ranging from pure mountain waters to polluted river waters. The temperature may be anywhere in the range  $0^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ . There is always the possibility of a fairly large common mode voltage being present whenever one attempts to measure potential differences between two in situ electrodes. Generally, the common mode voltage can be reduced to acceptable levels by isolating the sensing head from major problem sources, such as power lines, and by establishing a local grounding electrode in the immediate vicinity of the sensing electrodes. For this system design, the common mode voltage is estimated to have a maximum value of  $\pm 3.5$  volts ( $\pm 2$  volts from metal to water interfaces and  $\pm 1.5$  volts superimposed by the working electrode). If the system is to be able to measure the electrode potentials to within 1 mv (0.02 pH units) in the presence of the maximum estimated common mode voltage, then it must have a common mode rejection ratio of at least 70 db.

The desire to employ selective ion electrodes as sensing elements, presents some of the most critical requirements on the readout network. Firstly, there is the requirement for a differential measurement. This need exists because the selective ion electrode develops its potential relative to the water so that a reference electrode must be used to simultaneously sense the potential of the water. Secondly, these electrodes have high source impedances which places

a dual requirement for ultra high input impedance and infinitesimal bias currents. The glass pH electrodes used have a resistance of about 550 megohms, at 0 °C, and about 18 megohms, at 30 °C. In order that the error voltages generated in this source resistance can be held below 1 mv, (0.02 pH units) then the electrode current must be kept under  $2 \times 10^{-12}$  amps. (1 mv.  $\times$  550 megohms). By assigning 0.5 picoamperes as the maximum permissible bias current, then 1.5 picoamperes remain as allowable signal current. The worst case signal current will result when the maximum common mode voltage, 3.5 volts, appears across the common mode input resistance of the amplifier. Consequently, the input resistance should be greater than  $2.3 \times 10^{12}$  ohms. Thirdly, the basic accuracy of the system can be defined in terms of the accuracy desired from the potentiometric analysis. In this case, an analytical accuracy of  $\pm 2\%$  is desirable and about as good as one can hope to achieve by this method. To realize this accuracy, the potential must be measured to better than 1 mv. The maximum range over which this accuracy is needed is 0 to 510 mv. in order to accomodate the pH range from 1 to 9.5.<sup>5/</sup> All other anticipated ranges will be within an overall range of  $\pm 0.51$  volts.

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<sup>5/</sup> This range covers the pH range from the pH of the standard acid reagent (pH) to the maximum expected value expected in Nature (pH 9.5).

In summary, the following minimum specifications must be met by the readout network:

common mode rejection ratio; 70 db.

input impedance:  $2.3 \times 10^{12}$  ohms

input bias current:  $5 \times 10^{-13}$  amps.

accuracy:  $\pm 1$  mv. over  $\pm 510$  mv. range

No mention has been made, so far, about response time or bandwidth. This is largely because the telemetry link was considered to be the major limitation, setting a maximum sampling rate of about ten characters or instructions per second. However, it was noticed, in preliminary experiments, that it seemed to occasionally take many seconds for the differential electrode configuration to produce a stable output after some small electrical disturbance of the high impedance input circuit.

An experiment was conducted to evaluate the problem that might arise in the system operation if the input buses carried sufficient charge to generate such disturbances when switched from one electrode to another. A circuit, essentially that shown in Figure 5, was set up so that the potential of a pH electrode could be observed relative to a reference electrode. The positive input of the amplifier was loaded with a 1000 pf polystyrene capacitor and arranged so that it could be alternately switched between a 1.5 volt dry cell and the pH electrode. The initial response appeared to be a typical RC network

response to an impulse. The time constant, determined from a logarithmic plot of the response, was 77 ms. This agrees with the expected response based on an electrode resistance of about 65 megohms<sup>6/</sup> and an electrode capacitance of about 85 pf.<sup>7/</sup> in parallel with the 1000 pf. After this initial response had died away, there remained a secondary response having about one hundredth the amplitude and lasting 15 seconds before the voltage stabilized within 1 mv. of its final value. It is thought that this secondary response is due to a disturbance of the charge diffusion equilibrium which establishes the electrode potential. Other tests with smaller input capacitors across the amplifier input, showed that the apparent time constant of the secondary response was independent of the size of the input capacitance, but that the amplitude of the response was roughly proportional to the charge unbalance that the electrode had to dissipate. It was therefore concluded, that the total effective capacitance associated with the input buses would have to be in the order of 50 pf, or less, if the electrode potentials were to be read after 0.1 second pause.

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<sup>6/</sup> At the test temperature of 15°C, the electrode resistance was calculated from the value at 25°C, given by the manufacturer as 30 megohms, using the fact that the electrode resistance doubles about every 7 degrees drop in temperature.

<sup>7/</sup> The value of electrode capacitance is taken from the Table 1 of Buck and Krull (1968) as that for the Beckman #41263 pH electrode, a general purpose pH electrode with the same bulb dimensions.

The straight forward, direct coupled configuration, originally proposed in Figure 5, would not likely result in very practical design for several reasons. Firstly, the amplifier would have to be a differential electrometer in order to meet the input requirements outlined above. In addition, it would have to have a precision of 1 part in 10,000 or some means changing the gain to permit full resolution at  $\pm 10$  volts as well as at  $\pm 510$  millivolts. Secondly, it would be difficult to construct a multi-point switching network to serve all points in the system and still maintain the ultra high impedance levels, considering that the system must operate under water. Even with careful guarding, insulating, tactical wire routing and special, low leakage relays, there would be too many opportunities for electrical leakage paths to develop. Thirdly, there is the danger, previously discussed, of coupling transient charges onto the electrodes and deteriorating their responses.

Recent availability of a low cost, high performance, FET operational amplifiers, has made it reasonable to consider a configuration of the type shown in Figure 6. The advanced input characteristics of the Bell and Howell F-318 ( $2 \times 10^{-13}$  amps bias current,  $10^{12}$  ohms and 80 db of common mode rejection), make it suitable for buffering all electrodes, including the glass pH electrode at the low temperatures. The chief advantage of these devices is that they are hybrid microcircuits which are small enough to be built right into

the individual electrode assemblies. In this way, the high impedance portion of the circuit can be confined to a small, easily guarded and insulated zone about the electrode tip itself. With each of the high impedance sources individually buffered by one of these micro-circuit amplifiers, arranged as a high impedance follower, the multiplexing can be done using ordinary relays and ordinary caution. However, to achieve the desired differential measurement with high common mode rejection, it was necessary to use a feedback arrangement commonly employed in instrument amplifiers (Burr Brown, Operational Amplifier Handbook, 1970).

Figure 7 shows the circuit arrangement that is commonly referred to as a data amplifier or an instrument amplifier. It is the basic form of the differential measuring circuit which is formed in the sensing head by the closing of appropriate relays onto the "Read (+)", "Read (-)", and the "read-aux" buses. The primary advantage of this circuit is that a high common mode rejection ratio can be realized with ordinary precision resistors mounted directly onto printed circuit boards, and with ordinary, printed circuit, reed relays. The gain of the circuit to a difference signal is

$$G_{\text{diff.}} = \frac{e_o}{e_1 - e_2} = \frac{R_4}{R_3} \left\{ 1 + \frac{2R_1}{R_2} \right\}$$

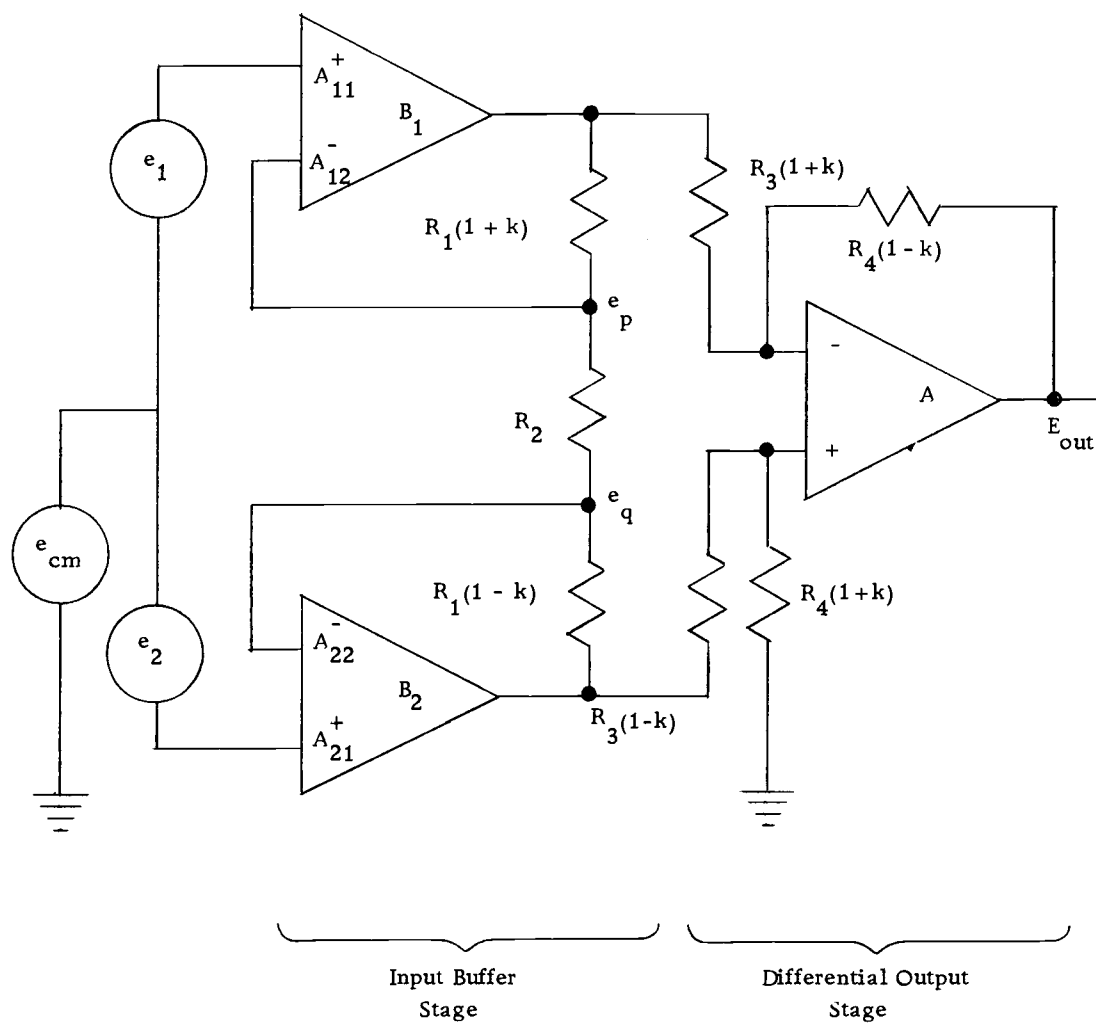


Figure 7. Instrument Amplifier Configuration



The common mode gain of the circuit is;

$$G_{c.m.} = \frac{e_o}{e_{cm}} = \frac{4k R_4}{R_3 + R_4}$$

where  $k$  is the deviation of the stated resistor value, taken in the worst sense. The theoretical common mode rejection due to resistor deviation is;

$$\begin{aligned} CMRR &= \frac{G_{diff}}{G_{c.m.}} = \left(1 + \frac{2R_1}{R_2}\right) \cdot \left\{ \frac{1 + \frac{R_4}{R_3}}{4k} \right\} \\ &= (GAIN_{stage\ 1}) \cdot \left\{ \frac{1 + GAIN_{stage\ 2}}{4k} \right\} \end{aligned}$$

The gain of the differential amplifier (second stage) was set at unity so that only high level signals would be handled on the relay multiplexer. The gain of the electrode buffer amplifiers (first stage) was set at a gain of 21 so that the electrode signal range  $\pm 480$  mv. could be boosted to  $\pm 10$  volts. Placing the highest gain in the first stage produces the best common mode rejection ratio and permits the assignment of the total gain to individual buffer amplifiers to suit the range of potential expected from each source. The two pH electrodes and the two chloride electrodes were all buffered with amplifiers having matched gains to 0.05%. Resistors  $R_1$  and  $R_2$  were chosen just large enough so that variations in the order of an

ohm could be tolerated in the relay contacts. As they stand now, with  $R_1 = 3.92 \text{ K}$  and  $R_2 = 392 \text{ ohms}$ , leakage paths between the auxiliary bus and common ground can cause degradation of the common mode rejection if the leakage path is less than 20 megohms.

To effect this data amplifier circuit in general so that various pairs of inputs could be handled, it was necessary to introduce the auxiliary bus.  $R_2$  was split into two equal halves, one half associated with each buffer amplifier. Connections to the auxiliary bus were made by separate relays closed in tandem with the respective relays for the "read (+)" and "read (-)" buses. The simple, three electrode example is that shown in Figure 6 and the detailed arrangement used in the sensing head is shown in Figure 2. As a result of this switching scheme, the buffer amplifiers have two gains; a gain of 1 when switched out and a gain of 21 when switched in (provided, of course, that the other half of the input stage is also switched in).

With the entire system operational and distilled water pumped into the test cell, a series of recordings were made to check the system response time and the ability to reject common mode voltage. Figure 8 shows the output of the differential amplifier module under four example switching situations.

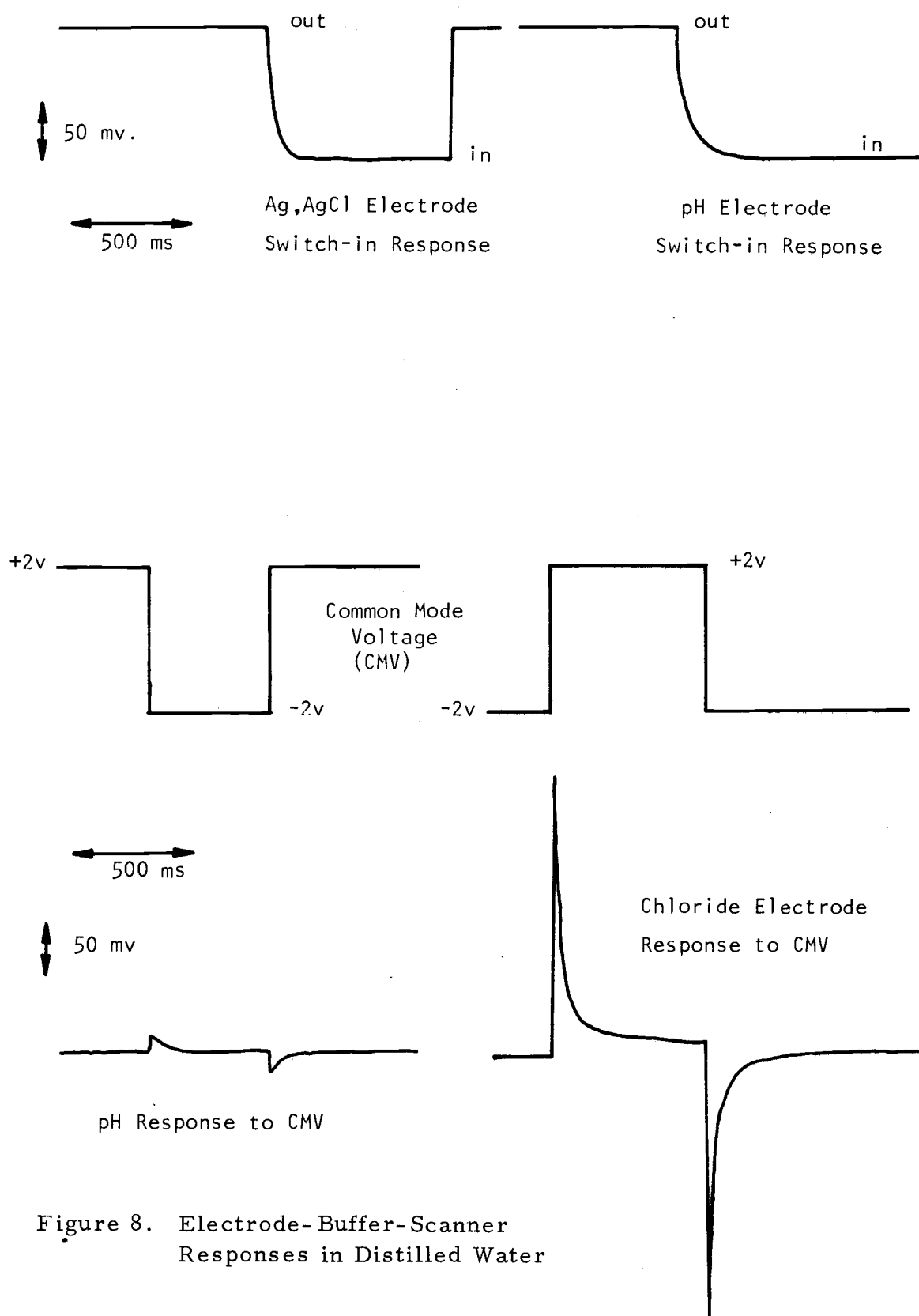


Figure 8. Electrode-Buffer-Scanner Responses in Distilled Water

Floating Controlled Current/Voltage Driver  
For Working Electrode

The working electrode and its associated driving and buffer amplifiers, were designed to provide the system with a capability for performing a wide range of electrochemical experiments. This module has three control modes; controlled current, controlled voltage and potentiometric. It also provides two outputs; the potential of the electrode, and a voltage proportional to the current through the electrode. Unlike the usual circuits for potentiostats and constant current sources found in electrochemical textbooks, all the control modes are floating with respect to the common ground of the system. The output of the programmable voltage source module becomes the input to the control circuit so that the computer can force any current or voltage condition that is desired for the working electrode. In other words, the system has the capability of such experiments as polarography on a stationary or moving electrode, chronoamperometry, chronopotentiometry, and some slow sweep voltammetry.

Figure 9 shows the working electrode module, configured in the controlled current mode (command 42<sub>g</sub>). Also shown is the reference silver/silver chloride electrode module as it would be connected in conjunction with the working electrode for the purpose of measuring

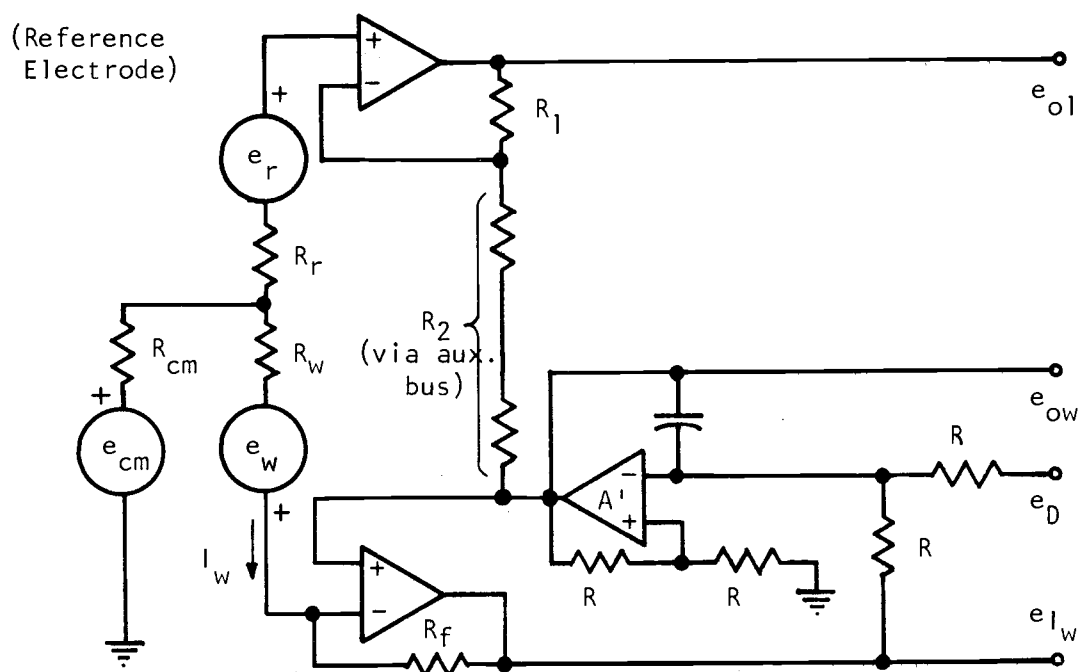


Figure 9. Working Electrode (Controlled Current Configuration)

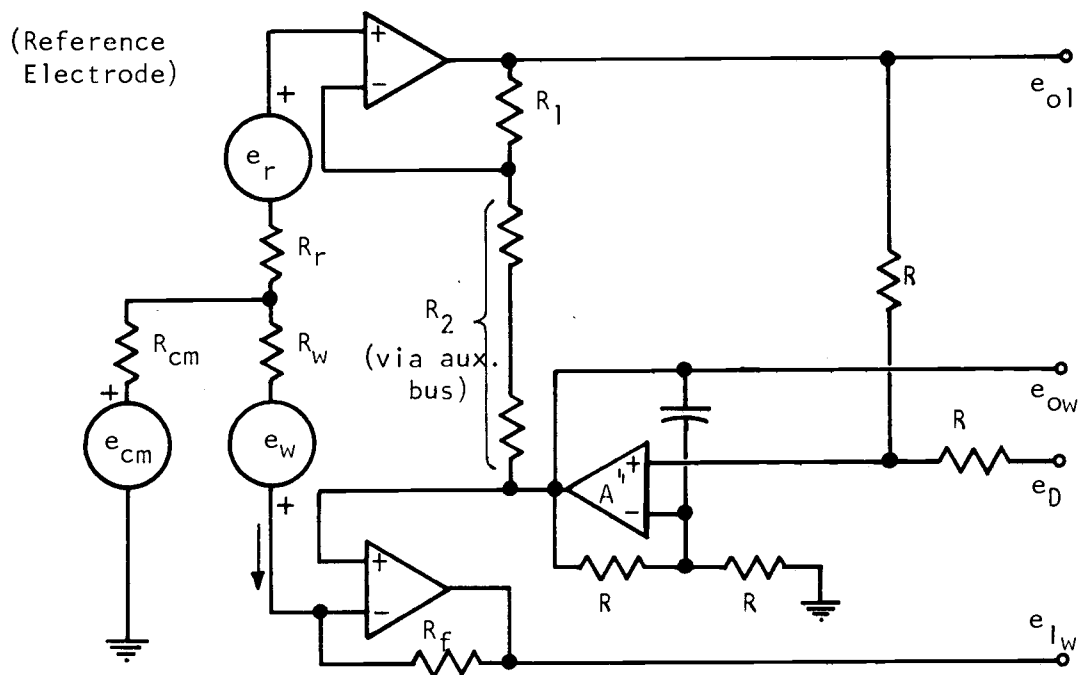


Figure 10. Working Electrode (Controlled Potential Configuration)

the potential of the working electrode (commands  $11_g$  and  $23_g$ ). Amplifier A' is shown as a single amplifier, where in fact it is a composite of two separate microcircuit amplifiers (amplifiers  $A_1$  and  $A_2$  in Figure 2). The actual working and reference electrodes are represented by their approximate Thevinin sources. The connection between the common of the operational amplifier network and the effective water potential is shown as a third electrode which develops a common mode potential,  $e_{cm}$ , as a result of electrochemical effects and local noise currents.

The control desired is that the current through the working electrode becomes a direct function of the drive voltage,  $e_D$ , derived from the programmed voltage source. By assuming all operational amplifier gains and input impedances are infinite, one can write simple expressions for the function of the circuit at low frequency. The working electrode buffer amplifier is configured as a current-to-voltage follower such that

$$e_{Iw} = e_{ow} - R_f I_w$$

Amplifier A' serves as a servo amplifier to force  $e_{ow}$  to a potential such that

$$I_w = e_D / R_f$$

which is the desired control relationship. The value of  $R_f$  was chosen to be 10 megohms, making the control factor  $10^{-7}$  amps per volt.

The usual laboratory electrochemical practice is to drive a counter electrode to achieve the current control. However, the effective counter electrode in this case is the grounding point. It was considered poor practice to attempt to drive ground when it was difficult to adequately control just where this grounding electrode was in this in situ environment.

The potential of the working electrode with respect to the reference electrode can be observed while the working electrode is in its controlled current mode. Noting that the reference electrode is buffered by a very high impedance, low bias current amplifier, one can neglect the voltage drop across  $R_r$ . Also, the effective working electrode potential, as normally observed in electrochemical methods, is really the sum:

$$e_w' \equiv e_w + I_w R_w$$

Writing an expression for the output of the reference electrode buffer;

$$e_{ol} = (e_{cm} - I_w R_{cm} + e_r) \cdot (1 + R_1/R_2) - e_{ow} R_1/R_2$$

and for the output of the driver servo amplifier;

$$e_{ow} = e_{cm} - I_w R_{cm} + e_w'$$

shows that if the difference voltage,  $e_{ol} - e_{ow}$ , is measured by the readout network, then

$$e_{ol} - e_{ow} = (e_r - e_w') \cdot (1 + R_1/R_2)$$

In other words the working electrode potential is a simple function of the observable difference voltage,  $e_{ol} - e_{ow}$ .

Figure 10 shows the same components configured into the controlled potential made by the command  $4l_8$ . The polarity of the servo amplifier is now inverted with respect to the current configuration, and the feedback point is now  $e_{ol}$ , instead of  $e_{Iw}$ . In this configuration, the potential of the working electrode  $e_w'$  can be driven as a direct function of  $e_D$  and the potential of the reference electrode,  $e_r$ . The operation of this circuit can be explained by writing the low frequency expression for the servo amplifier ( $A''$ ) output under these new conditions:

$$e_{ow} = e_D + e_{ol}$$

By substituting the expressions for  $e_{ol}$  and  $e_{ow}$  into this expression and solving for  $e_w'$ , yields

$$e_w' = e_r + e_D \left\{ \frac{R_2}{R_1 + R_2} \right\}$$

Hence, the working electrode potential can be controlled to any value



in the range of the circuit, independently of the electrode current,  $I_w$ , or the effective common mode voltage,  $e_{cm}$ .

The usual observations made in voltammetric experiments at controlled potential is the current delivered by the working electrode. This can be done here by measuring the difference potential,  $e_{Iw} - e_{ow}$ , which is directly related to the working electrode current by

$$I_w = -(e_{Iw} - e_{ow})/R_f$$

It was decided to scale the voltage drive of the working electrode so that it would be  $\pm 1.5$  volts about the reference electrode. Since  $R_1$  and a portion of  $R_2$  are associated with the reference electrode buffer, they have been chosen previously as 3920 and 196 ohms, respectively. The only resistance left to choose is the other part of  $R_2$  which is to be associated with the working electrode circuit and joined to the reference electrode circuit through the auxiliary bus. Since  $e_D$  has the range  $\pm 10$  volts, a gain factor of 6.5 is needed and a value of 509.4 ohms was selected as a convenient precision resistor to use. Consequently, the total value of  $R_2$ , as it appears in these equations, was 705.4 ohms which yields a control coefficient of 0.1525 volts per volt.

The third control mode for the working electrode is the potentiometric mode where the current through the working electrode is held at zero. The command, 43<sub>g</sub>, puts the working electrode into

its controlled current mode but forces  $e_D$  to be zero by connecting this input to common instead of to the programmed voltage bus. In this mode the working electrode behaves as a potentiometric electrode and the programmed voltage bus is free for other service. The working electrode is normally left in its potentiometric mode as this condition does not inject unwanted currents into the test cell to confound other experiments.

The foregoing explanation has considered the function in a rather idealized manner. Practical considerations of common mode rejection due to the amplifiers and their resistor networks limit the performance to about 63db rejection of the common mode voltage. The "leakage" current in potentiometric mode was below  $10^{-10}$  amps.

#### The Command Structure and the Logical Control of the Switching

The philosophy of the command structure and the switching logic design was to achieve the required switching as quickly as possible, within the limitation imposed by the telemetry link, and as simply as possible, within functional modular framework of the system. In order to make efficient use of the 110 baud telemetry link, it was desired to minimize the product of the bits per command, times the number of commands to effect a new setup or condition in the sensing head. In other words, there should be a few bits

transmitted as would be necessary to clear the previous conditions and establish the new conditions. On the other hand, the command structure must not be so complex that it involves extensive logic circuitry or makes it difficult to implement it on the functional module basis. This means that the format of the command should lend itself to a simple decoding scheme that would permit the decoding logic to be placed on the same circuit board as the buffer amplifiers and relay networks for any one particular functional module. It was estimated that the entire sensing head could be adequately served, with a little to spare, by a total set of 64 discrete control states (e. g. 32 relays) which would permit a total of 32 different, mutually exclusive, conditions.

Assigning each of the 32 relays an address and two states, would result in a simple scheme that could be simply effected within each module. However, it would require an average of four commands to effect a typical condition change involving the clearing of two relays and the setting of two others. Allowing provision for a parity bit plus a command word separation of two bit spaces, the total transmission would require the equivalent of 44 bits to effect a typical condition change by this command structure.

Another approach would be to assign a command to each condition that was desired. Such a scheme would require only 8 bits in a transmission per condition change. However, the logic

circuitry for this scheme was thought to be too complex to provide the degree of flexibility, modularity and logic circuit density that was desired.

The scheme employed in this design was a compromise between these two schemes. It was found that the entire set of conditions, desired for the immediate and envisaged for future projects, could be divided into eight groups. Those conditions, within any one group were mutually exclusive in that no two of them would be used at the same time. For example, all those conditions which involved a connection to the positive input bus would be placed in the "read (+)" group since the connection of more than one source to this bus would be meaningless. Once the conditions were grouped, it became apparent that there was generally just one relay, or at the most a pair of relays, that needed to be closed to form the desired condition. A six bit binary word was chosen as the command format. This was broken down into two octal bites, the first three bits defining the group type and the last three bits defining the number of the specific condition within that group. It was arranged for the command type and number to be decoded separately, so that the control flip-flops would be set on the condition that both the command type AND the command number for a given flip-flop had been decoded from the command. However, the clearing of a control flip-flop would occur whenever its group type was decoded, with the exception of the case

when its number was also decoded. Thus, it was arranged that when a new condition was desired, the issuing of the command to setup that condition also cleared any previous conditions which would have conflicted with the new condition.

Decoding of commands begins in the telemetry interface module. Here the six bit command code is broken into its two octal parts which are subsequently decoded into 8-line. These two 8-line groups are buffered out onto 16 buses, common to all functional modules. A one millisecond clock pulse, to signify the arrival of a new command, is generated and buffered out onto a separate bus. Any of the possible 64 commands can be applied to any given control flip-flop by selecting two lines (one from each of the 8-line groups) and ANDing them to enable the appropriate gate of the control flip-flop. Since only one of the eight lines in each 8-line group will be high for any given command, then only the control flip-flops controlled by both these lines will be affected at the fall of the clock pulse.

Each condition has its own control flip-flop. The status of this flip-flop maintains a number of relays or logic gates in states which determine the presence or absence of that particular condition within the sensing head. The logic circuitry for a typical control flip-flop and its associated steering gates and relay drivers are shown in Figure 11. Gates #1, #2, and #3, are part of the command

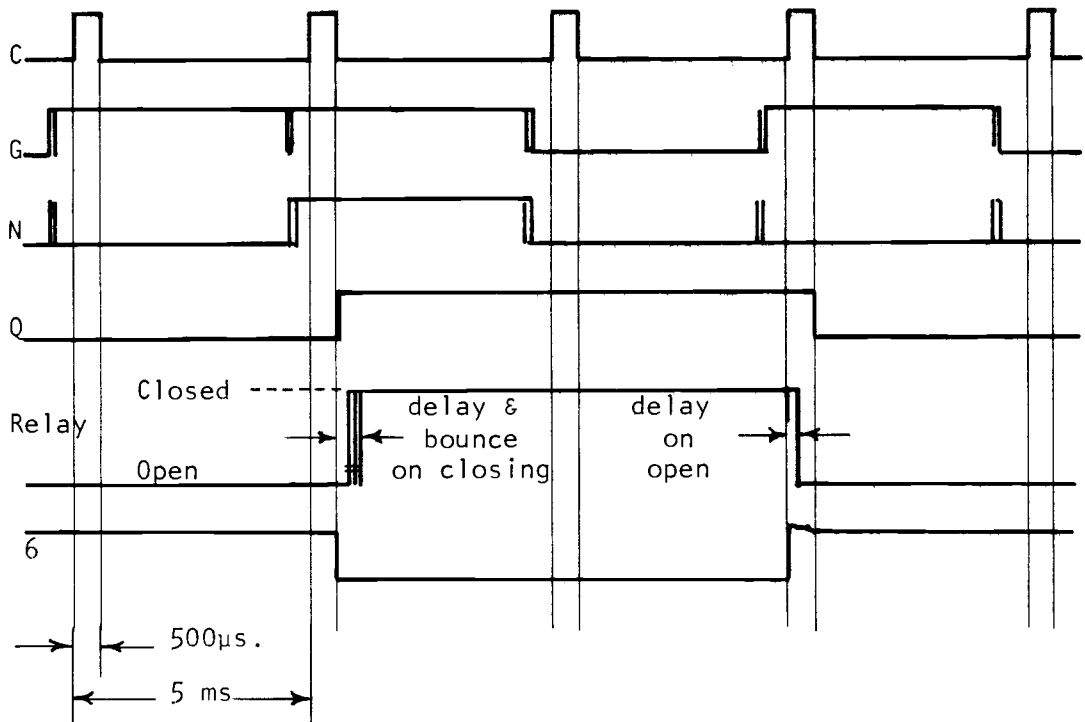
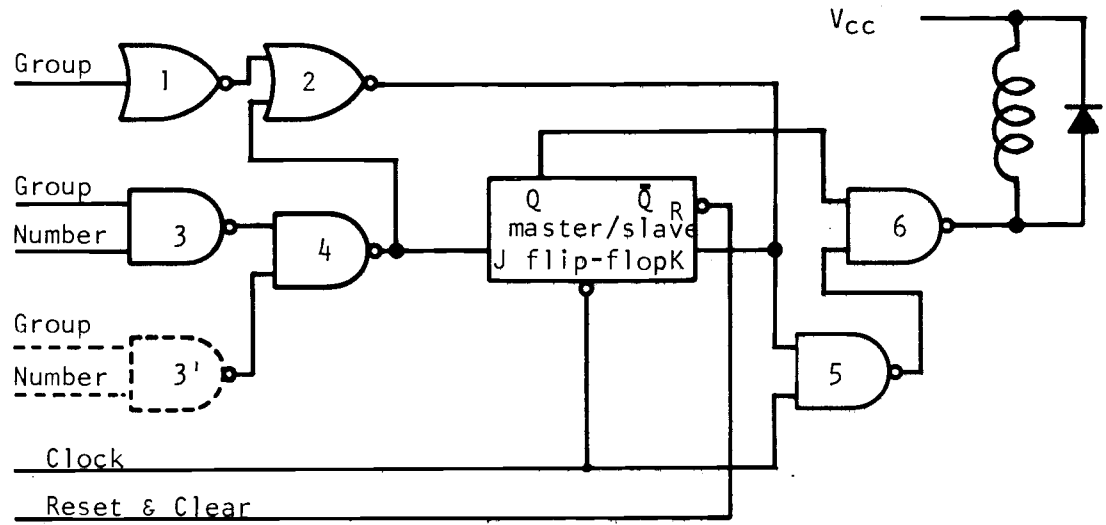


Figure 11. Logic and Timing Diagram for a Generalized Control Flip-Flop

decoding structure, but are physically located on the circuit board holding the control flip-flop. Setting the flip-flop in response to a specific command is accomplished by driving the inputs to NAND gate #3, from a selected pair of the two, 8-lines which carry the partially decoded command. Clearing the flip-flop in response to any command within a specific command group is accomplished by wiring the reset gate of the flip-flop to the appropriate 8-line decode of that command group. NOR Gate #2, forces the set condition to over ride the clear condition which, in general occurs coincidently. Since the control flip-flops are of the J-K, master/slave type, they will change their state following the fall of the clock pulse, provided that the appropriate conditions on their input gates were established prior to the rise of the clock pulse. This operation was exploited to effect a delay between the time a relay was disconnected from a bus to the time another was connected. Logic gates #5 and #6 drive the relay in such a manner that the disconnect occurs on the rise of the clock pulse and the closure occurs on the fall of the clock pulse. Thus the potential problem of momentarily shorting the outputs of the buffer amplifiers is avoided.

The logic is conventional transistor-transistor logic manufactured by Texas Instruments (7400 series TTL). The relays are all single pole, picoreed relays manufactured by C. P. Clare Company (PRB-3009H). This type has a five volt, 535 ohm coil so that it can

operate directly off the standard TTL output, however, a diode is placed across the coil to suppress the turn off transient. The logic gates, flip-flops, picoreed relays and other parts that constitute a given functional module, were mounted on one circuit board, which had a plug configuration in common with all other such functional modules.

Table 1 outlines the command set and coding assignment mode for this working model. Each line across in the table defines the command set which has members whose effect is mutually exclusive from the other members of that set. The assignments made were found to be very effective and no problems were ever attributed to this control scheme. The "mode" control set was introduced to provide a facility for controlling up to five other sensing heads from the same telemetry terminal. The effect of the mode control was to enable the command set for the respective sensing head. If the mode flip-flop is not set through this mode command, clock pulses to the functional modules are inhibited. The "reset" command in the mode set, not only clears a previous mode, but causes a reset pulse to be applied to all control flip-flops in the system. All control flip-flops were wired so that their "reset" state would effect a safe state in the device it controlled; either disconnect, stopped, zeroed or otherwise prevented from causing problems to the system. Needless to say, this is an effective "panic button" and is



Table 1. Command set for robot water quality analyzer

Octal code	Command Group Description	X0	X1	X2	X3	X4	X5	X6	X7
0X	System mode control	Clear	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Power on	Power off
1X	Read (+) after clearing (+) bus	$pH_R$	$Cl_R^-$	$pH_A$					Common Ground
2X	Read (-) after clearing (-) bus	$pH_R$	$Cl_R^-$	$Cl_A^-$	$E_w$				Common Ground
3X	Read (+) & (-) after clearing (+) & (-) bus.		Program volts	$I_{work}$	Ref. volts		Temperature		Valve pos.
4X	Set Up new configuration, clear old.	Control $E_w - E_{pH_A}$	Control $E_w - E_{Cl_A^-}$	Control $I_w$	Control $I_w = 0$	Free Drive bus.	Drive Aux. Elec.	Ground Aux. Elec.	
5X	Mechanical control	Stop	Pump fwd.	Pump rev.	Pump fast	Valve c. w.	Valve c. c. w.		
6X	Programmable voltage and D/A controls	Zero	+ polar.	- polar.	Set A/D = .003	Set A/D = 1.			
7X	Programmable voltage value setting								

programmed as the first step in the error recovery sequence.

### The In Situ Design

The design of the in situ sensing head was undertaken with a dual purpose in mind. The primary objective was to provide the apparatus needed to demonstrate the methodology proposed in this thesis. The second objective was to produce functional hardware that would represent one practical example of such apparatus which could eventually be operated in situ at 100 meter depths. The working model that resulted took the form of an incomplete prototype, lacking pressure cases, underwater cables and power supplies. The peristaltic pump, servo positioned valve, and all the electrodes were designed and constructed for operation by remote control under in situ environmental conditions.

Each electrode is packaged into a standard electrode assembly which houses the buffer amplifier and provides a guarded, high impedance connection through the pressure bulkhead. Figure 12 shows two examples of the electrode assemblies; the pH electrode on the left and the Ag, AgCl ("chloride") electrode on the right. Outwardly all electrode assemblies are identical, except in length and the particular detail of the active tip. Each one fits into a one inch diameter hole, made in the upper bulkhead and sealed by a double "O" ring. A flow cell screws onto the underside of each

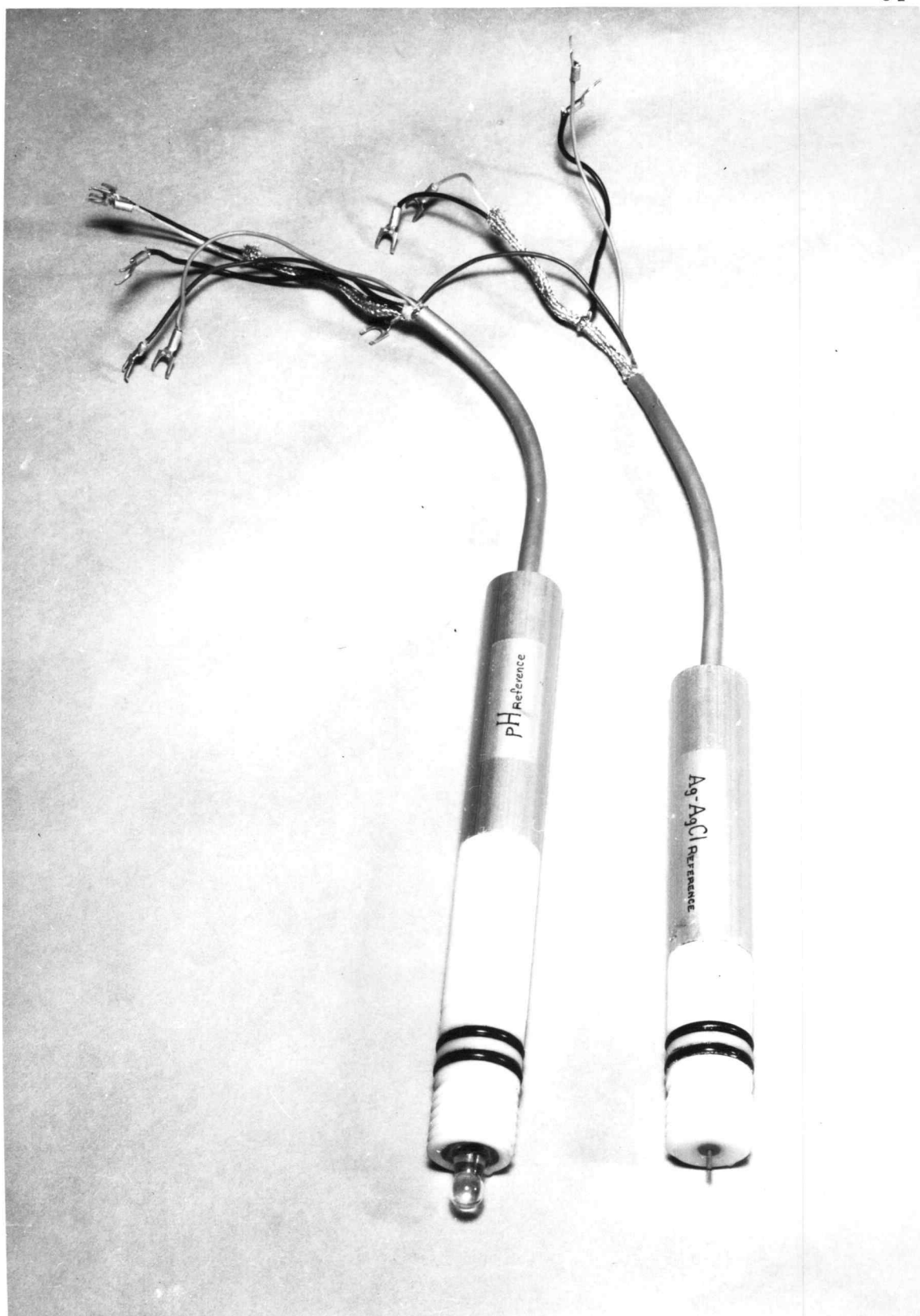


Figure 12. Electrode assemblies, pH and chloride.

electrode assembly, forming a nut which prevents it from being forced back inside by the external pressure.

The six electrode assemblies are arranged in a hexagonal pattern so that their active tips protrude through the upper bulkhead and their buffer amplifier portions remain above, in what would be the inside of the pressure case. See photograph in Figure 13.

Each flow cell is individually tailored to the shape of the electrode it houses and to the functional position it occupies in the test cell configuration. The cells are interconnected by either 1/4 inch Nylon or glass capillary tubing to form the test cell configuration in Figure 2. Efficient flushing was realized by designing the inflow and outflow ports so that a vigorous spiral circulation would result when the pump was operating in either direction. When an electrode assembly is mated with its flow cell, a Tygon washer<sup>8/</sup> is compressed against the shoulder of the flow cell, forming a seal with good electrical insulation between the water in the test cell and the surrounding lake water. Flow cell to tubing connections were made as compression fittings, reinforced with Silastic. Although, this means of making the fittings appeared to work well initially, it was later found that small electrical leakage paths developed through several

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<sup>8/</sup> The washer is made from a 1/16 inch slice of 3/4 inch Tygon tubing.

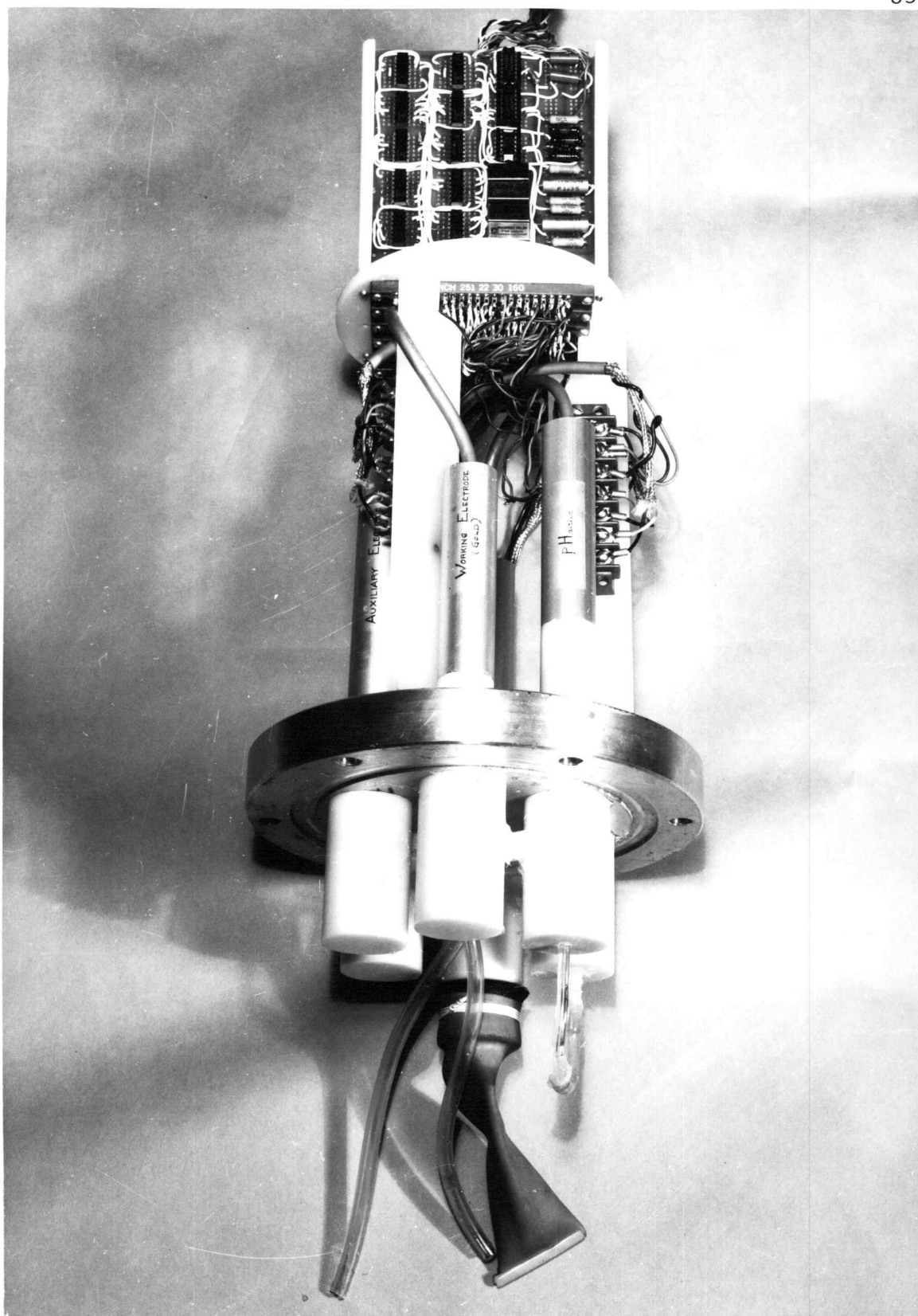


Figure 13. Electrode array portion of robot sensing head.

of these fittings which had been broken and remade during the course of development.

A peristaltic pump was selected for several reasons. Its main advantage in this system is that the water being pumped is kept inside Tygon tubing where it is electrically insulated from the outside water. Further, the roller pinching action effectively isolates<sup>9/</sup> the inflow and outflow streams, a fact upon which the conductivity measuring scheme depends. Since this kind of pump can move sufficient water against pressure heads in the order 20 psi., it was felt that a degree of electrode cleaning action could be realized with appropriately designed flowcells. Finally, there is the inherent advantage of peristaltic pumps that eliminate contamination from lubricating and sealing compounds, a problem with most other pump types.

The pump installed in this working model system was a laboratory peristaltic pump<sup>10/</sup> which had been specially ordered with all metal parts made from stainless steel. The pump head takes 1/4

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<sup>9/</sup> Input to output resistance was measured to be typically  $10^{10}$  ohms, with an extreme range from  $10^9$  to  $10^{11}$  ohms. These values were measured with 0.001 molar HCl in the pump after approximately 20 hours of continuous life on the tubing.

<sup>10/</sup> The unit was a Msterflex pump head #7017-1, manufactured by Cole-Parmer Instrument Company, Chicago.

inch Tygon tubing and delivers approximately 300 milliliters per second at 120 rpm.

The motor used to drive the pump in this working model was the same gearmotor assembly that normally drives the laboratory version of this pump. Since one of these motors and the associated speed controller were available, they were temporarily modified to serve in this apparatus. Later, with the experience gained from operating the working model, it would be a simple matter to procure a d. c. motor for the prototype which would drive the pump efficiently. The speed controller was modified by the addition of three relays which were driven from control flip-flops in the pump control module of the sensing head. These relays provided for forward-reverse control, plus a high (120 rpm) and a low (40 rpm) speed. The logic in the pump control module was interlocked to insure that the polarity reversing relay could not be changed while the motor was running.

Figure 14 shows the detail of the pump mechanism. The pump-head is mounted on the outside of the pressure bulkhead while the gearmotor assembly is on the inside of what would be the lower pressure case. A stainless steel shaft, with a rotary seal, couples the drive torque through the bulkhead.

A rotary plug valve was selected for this system because it was easy to mechanize within the system concept and because it

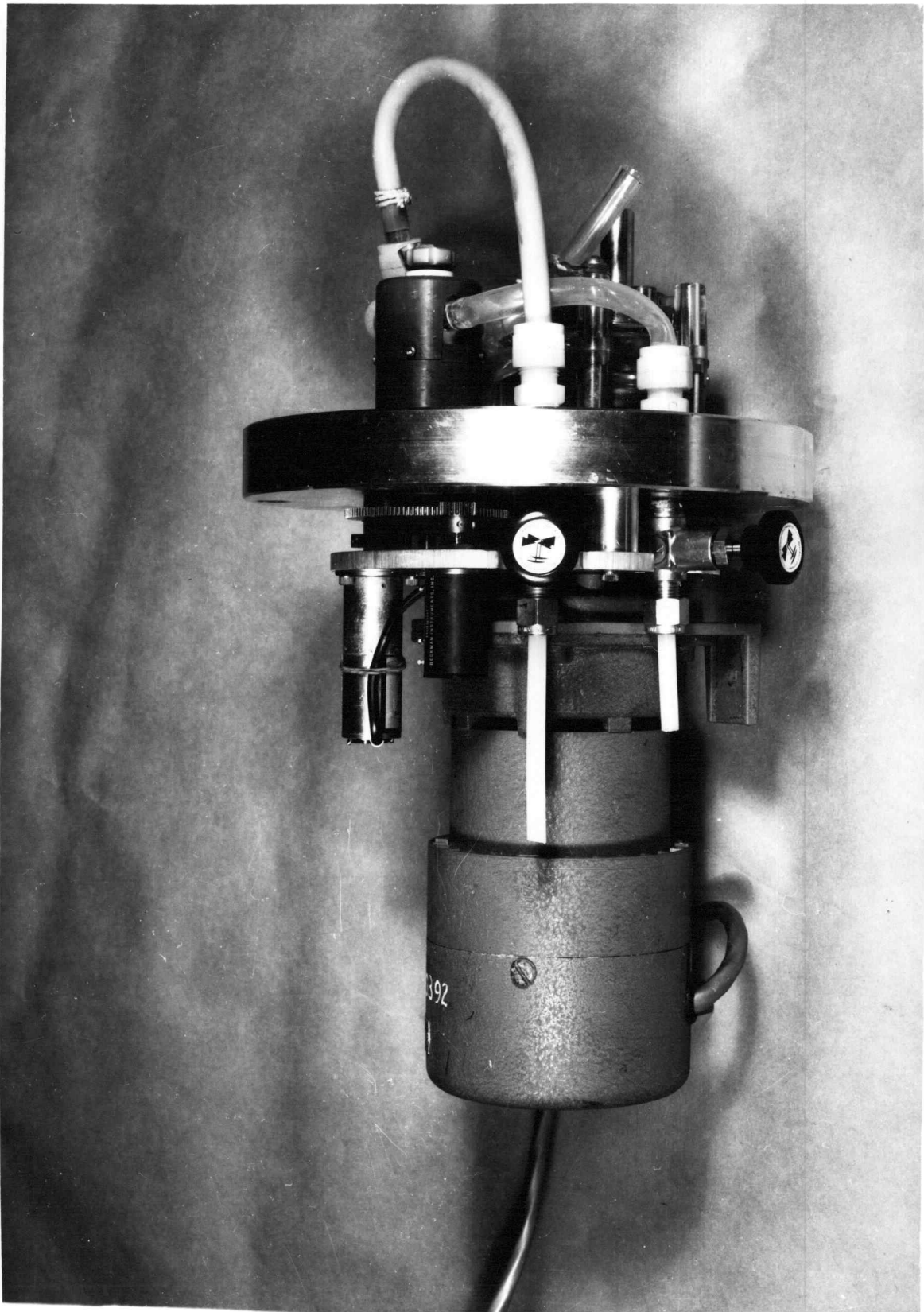


Figure 14. Pump and valve mechanism.



offered the possibility for multiple inputs and outputs with a single servo control. The valve was a conventional, Teflon in glass, stop cock fitted into a plastic holder which was mounted on the outside of the lower bulkhead. A d.c. gearmotor was arranged to turn the valve while a ten turn potentiometer, also geared to the same shaft, provided position feedback to the computer.

Two relays, driven from control flip-flops in the valve control module of the sensing head, provided three control states for the gearmotor: slew clockwise, slew counter-clockwise, and stop with brake. The drive circuits to these relays were interlocked with the pump motor stop command so that the pump had to be at rest before the valve could be moved.

The valve is set by a sequence of commands from the computer. Initially the valve position is sensed by switching the feedback potentiometer onto the "read (+)" bus and its position transmitted to the computer (command code  $37_8$ ). The computer then issues commands to the motor relays to cause rotation of the valve towards the desired position. In other words, this is a simple "bang-bang," relay servo system with feedback through a remote computer. There was an initial problem with this servo which resulted from the motor speed being too fast for the rate at which control commands could be sent over the low speed telemetry line. The situation was corrected by inserting resistance in series with the motor to reduce its

acceleration and by introducing, what amounted to, rate feedback into the digital control program. The maximum slew rate was thus reduced by only 10%, whereas the overshoot was reduced by 300%.

A key feature of the mechanical design was the means for coupling drive torques through the pressure bulkhead. A 5/16 inch diameter shaft, made of stainless steel was passed through the pressure bulkhead in a Turcite<sup>11/</sup> bearing. Two "Quad"<sup>12/</sup> rings, set in grooves in this shaft, formed a double seal against the inner diameter of the bearing. The Turcite bearing fittings are set into larger holes in the pressure bulkhead and sealed against the pressure by a conventional double "O" ring piston seal.

### The Liquid Junction

In this system, the reference solution serves the dual purpose of establishing the reference potentials for the potentiometric electrodes, and of supplying the hydrogen ion as a titrant for the alkalinity titration. The chemical composition of this solution and the physical structure of the interface between this solution and the water

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<sup>11/</sup> Turcite is a Teflon based material manufactured by W. S. Shamban and Co., California as "self-lubricating" bearing material.

<sup>12/</sup> Quad rings are the trade name for a special design of sealing ring having a cross-section like a four leaf clover. They offer better sealing and friction properties than conventional "O" rings in dynamic applications such as this one.

in the test cell were the design variables to be optimized.

To serve as a titrant in the "chloride tag" method, the reference solution must contain at least .01 N hydrochloric acid. However, the solution must also lend itself to the formation of a liquid junction having a potential associated with it which was either negligible (below  $\pm 1$  mv) or known by some calculation method. Since acid was an essential component of this solution, it was considered beyond reasonable expectations to expect to formulate a solution which would always provide a negligible junction potential. Therefore, it was decided to take the calculation route by attempting to make the junction simple so that it could be treated as a concentration cell with transference and its potential estimated with the Henderson equation.

Discussion of the Henderson equation can be found in most texts on physical chemistry such as Kortum and Bockris (1951). The equation used here was the general ion, integrated form based on an assumed linear diffusion model of the junction:

$$E_J \approx - \frac{RT}{F} \cdot \left\{ \frac{\sum \frac{\lambda_i}{z_i} (c_i'' - c_i')}{\sum \lambda_i (c_i'' - c_i')} \right\} \ln \left\{ \frac{\sum c_i'' \lambda_i}{\sum c_i' \lambda_i} \right\}$$

where  $E_J$  = diffusion potential (herein referred to as the junction potential.)

$\lambda$  = equivalent ionic conductance

$z$  = valence of ion

$c'$  = concentration of stronger solution

$c''$  = concentration of weaker solution

$i$  = subscript denoting  $i^{\text{th}}$  ion.

Underlying this equation are the following assumptions.

1. Concentrations of the solutions on either side of the junction are in range where the Debye-Hückel limiting law is valid.
2. Concentrations are low enough to permit equating concentration and activity terms.
3. A linear diffusion gradient exists between the two solutions.

A simple solution of hydrochloric acid was chosen as the reference solution. The concentration was made one tenth normal as a compromise between two factors. In order for the junction potential to be relatively insensitive to the usual variety and concentrations of ions in natural water, then the reference solution concentration,  $c'$ , was made about two orders of magnitude larger than the mean ionic strength of 0.002 M expected in the natural waters. Setting  $c'$  much greater than  $c''$  in the Henderson equation reduces the influence from the ions in the test water. It was hoped that by making the concentration 0.1 molar, the first two assumptions in the Henderson equation would be sufficiently valid that the equation could be used to calculate the junction potential in this system.

The structure of the water-reference solution interface was designed to approximate the linear diffusion assumption made by Henderson. The junction was made in a 1 mm. glass capillary tubing about 15 cm. long. A gold plug, 1/8 inch long, was placed in the capillary at the reference solution end to reduce free flow through the tube. A slow leak of reference solution by the gold plug was arranged for by making longitudinal scratches along the gold surface. Since the reference solution is stored in a flexible reservoir, buoyed up by the surrounding water in which it sits, there is little pressure difference across this capillary tubing under normal conditions. Figure 2 shows the schematic of this plumbing arrangement. However, when the pump is running in the forward direction at high speed, a pressure drop is induced inside the test cell which tends to draw reference solution into the test cell at a rate of about eight microliters per second. Similarly, the running of the pump in high speed reverse, induces the opposite situation where test water is pushed into the capillary towards the reference solution. A sequence of pump and valve operations was devised whereby the mean interface between the two solutions could be set up about half way in this capillary tubing. The position and diffuse nature of this junction was verified by direct observation with a test water containing a pH color indicator. A set of operations and timing intervals were selected from hours of trial and error testing as that which gave

stable and reproducible potentials. With most solutions, including tap water, the potentials observed for pH and chloride measurements were reproducible within 200 microvolts.

### The Titration Interpreter Program

The titration experiment for the determination of total alkalinity and total inorganic carbon, as presented in Chapter IV, is quite complex. It was decided that this experiment constituted a good example on which to attempt an interpretation incorporating the methods proposed in Chapter III for the INTERPRETER program. The actual program was written in FORTRAN IV and run on a Control Data Corporation 3300 Computer. The following is a brief report on the interpretation programming as developed to evaluate the working model system and to produce the results for this thesis.

For convenience of expression, the data table from the titration experiment is treated as an  $n \times 4$  matrix called,  $\bar{X}$ . The first row in this matrix is the set of readings;  $E_{pH}$ ,  $E_{Cl}$ ,  $C_{ond}$  and  $T$ , which were made by the ROBOT OPERATOR on the natural water sample (i.e. the initial readings). Each successive row is a similar set of readings taken after each successive addition of HCl titrant.

It is also convenient to create a coefficient vector,  $\bar{\theta}$ , which contains all the significant parameters and calibration coefficients needed in the interpretation process. Here, this vector is

specifically defined to contain the water parameters:  $C_{\text{Tot}}$ ,  $C_X$ ,  $\text{pH}_i$  (the initial pH),  $\text{pCl}_i$  (the initial pCl) plus the calibration coefficients:  $K_{\text{pH}}$ ,  $E_{\text{PZ}}$ ,  $K_{\text{Cl}}$ ,  $E_{\text{CZ}}$  and  $K_{\text{cell}}$ . Initially, each of these variables is assigned the best value known for that parameter or coefficient. A good guess is usually available as a previous value or from a recent calibration test.

The first stage of the interpreting program is the application of the transfer functions which are summarized in Table 2 in the order that they are processed. Since the first functions require variables for which the exact values are unknown initially, the solution of the equations is iterative. For the first pass, values for  $E_J$  and  $\gamma$  are guessed to be 0.080 volts and 1, respectively. Values for  $C_{\text{Tot}}$  and  $C_X$  are taken from the coefficient vector  $\bar{\theta}$  and not improved by the iterative procedure at this stage. Fairly large errors (10 - 30%) in the estimation of these two variables cause little change in the computed values for pH, pCl and K. An iterative solution to the equations in Table 2 is found for each of the  $n$  rows in the  $\bar{X}$  matrix. The solution of each set of input readings results in values being assigned to the variables pH, pCl, K,  $\gamma$ ,  $I$ , and  $E_J$ . The matrix formed by these solution vectors is designated  $\bar{Y}$  and has the dimensions  $n \times 6$ .

The functions in Table 2 involve a number of factors which are usually regarded as constants at 25°C. In practice the system

Table 2. Summary of basic equations.

$$\text{pH} = (E_R - E_{\text{pH}} + E_{\text{PZ}} + E_J) / K_{\text{pH}} \quad (1)$$

$$a_{\text{H}^+} = 10^{-\text{pH}} \quad (2)$$

$$[\text{H}^+] = a_{\text{H}^+} / \gamma \quad (3)$$

$$[\text{OH}^-] = K_w / (a_{\text{H}^+} \gamma) \quad (4)$$

$$\text{pCl} = (E_R + E_{\text{Cl}} - E_{\text{CZ}} - E_J) / K_{\text{Cl}} \quad (5)$$

$$a_{\text{Cl}^-}^* = 10^{-\text{pCl}} \quad (6)$$

$$a_{\text{Cl}^-} = a_{\text{Cl}^-}^* - K_{\text{SP}} / a_{\text{Cl}^-}^* \quad (7)$$

$$[\text{Cl}^-] = a_{\text{Cl}^-} / \gamma \quad (8)$$

$$[\text{CO}_3^{=}] = C_{\text{Tot}} / (1 + \beta_1^* a_{\text{H}^+} + \beta_2^* a_{\text{H}^+}^2) \quad (9)$$

$$[\text{HCO}_3^-] = \beta_1^* \cdot a_{\text{H}^+} [\text{CO}_3^{=}] \quad (10)$$

$$[\text{H}_2\text{CO}_3] = \beta_2^* a_{\text{H}^+}^2 [\text{CO}_3^{=}] \quad (11)$$

$$\text{where } \beta_1 = \beta_1 \gamma^{3/2} \quad \text{and} \quad \beta_2^* = \beta_2 \gamma^{5/2}$$

$$K = \text{Cond} \cdot K_{\text{cell}} \quad (12)$$

$$E_J = -0.0591 \frac{\phi_N}{\phi_D} \log_{10} \left\{ \frac{1000 K}{0.1 (\lambda_{\text{H}} + \lambda_{\text{Cl}})} \right\} \quad (13)$$

$$\begin{aligned} \text{where } \phi_N = & \lambda_{\text{H}} [\text{H}^+] + \lambda_{\text{x}} [\text{C}_{\text{x}}] - \lambda_{\text{OH}} [\text{OH}^-] - \lambda_{\text{Cl}} [\text{Cl}^-] \\ & - \lambda_{\text{HCO}_3} [\text{HCO}_3^-] - 1/2 \lambda_{\text{CO}_3} [\text{CO}_3^{=}] \\ & - 0.1 (\lambda_{\text{H}} - \lambda_{\text{Cl}}) \end{aligned}$$



Table 2. Continued.

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$$\text{and } \phi_D = 1000 \text{ K} - 0.1 (\lambda_H + \lambda_{Cl})$$

$$I = \frac{1}{2} \left\{ [H^+] + [C_x] + [OH^-] + [Cl^-] + [HCO_3^-] + 4[CO_3^{=}] \right\} \quad (14)$$

$$\gamma = 10^{-0.509 \sqrt{I}} \quad (15)$$


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obtains its measurements at the in situ temperature. Hence, all constants appearing in Table 2 are adjusted to the in situ temperature by appropriate methods (detail of these methods is given in appendix G). These adjusted values are stored in the constant<sup>13/</sup> vector  $\bar{B}$ .

The computational process for this first stage of the titration interpreter program can be summarized as the iterative solution of:

$$\bar{Y} = (\bar{X}, \bar{\theta}, \bar{B}, \bar{Y}^*)$$

where  $\bar{Y}^*$  is the first approximation of  $\bar{Y}$ .

The second stage of the interpreting program is the computation of better elements of the coefficient vector,  $\bar{\theta}$ , by the method of nonlinear regression with parameter estimation. A thorough discussion of regression analysis, as it pertains here, falls outside the scope of this thesis. Nevertheless, direct application of an I. B. M. subroutine<sup>14/</sup> called nonlinear regression with parameter estimation

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<sup>13/</sup> In the program it was found necessary to compute a new B vector for each set of readings because the temperature of the water in the test cell exhibited a significant rise during the titration experiment. The rise in temperature is attributed to the pressure test vessel, in which the simulation took place, being above sample temperature. In actual field operation the surrounding water will provide a heat sink at the in situ temperature and only one B vector would be computed.

<sup>14/</sup> NLREG is based on the modified Gauss-Newton method for fitting of nonlinear regression functions as described by Hartley (1961). The actual listing for this subroutine cannot be made available as it is part of a commercial Numerical Subroutine Package.

(NLREG), was made to demonstrate some of the unique advantages to be realized from this analytical experiment approach. In particular, it was intended to show one method for observing water quality parameters for which there are no specific sensors, and to give examples of autoverification and autocalibration.

The method of nonlinear regression takes a limited subset of the coefficient vector  $\bar{\theta}$  and finds improved values for each. Improvement is defined to be a reduction in the mean square error between readings from the matrix,  $\bar{X}$ , and theoretical values generated from mathematical models. These mathematical models take into account all significant descriptions of the water chemistry and the processes involved in the analytical experiment. Normally one of the columns from the input matrix (i. e. all successive readings of one observation such as  $E_{\text{pH}}$ ) is regarded as the dependent variable, while the other columns of  $\bar{X}$  are regarded as independent variables and used as driving inputs to the mathematical model. Both the models, themselves, and the manner in which the "error" is defined are the important aspects in the application of nonlinear regression to this interpretation problem. Hence, brief descriptions will be presented on the "conductivity" and "alkalinity conservation" models used in the interpretation of data from the simulated operation of the working system.

The conductivity of dilute solutions can be estimated by taking

the sum of all significant ionic concentrations, multiplied by their respective equivalent ionic conductances ( $\lambda$ ). Hence the first model applied was based on the theoretical conductivity,  $K_T$ , using the following series of equations:

$$K_T^* = \left\{ \lambda_H [H^+] + \lambda_{OH} [OH^-] + \lambda_{Cl} [Cl^-] + \lambda_{HCO_3} [HCO_3^-] + 2 \lambda_{CO_3} [CO_3^{--}] + \lambda_{C_x} C_x \right\} \div 1000 \quad (16)$$

$$\Lambda_T^* = 1000 K_T^* \div I \quad (17)$$

$$\Lambda_T = \Lambda_T^* - (60.2 + 0.229 \Lambda_T^*) \sqrt{I} \quad (18)$$

$$K_T = \Lambda_T \div 1000 \quad (19)$$

Equation (18) is the Onsager equation employed to correct the theoretical conductivity for interionic effects in weak electrolyte solutions. All the terms in these equations are either used or calculated in the first stage of this interpreter program. The error term for the regression analysis is

$$\epsilon_C = K - K_T$$

and the quality of the fit between theory and observation is

$$Q_C = \sqrt{\frac{1}{n} \sum_{j=1}^n \epsilon_{cj}^2}$$

The conservation of alkalinity provides another base for a theoretical model. For a water having significant amounts of carbonate and bicarbonate alkalinity only, one can define the total alkalinity to be:

$$A = [\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{H}^+] - [\text{OH}^+]$$

which can be written as a function of hydrogen ion activity;

$$A = \frac{C_{\text{Tot}} \left\{ \beta_1^* a_{\text{H}^+} + 2\beta_2^* a_{\text{H}^+}^2 \right\}}{1 + \beta_1^* a_{\text{H}^+} + \beta_2^* a_{\text{H}^+}^2} + \frac{a_{\text{H}^+}}{\gamma} - \frac{K_w}{a_{\text{H}^+} \gamma}$$

When  $a_{\text{H}^+}$  is computed from the original pH of the water, then  $A$  is the initial or total Alkalinity,  $A_i$ . After some HCl titrant has been added, one can still compute an alkalinity value for this solution using the actual pH as computed from the  $E_{\text{pH}}$  reading for that stage in the titration.  $C_{\text{Tot}}$ , as a parametric property of the water, remains unchanged. The initial alkalinity and subsequent values of computed alkalinity are related by:

$$A_j = A_i - [\text{HCl}]$$

where  $[\text{HCl}]$  = the effective concentration of added acid

which may be regarded as the number of equivalents of HCl added divided by the volume of the test cell.

A value for  $[HCl]$  can be computed using the chloride ion as a tag, by regarding the increase in chloride ion concentration as a direct measure of the effective HCl concentration, i. e.

$$[HCl] \equiv [Cl^-]_j - [Cl^-]_i$$

With this, it is now possible to define another error term for regression analysis as

$$\epsilon_A = \frac{A_i - A_j - [HCl]}{A_i + A_j + [HCl]}$$

and the quality fit between theory and observation is:

$$Q_A = \sqrt{\frac{1}{n} \sum_{j=1}^n \epsilon_{Aj}^2}$$

If the first reading of  $E_{pH}$  includes a measurement error then the effect of this error is multiplied since it is used to compute  $A_i$ . Consequently, the term,  $pH_i$  was introduced into  $\theta$ . The regression subroutine will adjust a guess value for  $pH_i$  in the same manner as it will adjust all coefficients in  $\bar{\theta}$ . The same reasoning introduced  $pCl_i$  as a coefficient in  $\bar{\theta}$ .

As outlined to this point, the success of the method in converging on realistic values for  $C_{\text{Tot}}$ ,  $\text{pH}_i$ ,  $C_x$  and  $\text{pCl}_i$ , depends upon having good guesses for these values.

Therefore, these values are guessed from simple considerations. First,  $\text{pH}_i$  and  $\text{pCl}_i$  are assigned the corresponding values from the first solution vector,  $\bar{Y}$ . Next, an approximate value of total alkalinity is found, by a linear interpolation of the titration curve. The  $[\text{HCl}]$  value is taken when the pH reading is 4.5, the typical equivalence point of a total alkalinity titration.  $C_{\text{Tot}}$  is computed from this interpolated alkalinity value and put into the coefficient vector. Finally,  $C_x$  is computed as that value of equivalent concentration of  $\text{Na}^+$  ions which makes the theoretical conductivity equal to the measured conductivity. On the chance that one of these pre-guessed values may turn out to be less than zero, then the detection limit is inserted in the coefficient vector in its place.

The flow chart in Figure 15 summarizes the major steps of this interpreting program just described. The actual program used to interpret all the data presented in this thesis is listed in appendix "D" and its effectiveness is discussed in the next chapter.

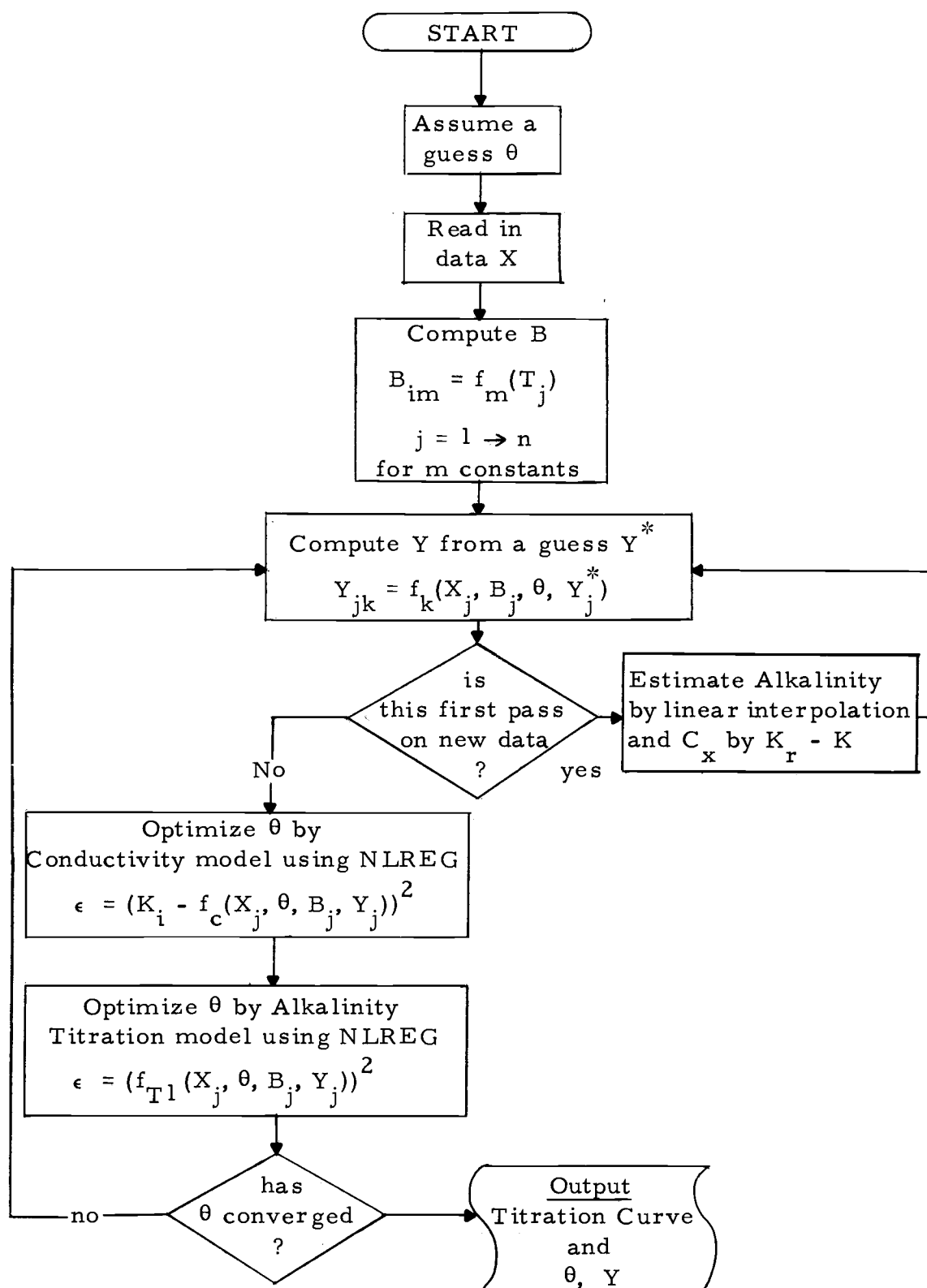


Figure 15. Flow chart of interpreter program.



## VI. SIMULATION OF A WORKING MONITOR STATION AND RESULTS

### Apparatus Configuration

Figure 16 shows the configuration of computer elements, the prototype sensing head and other apparatus which were used to simulate a complete working monitor system. The array of six electrodes with their buffer-drive circuitry were mounted above the pump-valve mechanisms with their controller circuits. The flow cells around each electrode, the valve and the pump were interconnected by sections of Nylon or Tygon tubing to form the "test cell" configuration depicted in Figure 2. The method of patching the sensing head into the EAI 690 Hybrid Computer is also shown. A strip-chart recorder, although not part of the simulated system, was occasionally used to provide a handy display of the detailed activities going on inside the sensing head. All data reported in this chapter was obtained from this test configuration. To simulate a lake environment a special pressure vessel was made. A short length of pressure casing was sandwiched between the two bulkheads and secured by six bolted rods. The upper bulkhead held the electrode array with the flow cells arranged so that they were inside the pressure vessel. The lower bulkhead held the pump and valve mechanism. Tap water was put inside this vessel and a means for

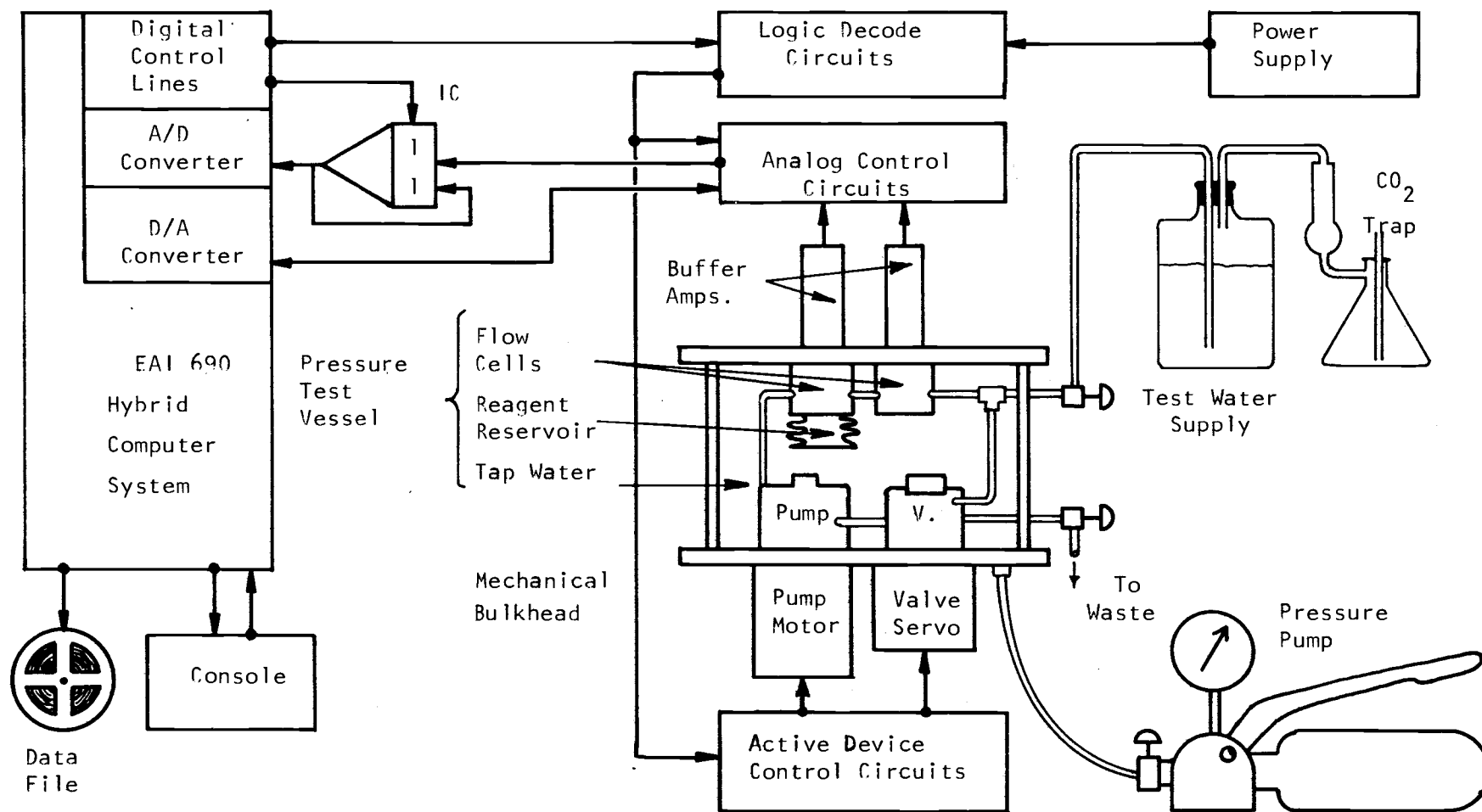


Figure 16. Apparatus Configuration for Working Model Simulation

pumping the hydrostatic pressure up to 150 psig was provided in order to simulate submergence to 100 meters in lake water. The test configuration may be considered as an "inside-out" configuration of the intended operational system where all critical aspects of the design are subjected to realistic in situ conditions.

Separate input and output ports to the test cell were provided so that known test solutions could be submitted to the robot sensing head without mixing with the water in pressure vessel. These ports were fitted with manual valves so that the vessel could be pressurized to its full range without generating large pressure differences between the water in the test cell and the tap water surrounding it. A short length of surgical rubber tubing formed the output section from test cell, thereby providing a mechanism for equalizing any residual pressure difference due to differential volumetric contraction on pressurization, (mostly due to tiny, trapped air bubbles). Outside the pressure case an enclosed system of tubing, including a caustic trap for CO<sub>2</sub>, was used to minimize atmospheric contamination of the fairly basic and poorly buffered test solutions.

### Calibration

A series of solutions were prepared (see appendix F) to test the working model system over its ranges for the parameters pH, conductivity and pCl. The data generated by the sensing head was

submitted to the interpreting program, stage one only. For each of these test solutions, the pH, conductivity and pCl values were known by the solution formula or by independent analysis. These known values were taken as standards and the coefficients,  $E_{PZ}$ ,  $E_{CZ}$ ,  $K_{pH}$ ,  $K_{Cl}$  and  $K_{cell}$  were found by conventional graphical techniques, using the computer generated values of  $E_j$ ,  $\gamma$  and  $\lambda$ 's where these factors were needed.

The cell constant of the conductivity configuration was found to be  $0.51 \text{ cm}^{-1}$  from the conventional calibration method using 0.01 M KCl as recommended by Jones and Bradshaw (1933). Before every set of system trials a series of 0.1, 0.01, 0.001 and 0.0001 N HCl solutions were run through the sensing head and the cell constant checked as function of concentration (and time since about 10 trials were attempted). The mid range (1000 to 100  $\mu\text{mhos}$ ) was good, repeating to within  $\pm 1\%$  of  $0.51 \text{ cm}^{-1}$ . The major factor limiting the repeatability in this conductivity experiment was the instability of the "chloride electrode" in dilute solutions which caused the measured quantity,  $E_{pH} - E_{Cl}$ , to change slightly during the experiment.

The pH configuration was tested with a series of diluted NBS buffer solutions (pH 4, 7 and 9), a dilution series of the standard 0.1 N HCl solution (0.01, 0.001 and 0.0001 N) and some other pH buffer solutions. As a result of the liquid junction potential having to be calculated from a simple model it was considered necessary to

keep the total ionic strengths of the test buffer solutions about 0.001 eq./l. A precision, Corning pH meter<sup>15/</sup> with documented electrodes and careful standard NBS calibration was used as the referee standard to determine the pH of the test solutions. Samples were taken in glass bottles and sealed with caps until the very moment of the referee testing. Despite this caution, it was found that for these weakly buffered, basic solutions, the change in pH reading during the referee testing itself was typically -0.05 pH units with fluctuations of  $\pm 0.02$  pH units, probably related to the gentle stirring action. This not only suggests the tolerance for these referee measurements but points out the difficulty encountered by conventional laboratory technique when working the high pH, low buffered natural waters.

Figure 17 shows the calibration curve that resulted from submitting these test solutions to the working model, sensing head. The millivolt readings on the ordinate in Figure 17 are computed from values, generated by the first stage<sup>16/</sup> of the interpreter program, as follows;

---

<sup>15/</sup> The assistance of Dr. Gordon, Dept. of Oceanography, Oregon State University is recognized for the loan of the pH meter and his consulting on this referee method.

<sup>16/</sup> The interpreter program was run with  $E_{PZ}$  and  $E_{CZ}$  forced to zero and  $K_{PH}$  and  $K_{Cl}$  forced to 59.16 mv./dec,  $C_{Tot}$  and  $C_x$  were forced to 0.001 effecting the ionic strength of 0.001 which was the approximate dilute strength of these dilute buffers. The acid solutions were run with  $C_{Tot}$  and  $C_x = 10^{-6}$ .

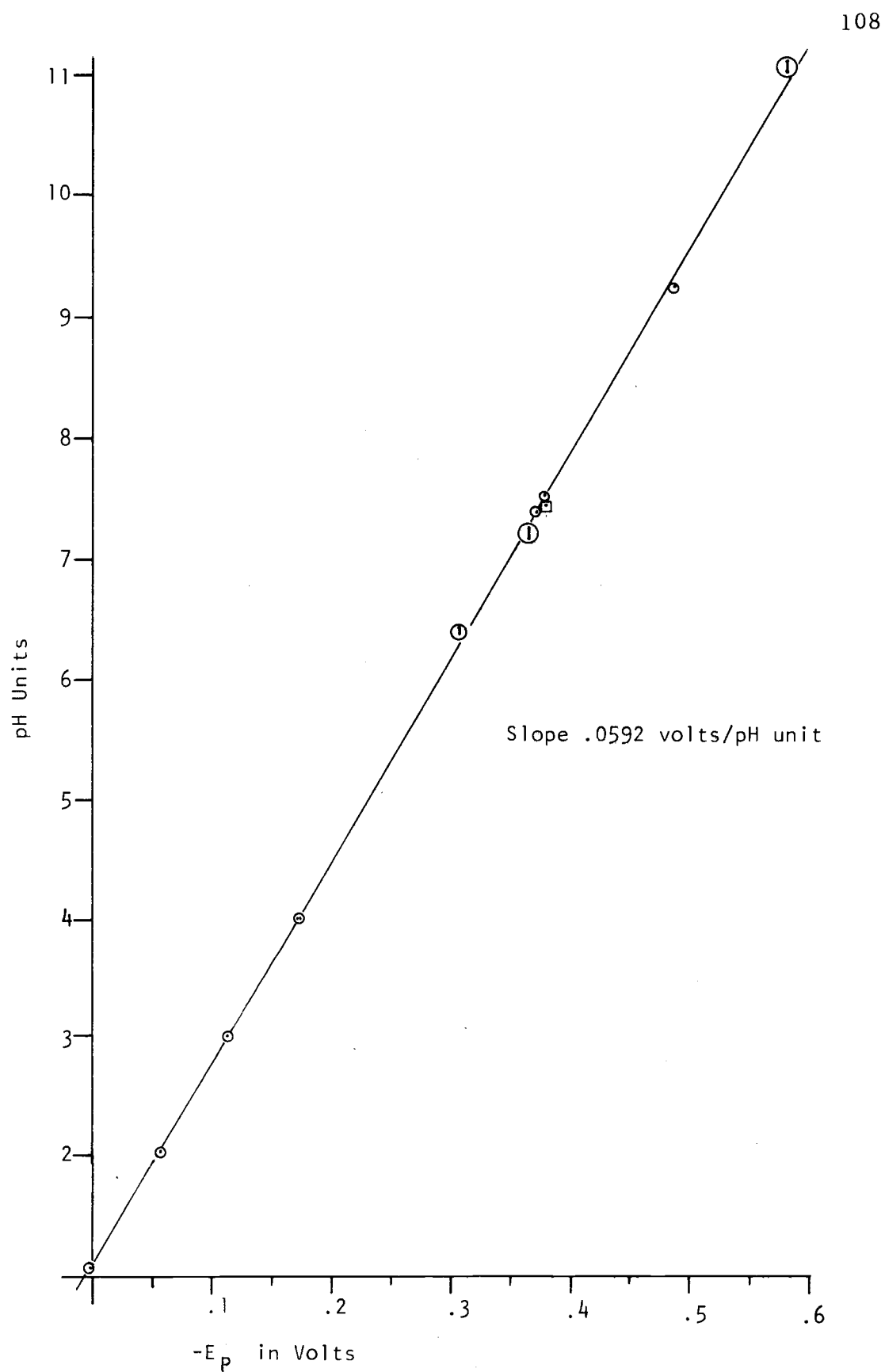


Figure 17. Calibration of pH Method

$$E_P = (-E_{pH} + E_J) \cdot \frac{298}{T + 273}$$

Hence,  $E_P$  is the voltage that the active pH electrode develops at 25°C with respect to the reference pH electrode, junction effects being effectively removed. The slope of this response curve was determined to be 59.2 mv/pH unit, with an apparent  $E_{PZ}$  potential of 0 mv. This curve demonstrates that the pH experiment produces pH values which correspond with standard pH measurement methods to within  $\pm 0.1$  pH units.

Figure 18 shows the response curve for the chloride ion experiment, as determined from two calibration runs, several days apart. The solutions were the same ones used for the pH calibration. Some of the diluted buffers also contained  $Cl^-$  at  $5 \times 10^{-5}$  N. The activities were calculated using the known  $[Cl^-]$  and the activity coefficient computed by the first stage interpreter. The values of  $E_C$  were computed from

$$E_C = (E_{Cl} - E_J) \cdot \frac{298}{T + 273}$$

Hence,  $E_C$  is the voltage that the active Ag, AgCl electrode develops at 25°C with respect to the reference Ag, AgCl electrode, junction effects being effectively removed. The slope of the response curve was found to be 57.6 mv/decade with an  $E_{CZ}$  offset of +0.001 mv. The curve demonstrates that reasonable performance was obtained

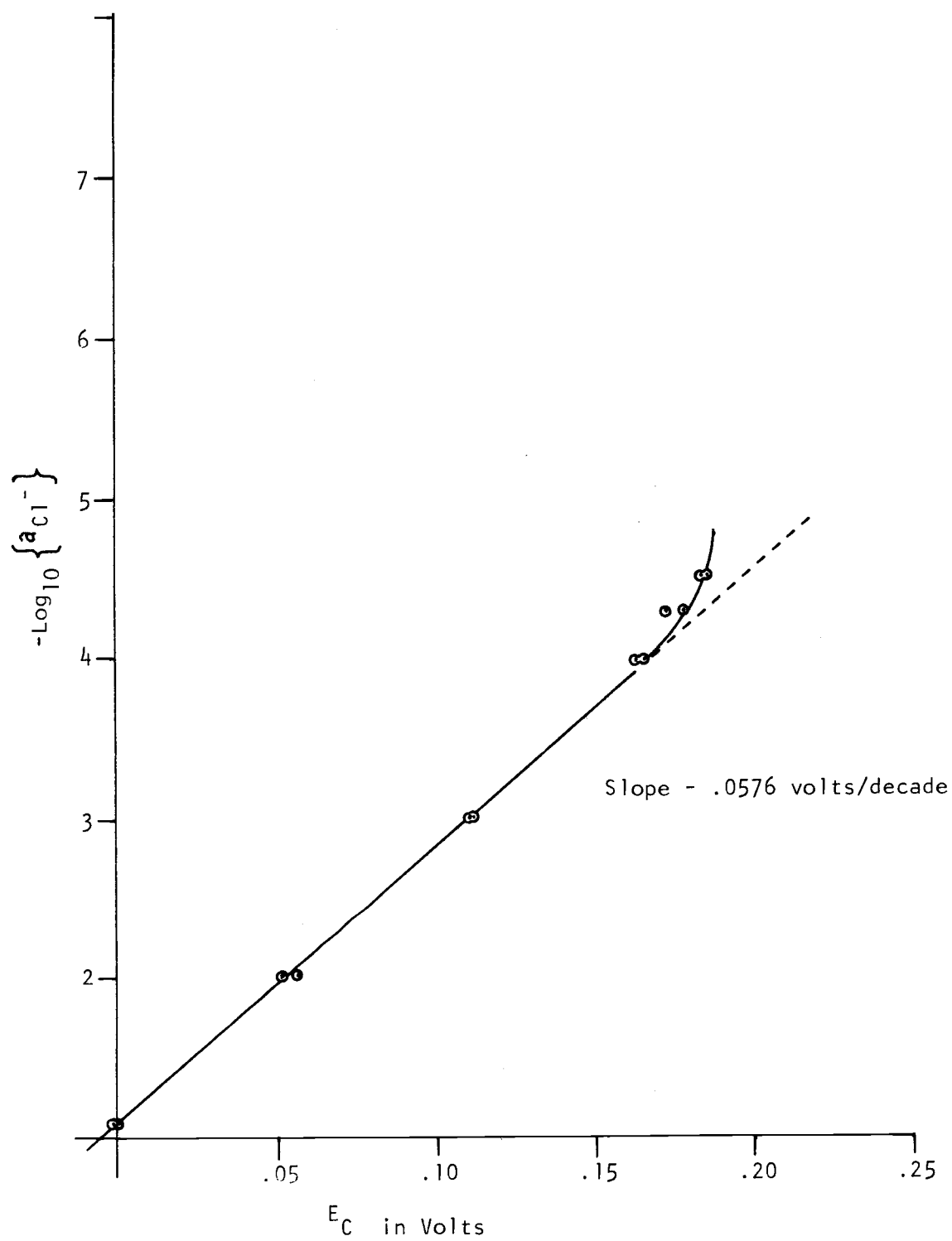


Figure 18. Calibration of Chloride Method



from the chloride experiment with a typical accuracy of  $\pm 5\%$  of reading. The more erratic performance at concentrations below  $10^{-4}$  N. is expected due to the reduced sensitivity at these levels and departure from the assumed thermodynamic conditions (i. e. the solution at the electrode surface is not necessarily saturated with AgCl such that the solubility product no longer controls the potential effectively).

An important conclusion to be drawn from these response curves is that the method for computing  $E_J$  is valid to within a few millivolts for most of the solutions used. One noticeable exception is the measurement on the full strength pH 7.4 buffer which deviated 6 mv. from the response curve.<sup>17/</sup>

### Operation and Results

A series of dilute  $\text{Na}_2\text{CO}_3$  solutions were made to 0.002, 0.001 and 0.0005 N and submitted to the robot sensing head. The RØBOT ØPERATØR program was directed to perform the following sequence:

---

<sup>17/</sup> For the case of the pH 7.4 buffer, full strength, the interpreting program was run with  $C_{\text{Tot}} = 0.1$  and  $C_X = 0.1$  to generate the approximate ionic strength; no attempt was made to supply the  $E_J$  computation with the actual buffer composition.

FLUSH

FILL

QUICKLOOK

TITRATE

on a sample of each test solution. The data generated by the working model was processed by the full interpreter program using the calibration coefficients determined by the methods just discussed. The INTERPRETER was later permitted to find "better" values for  $E_{PZ}$  and  $E_{CZ}$  since the calibration values were determined several days prior to the testing of these carbonate solutions. Figures 19, 20 and 21 show examples of the conductometric and pH titration curves which resulted.

The 0.002 N solution was also titrated at the simulated 100 meter depth conditions. Figure 22 shows the titration curves that were produced. The first data point was taken immediately after the FLUSH and FILL routines were completed. The rest of the data points were taken by the TITRATION routine after the internal pressure of the test cell was raised to 150 psig.

In order to evaluate the methods and equipment with natural water, arrangements were made to obtain duplicate samples of Willamette River water taken by the Department of Environmental Quality, State of Oregon. This agency provided their standard analysis of these water samples for comparison. The actual

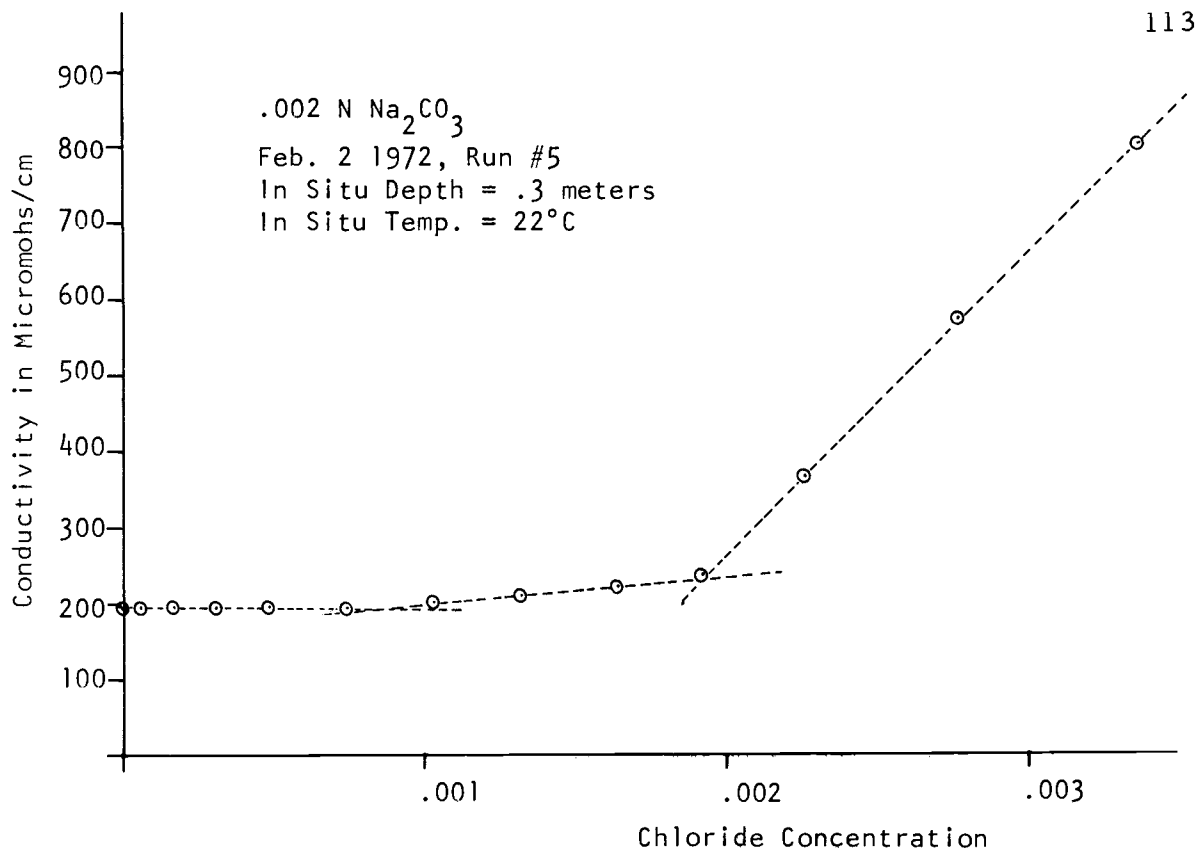


Figure 19a. Conductivity Titration

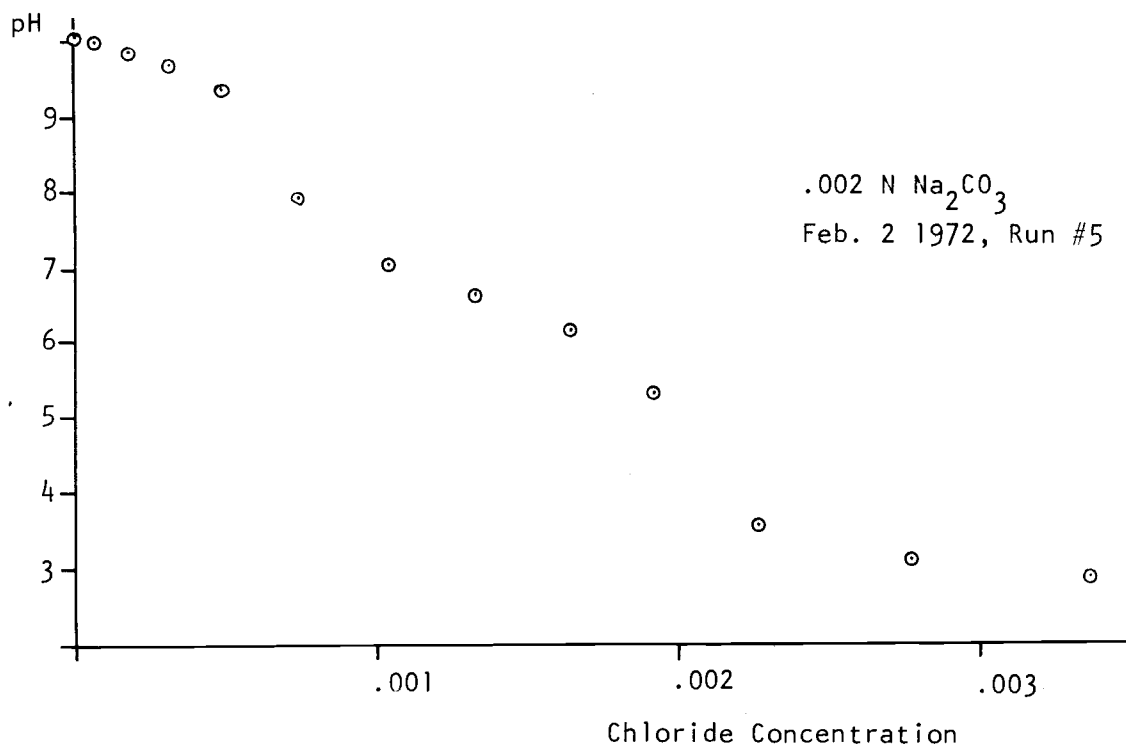


Figure 19b. pH Titration

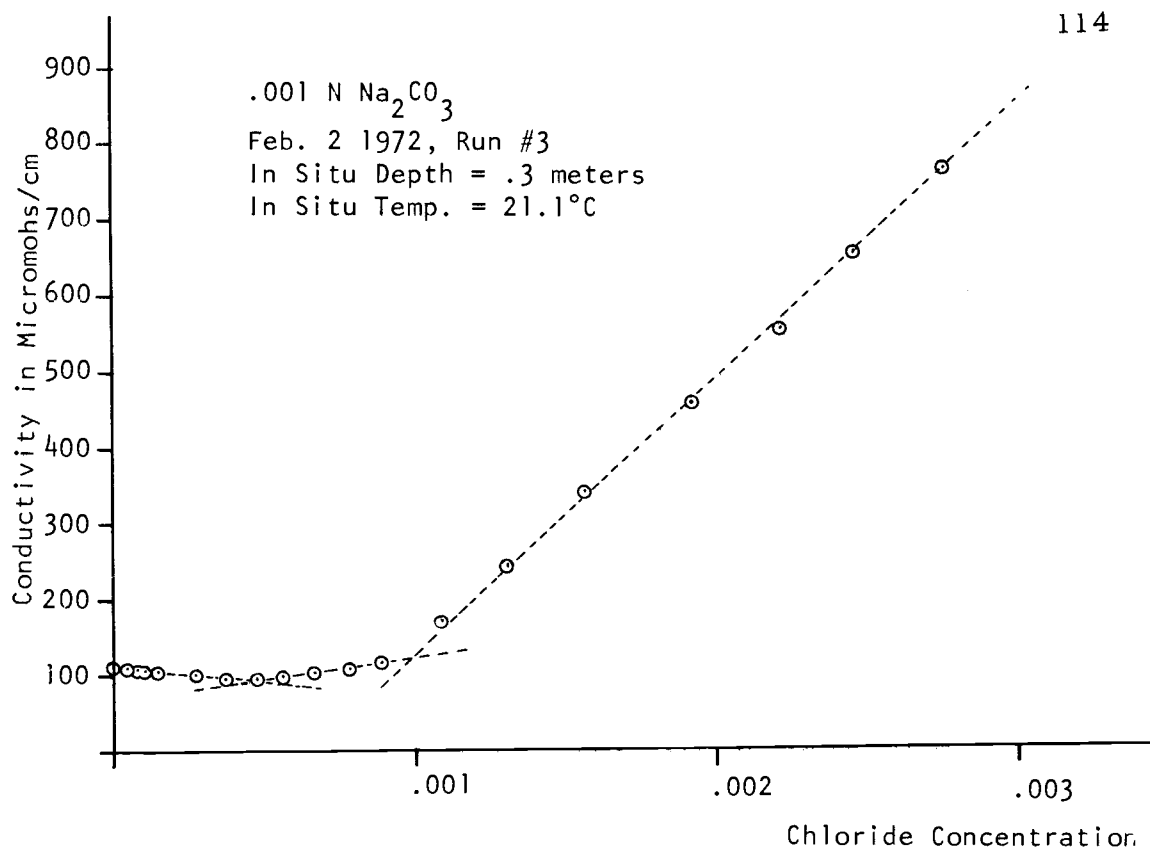


Figure 20a. Conductivity Titration

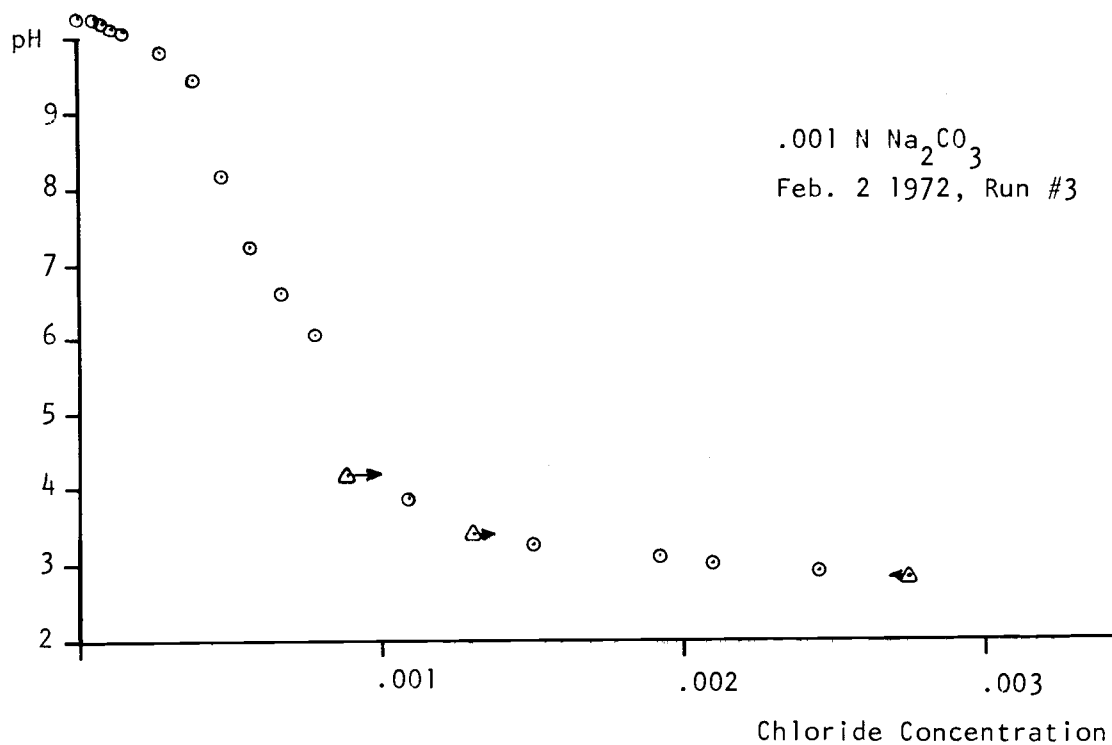


Figure 20b. pH Titration

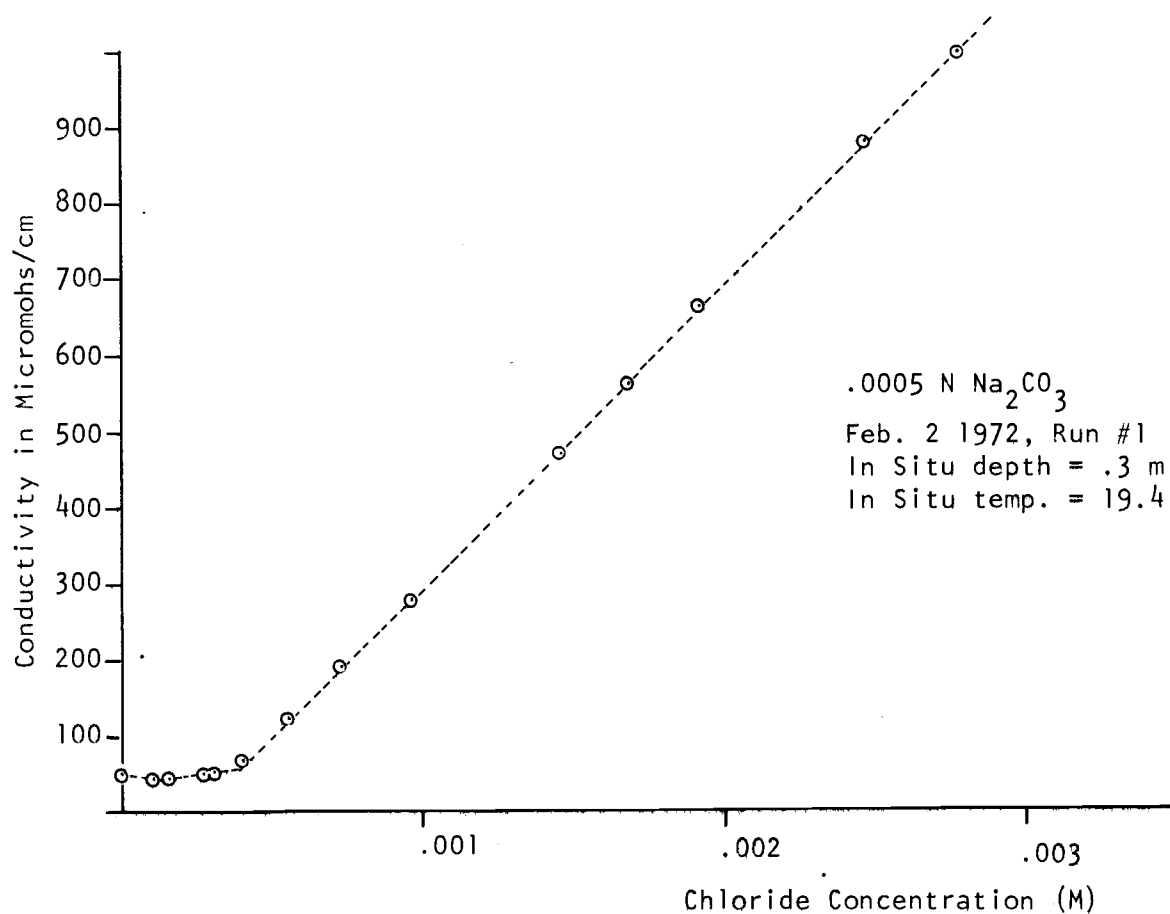


Figure 21a. Conductivity Titration

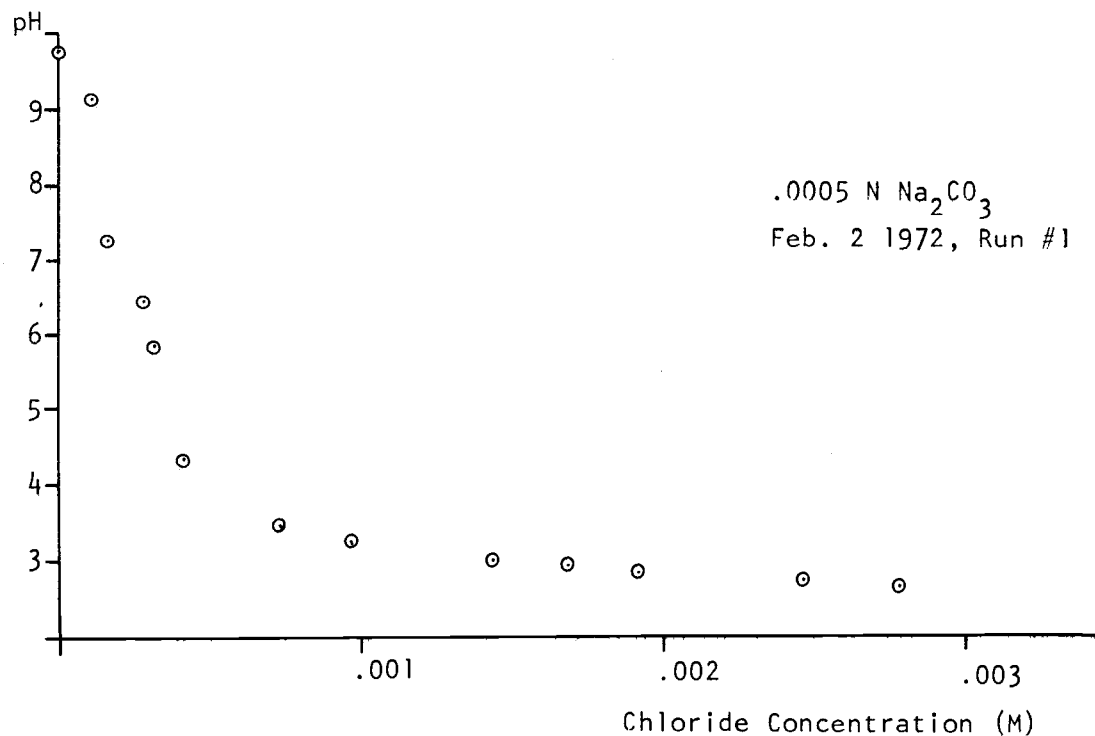


Figure 21b. pH Titration

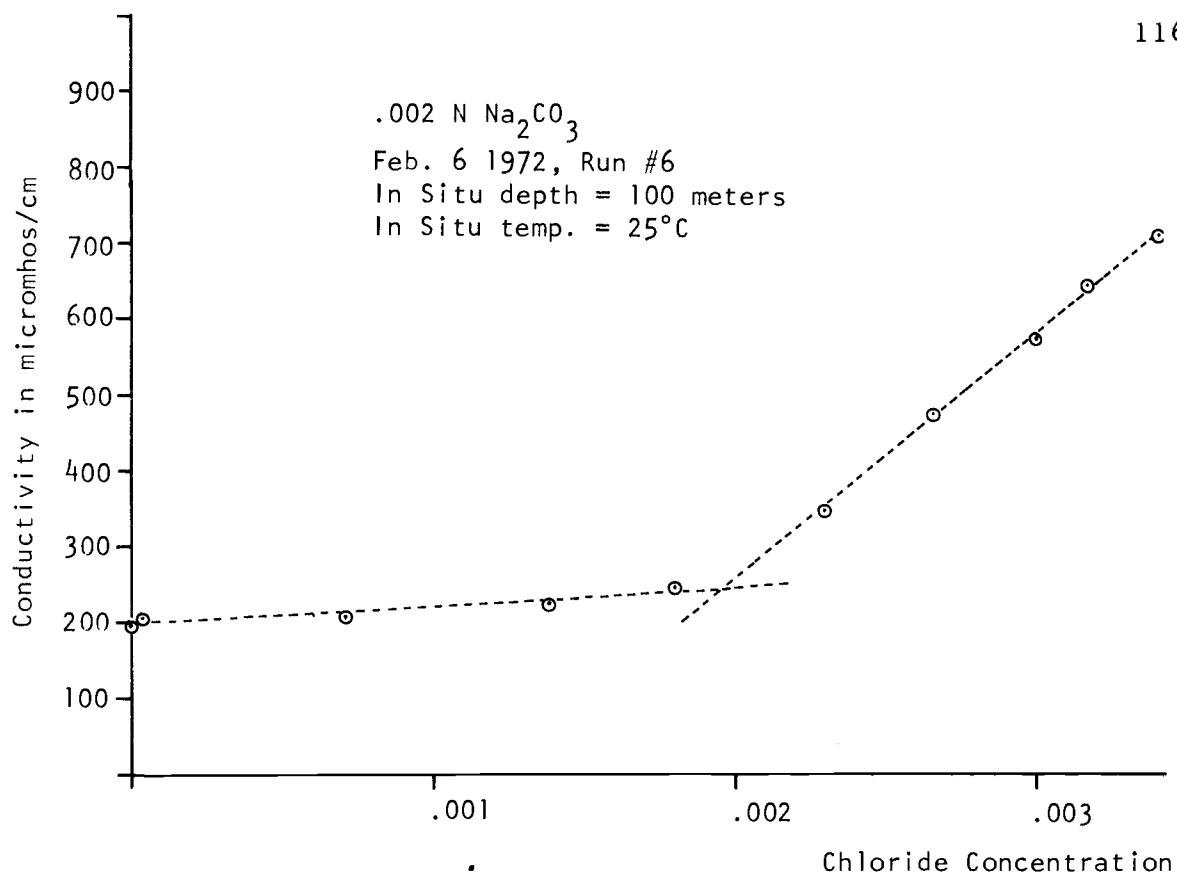


Figure 22a. Conductivity Titration at 150 psig

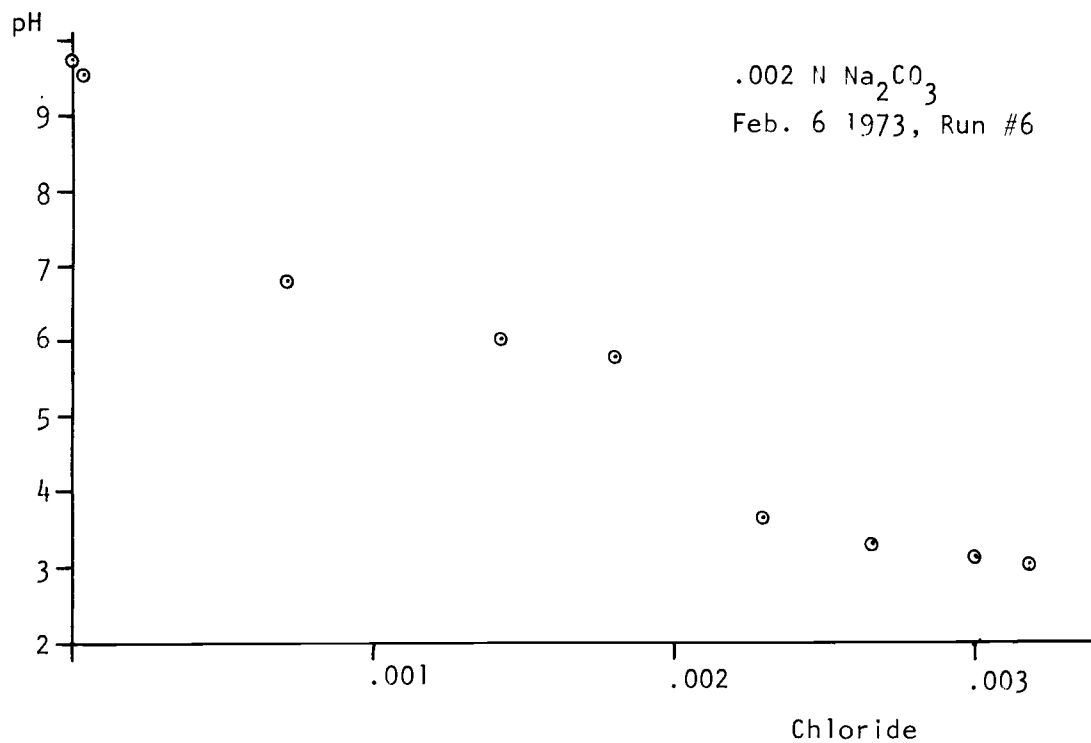


Figure 22b. pH Titration at 150 psig

titration curves were qualitatively the same as the standard carbonate solutions so that plots for these runs are not presented.

Table 3 summarizes the results of these titration experiments. The quality of fit factors  $Q_A$  and  $Q_C$  generated by the INTERPRETER are also presented.

### Discussion of Performance

In general the performance is considered good in view of the first prototype hardware design and use of dilute, low buffer capacity solutions. Repeatability and accuracy are about 2% to 6% of reading over a wide range of scale.

It is now recognized that the 0.005 N sodium carbonate solution was probably contaminated by  $\text{CO}_2$  as a result of the preparation method; a three fold dilution of a 0.1 N standard with distilled water not completely purged of  $\text{CO}_2$ . As a result, the  $\text{CO}_2$  would titrate the hydroxide ions and reduce the carbonate alkalinity by converting it to bicarbonate. The computed value for  $C_{\text{Tot}}$  was about 20 to 60% higher than expected from the sodium carbonate alone.

The main point to the pressurized tests was to show that the titration experiment could be done and to evaluate any problems the pressure would pose for the electrodes and mechanical devices. In this vein, the equipment was very successful. Full manipulation was realized without a drop of water seeping through any of the seals. To

Table 3. Summary of titration experiment results.

	Alk. (meq)	C <sub>Tot</sub> (meq)	C <sub>x</sub> (meq)	pH <sub>i</sub>	pCl <sub>i</sub>	E <sub>PZ</sub> (mv)	E <sub>CZ</sub> (mv)	Cond (μm)	Q <sub>C</sub> (μm)	Q <sub>A</sub> (%)
Guess θ	1.00	1.00	1.00	7.00	4.5	0.0#	+1 #	-	-	-
2 mN Na <sub>2</sub> CO <sub>3</sub>	1.81	1.01	1.01	10.49	4.4	0.0#	6. #	205.	70	3.9
2 mN Na <sub>2</sub> CO <sub>3</sub> at 100 meters	1.94	1.54	2.04	9.62	4.3	0.0#	6. #	197.	12	3.1
1 mN Na <sub>2</sub> CO <sub>3</sub>	1.00	0.56	0.63	10.25	4.4	0.0#	5. #	112.	22	2.9
0.5 mN Na <sub>2</sub> CO <sub>3</sub>	0.49	0.40	0.50	9.61	4.4	0.0#	5. #	53.	3	4.9
Willamette I (by analysis)	0.37 0.38	0.40 -	0.54 0.74	6.76 -	3.9	0.0#	4. #	54.	9	3.4
Willamette II (by analysis)	0.34 0.34	0.51 -	0.60 0.85	6.74 -	4.0	0.0#	4. #	53.	7	2.7

Key to Symbols and Abbreviations

# Value forced by calibration or other consideration

meq Milliequivalents

mv Millivolts

μm Micromhos cm<sup>-1</sup>



check that there was no problem with the electrodes, a standard pH 7.4 buffer solution, made 0.001 N in KCl, was submitted to the sensing head. Readings from the pH electrode pair remained constant ( $\pm 200 \mu\text{v}$ ) over several cycles from 0.5 psig to 150 psig. The chloride electrode pair showed a slow drift of less than 1 mv during these pressure cycles. The "reference potential" between the pH and the Ag, AgCl electrodes in the 0.1 N HCl solution also remained constant ( $\pm 200 \mu\text{v}$ ).

The titration of 0.002 N  $\text{Na}_2\text{CO}_3$  under 150 psig pressure (Figure 22) shows fair resemblance to the titration of the same solution at 0.5 psig (Figure 19). The noticeable differences are the fewer number of data points in the zone of interest and the fairly large errors in pH appearing at the "knees" of the titration curve. Both these effects are explained as result of non ideal test apparatus which subjected the test cell to a slightly lower pressure than the reference cell. The pressure control over the liquid junction, as exercised by the TITRATION routine, could not compensate for the small residual pressure difference. As a result, there was a faster than desired flow of acid into the test cell which increased the size of the acid addition steps. Instead of the liquid junction remaining fixed during the reading phase of the titration cycles, the mixture of liquids tended to seep towards the flow cell surrounding the active pH electrode. This seeping action advanced the titration of the test water,

in the vicinity of the active pH electrode, over the titration of the bulk of the test solution. Since the rate of change of pH with acid added is large at the knees of the curve, then the effect was considerable. No attempt to rewrite the TITRATION subroutine to compensate for these problems was made because the end result would only be correcting for a problem existing in this particular test apparatus, not expected to be present in true in situ operation.

The performance of the Ag, AgCl electrode as a selective ion electrode for chloride ion has been a limiting factor on the accuracy which can be realized by this equipment. It was perhaps unreasonable to expect better performance, but it was felt that this electrode would have been suitable to demonstrate the chloride tag method as a means for doing titrations in situ with mechanically simple apparatus. Presumably, a true selective ion electrode such as the Orion 94-17 would improve the performance, but its cost made it unaffordable for this project.

After running the working model system, some deficiencies in the system were noticed. A very common sequence of events (read a value, telemeter it, and execute two robot commands) required 500 ms. Since a next step cannot be started until this sequence is finished, the 500 ms is just a delay. Using a 20 point titration experiment as an example, it was found that 720 seconds of a total of 1080 seconds were spent in wait loops in which the telemetry

link was idle. It is estimated that almost all the commands and data could have been transmitted during the wait loops if some digital registers were to be incorporated to receive and hold them. A buffer that could hold three commands pending a fourth "go" command would serve all cases in the titration experiment. Only one data buffer would be needed to hold one 12 bit word from the A/D converter pending a free line. Another manipulation that consumed much of the experiment time was the indirect method for adding the titrant through the liquid junction capillary. Over one half the time in each addition-measurement cycle was spent just adding the reagent and reforming the liquid junction. Hence, it would be more efficient to have a second pump module to administer the titrant.

## VII. CONCLUSIONS

The apparatus which constituted the sensing head was a general success in that it performed satisfactorily in the simulated in situ environment. The seals and mechanical design worked well enough to permit operation of the sensing head under the equivalent of 100 meters of water. The blocked capillary junction joining the reference cells to the test cell produced repeatable stable liquid junction potentials even with very dilute test solutions. The differential electrode buffer design proved adequate to reject the significant 60 cycle background which was definitely present in this laboratory simulation. However, the in situ design was only a first attempt and several deficiencies were recognized. Perhaps the most serious problem was due to combining reference solution and titrant without providing direct controls over the flow in the capillary. A good portion of the variability between the tests is attributed to undetected contamination of the reference solution which occurred while the computer or the operator were servicing a flagged error condition. Flow cell-to-flow cell connections were prone to minor leaks which led to parasitic electrical paths of a highly unpredictable nature.

The concept of in situ experimenting has been demonstrated to be an effective and reasonable means for observing water quality parameters, including some for which specific sensors are not

available. High level computer languages, such as HOI, proved to be invaluable during the routine development stages.

Detailed and elaborated procedures were handled with ease by nested subroutines, which once devised, could be called by higher level routines to provide a simple, easy to understand RØBØT ØPERATØR program. The idea of performing a series of batch analysis in one test cell was no problem once good FLUSH and FILL routines were devised. Reagent consumption by this kind of batch analysis is only 1 millilitre per titration, meaning that one litre would be enough for a whole month of hourly titrations. As a result of this work it is felt that the computer controlled experiment approach opens the door to many innovative new methods to observe needed parameters. Novel techniques such as the chloride tag titration method can overcome the necessity for critical hardware design which would otherwise be required to directly implement conventional laboratory analysis.

Bringing the computer into the first stages of the analysis to work with primary observable quantities has been shown to offer possibilities beyond the expected ability to just utilize more precise formulations of transfer functions. A first example was the use of a multi-parameter, iterative method for adjusting the transfer relations to account for the "not necessarily minor" factors like ionic strength and changes in "physical constants" which are, in fact,

functions of temperature. Another example was the use of the computer to interpret data from analytical experiments. Although the direct programming of conventional graphical interpretation techniques produced the best results from this working model data, much promising capability was shown for nonlinear regression techniques. The concept of autoverification was demonstrated to provide a good index of the error factor involved in each experiment. The concept of autocalibration could not be conclusively demonstrated, although good values for ECZ and EPZ were produced for data sets with autovarification indexes less than 2.9%. It is felt that the attempt to apply nonlinear regression techniques was crude in that it did not take sufficient cognizance of the mathematical properties of the computer models in selecting the coefficients to be fitted, nor of the statistical properties of the data sets. It did, nevertheless, indicate some important capabilities that can be derived from a computer based monitoring system employing the "experiment concept".

The development and operation of this working model system has revealed several areas where the system architecture could be improved to facilitate remote in situ experimenting. If there were digital command and data buffer storage registers incorporated into the robot sensing head then it could make more efficient use of the telemetry link. It is hard to say just how fast the telemetry link should be to accommodate the wide range of experiments that may be

wanted. Yet, it is apparent that the 10 cps limitation imposed for this working model system was just too slow to permit effective closed loop servo controls for valves and electrode potentials. This leads one to suggest that rates in the order of 30 cps would be a minimum for this kind of system. Furthermore, the proposed "mini size" for the central computer is probably too small for a really effective system software package using high level languages like FORTRAN. All these points suggest that a "small", dedicated central computer and conventional telephone line telemetry scheme may not be the best system architecture for a remote experimenting system. Perhaps a better system architecture would be to have a very small "micro-computer" built into the robot sensing head and have it communicate with a full sized computer installation on a time-slice basis at 10 cps. Adopting such an architecture, one could realize the command and data buffers, and the high speed capability for simple servo loops. Removing the requirement for dedication of the central computer means that one could afford a very powerful central computer to direct the experiment procedure, to interpret the data, and to display and file the results.

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## APPENDICES

## APPENDIX A

### Discussion on a Linearizing Circuit for a Thermistor

## APPENDIX A

Discussion on a Linearizing Circuit for a ThermistorPart 1 - Circuit Analysis (Reference Figure 3)

Making the usual assumptions for analyzing circuits employing operational amplifiers (i.e. infinite gain and input impedance), and noting that,  $e_s \simeq e_2$ , then one can write

$$e_1 \simeq V_R \cdot \frac{R_i + \alpha R_1}{R_i + R_1 + R_i \cdot R_1 / R_T}$$

$$e_2 = \alpha V_R \text{ where } \alpha = \frac{R_2}{R_2 + R_3}$$

$$E_{out} = e_2 \left\{ 1 + \frac{R_f}{R_i} \right\} - e_1 \left\{ \frac{R_f}{R_i} \right\}$$

Combining these into an expression relating thermistor resistance,  $R_T$ , to output voltage,  $E_{out}$ , gives:

$$E_{out} = V_R \cdot \frac{R_f}{R_i} \left\{ \alpha \left( 1 + \frac{R_i}{R_f} \right) - \frac{R_i + \alpha R_1}{R_i + R_1 + \frac{R_1 R_i}{R_T}} \right\}$$

## Part 2 - Selecting Component Values

It is desired to select values for  $R_f$ ,  $R_i$ ,  $R_1$  and  $\alpha$  such that the calibration curve passes through -10 volts at  $0^\circ\text{C}$ , 0 volts at  $15^\circ\text{C}$ , and +10 volts at  $30^\circ\text{C}$ . It was also desired to make the curve relatively linear and to operate the thermistor with low enough voltage to maintain accuracy at  $\pm 0.05^\circ\text{C}$  or better. For convenience, the supply voltage, +15 volts, was taken as  $V_R$ . In order to keep self heating errors to a negligible level, 0.1 mw (corresponding to  $+0.03^\circ\text{C}$ ) was taken as the maximum power that could be dissipated by the thermistor. Anticipating that the maximum power would be delivered to the thermistor when it had its highest value,  $R_T = 9.8\text{K}$  at  $0^\circ\text{C}$ , then  $e_1$  should be no more than 1 volt when  $R_T = 9.8\text{K}$ . In order to keep amplifier drift and offset problems to a minimum, it was desired to make  $R_1$  approach the mean value of  $R_T$  (about 6K). This makes the bridge output voltage most sensitive to changes in  $R_T$  and reduces the gain required from the buffer amplifier to bring  $E_{\text{out}}$  to the desired  $\pm 10$  volt swing. Making  $e_1 = 1$  volt was the best compromise.

At this point the design problem reduces to selecting  $R_f$ ,  $R_i$ ,  $R_1$  and  $\alpha$ . These values were found by making a breadboard of the circuit. A number of  $R_i$  values were taken in turn.  $R_1$  was selected to make  $e_1$  about 1 volt when  $R_T = 9.8\text{K}$ . Next,  $R_T$  was

set at 4.7K (corresponding to 15°C) and  $\alpha$  was adjusted to make  $E_{out}$  zero. Then with  $R_T$  set at 9.8K again,  $e_1$  was checked and  $R_f$  was chosen to make  $E_{out}$  go to -10 volts. After carefully readjusting  $E_{out}$  to zero ( $R_T = 4.7K$ ), the symmetry was measured when making  $R_T = 2.417K$  (corresponding to 30°C). These steps were repeated for several  $R_i$  values until acceptable symmetry was realized. Precision resistors were found for  $R_f$ ,  $R_1$  and  $R_i$  which were close to the best values obtained from this exercise. The value of  $\alpha$  was trimmed to make  $E_{out}$  zero when  $R_T$  was 4.717K.

The degree of linearity realized by this circuit was considered acceptable so no attempt was made to improve the linearity by trying other values for  $V_R$  and maximum power dissipation. It was noted that power dissipation in the thermistor was not only very low, but also relatively constant across the range compared to more common bridge circuits. The transfer equation;

$$T = 15 + 0.1501 E_{out} + 0.0076.4 E_{out}^3$$

was determined from a regression analysis on a table of  $E_{out}$  vs temperature values, generated by applying the standard thermistor calibration ( $R_T$  vs. temperature) to the completed circuit (in place of the thermistor).

## APPENDIX B

Summary of Subroutines in

RØBØT ØPERATØR



## APPENDIX B

Summary of Subroutines in  
ROBOT OPERATOR

Name	Nest level	Description	Execute time
CARETAKER	3	clear liquid junction, clean electrodes	60 sec.
ENCODE	0	ask robot to do A/D conversion and transmit, reading corrected for offset in A/D, and value in volts assigned to variable E	0.3
EXECUTE	0	transmit last eight bits of the value in variable I, i.e. execute robot instruction I	0.1
FILL	3	cause robot to take a fresh sample of water and establish liquid junction	10.0
FLUSH	3	cause robot to take a fresh sample and thoroughly rinse the flow cell	15.0
HELLO	3	establish initial conditions and check zero offsets, reference voltages, leakage currents through working electrode and ask computer operator to supply control flags and control constants. Unsatisfactory status is reported on computer console.	10 to 30
PUMPON	2	run main pump according to value in variable S; S = 0 is stop, S = +2 is full speed forward, S = +1 is slow speed forward, S = -1 is slow speed reverse, S = -2 full speed reverse. Includes valve and timing checks.	0.3
QUICKLOOK	3	execute a sequence of experiments to measure, temperature, pH, Cl <sup>-</sup> ion, conductivity, and reference potential, and print out values of T, EPH, ECL, COND, and ER on computer console.	24.0

## Summary of Subroutines in RØBØT ØPERATØR (cont.)

Name	Nest level	Description	Execute time
READCOND	2	conduct conductivity measurement	8.0 sec.
READECL	2	measure ECL, wait, average and scale	4.0
READEPH	2	measure EPH, wait, average and scale	4.0
READER	2	measure ER (potential between two reference electrodes) scale	0.7
READEW	2	measure EW (potential of working electrode relative to reference chloride)	0.7
READIW	2	measure current through working electrode, scale in $\mu$ amps	0.5
READO2	2	conduct polarographic experiment for dissolved oxygen	not finished
READT	2	measure temperature of water	0.8
RESET	3	clear sensor head to safe state, reinitialize and check status. (first stage in error recovery)	5.0
TITRATE	3	conduct titration experiment (assumes FLUSH and FILL executed previously)	200.0 to 600.0
VALUE	1	obtain E averaged over 2 seconds	2.5
VALVSET	2	position valve according to P, if P = 0.402, "open" if P = 0.168, "closed circuit" if P = 0.520, "block flow"	3.0
VOLTSET	1	set programmable voltage source to V volts ( $-10.0 < V < +10.0$ )	0.3
WAIT	0	cause delay of W seconds ( $100 < W < 0.1$ )	W sec.

## APPENDIX C

### A Discussion of Volumetric Independence

#### In the Chloride Tag Method

## APPENDIX C

A Discussion of Volumetric Independence  
In the Chloride Tag Method

It is desired to show that the chloride tag method, as used in this working model, is independent of volumetric measurements. To do this, it is necessary to consider the material balance problem where a flow of  $x$  ml/second of an acid reagent of normality  $N$  is forced into a full volume,  $V$ , which then overflows by an equal amount of  $x$  ml/second. The fixed volume,  $V$ , is the effective volume of the test water circuit comprised of the pump, tubing and the flow cells (reference Figure 2). During the forward running of the pump a slow flow of acid reagent enters the test water circuit, and is mixed thoroughly. The "T" junction shown in Figure 2 has the "stem" made of a 1 mm diameter capillary tube, through which excess, mixed solution is expelled so as to maintain the volume in test water circuit constant.

If  $Q_A(t)$  is the number of equivalents of alkalinity in the test water solution after  $t$  seconds of dilution by another solution at the rate  $x$  ml/second, then one can write the differential equation describing this situation:

$$\frac{d}{dt} Q_A(t) = -\frac{x}{V} Q_A(t)$$

Initially,

$$Q_A(0^+) = Q_A^*$$

where  $Q_A^*/V$  is the alkalinity of the natural water, and the solution of the describing equation is:

$$Q_A(t) = Q_A^* \exp(-xt/V)$$

A similar equation can be derived for the number of equivalents of added agent,  $Q_a$ , which is  $N$  normal in its bulk concentration. Beginning with the input-output balance,

$$\frac{d}{dt} Q_a(t) = x(N - Q_a(t)/V)$$

and solving using  $Q_a(0^+) = 0$ , yields:

$$Q_a(t) = NV \left\{ 1 - \exp(-xt/V) \right\}$$

By noting,

$$\frac{Q_A(t)}{Q_A^*} = \exp(-xt/V)$$

the substitution can be made in the expression for  $Q_a(t)$  and the equation solved for the equivalents of alkalinity as a function of time;

$$Q_A(t) = Q_A^* \left\{ 1 - Q_a(t)/NV \right\}$$

Since the concentration of added agent,  $C_a(t)$  is just  $Q_a(t)/V$ , and the alkalinity,  $A(t)$ , is  $Q_A(t)/V$ , then this expression can be stated in concentration terms as follows:

$$A(t) = A^* \left\{ 1 - C_a(t)/N \right\}$$

In other words, the effective alkalinity at time  $t$  is a function of the original alkalinity and the ratio of the concentration of the added agent in the mixed solution over its base concentration.

The discussion so far has not been concerned with the fact that when the agent is HCl, titration is taking place. This fact does not change the dilution situation that occurs and is essentially all that the above equation describes.

At the equivalence point in the titration the equivalence of the terms  $Q_a(t_e)$  and  $Q_A(t_e)$  is implied. Thus, if one can detect the equivalence point and measure  $C_a(t_e)$  at this point, then one can calculate the bulk solution alkalinity,  $A^*$ , by

$$A^* = C_a(t_e) \frac{N}{N - C_a(t_e)}$$

Provided one chooses  $N$  to be much greater than the maximum alkalinity expected, then the above expression reduces to the approximation:

$$A^* = C_a(t_e)$$

In any event, these expressions contain no volumetric quantities at all. Furthermore, the tolerance on N can be quite loose.

Whereas, the conventional volumetric method includes the combined effect of errors in three volumetric measurements; the sample aliquot; the amount of reagent added and the weight to volume ratio which defines the normality of the reagent. The precision of this chloride tag method depends upon the precision of the Chloride ion concentration determination.

Selective ion potentiometry for this ion measurement provides a method with a precision of about  $\pm 4\%$  of the value being measured.

## APPENDIX D

An INTERPRETER Program

(FØRTRAN Listing)



```

C      WATER QUALITY  ROBOT  TITRATION CURVE FIT ROUTINE
C
C      VERSION  NO.1 - IN SITU CHLORIDE-TAG METHOD
C      INPUT DATA
C          EPH= POTENTIAL OF PH-REF ELECTRODE PAIR IN VOLTS
C          ECL= POTENTIAL OF AG/AGCL- REF ELECTRODE PAIR IN VOLTS
C          SK = CONDUCTIVITY OF SOLUTION IN MHOS
C          I  = TEMPERATURE OF SOLUTION IN DEG. C.
C      PLUS COEFFICIENT VECTOR THEIA, PARTITIONED INTO THP(6) AND THC(6)
C          WHERE THP(1)= TOTAL CO2 CONCENTRATION IN MOLES
C          THP(2)= INSITU PH
C          THP(3) = IN SITU PCL
C          THP(4)= OFFSET POTENTIAL OF PH ELECTRODE IN VOLTS
C          THP(5) = SENSITIVITY OF PH ELECTRODE IN V./PH UNIT
C
C          THC(1) = CONCENTRATION OF OTHER IONS EXPRESSED AS
C                  EQUIVALENT SODIUM
C          THC(2)= SAME AS THP(4), EPZ
C      AND  THC(3)= CHLORIDE ELECTRODE OFFSET IN VOLTS
C          P.C(4) = SENSITIVITY OF CHLORIDE ELECTRODE V./PCL
C          THP(5) = CONDUCTIVITY CELL CONSTANT
C
C      PLUS  A CONTROL/COEF. CARD IN 215,F10.5,15
C          NRX= NUMBER OF OBSERVATIONS (NRX=0 CALLS EXIT)
C          NTHPN = NUMBER OF COEFFICIENTS OF THP VECTOR TO BE FITTED
C          NTHCJ = NUMBER OF COEFFICIENTS OF THC VECTOR TO BE FITTED
C          NITER=NUMBER OF ITERATIONS MAX.
C
C      DIMENSION THP(8), PH(20), PCL(20), COND(20), TR(20), EJ(20
C      $), Z(20), G(20), ALFA(20), Y(12), RB1X25(20), RB2X25(20), RKX25
C      $(20), ECL(20), EPH(20), I(20), ST(2,8), STP(2,8), GGG(20), GGGG(20
C      $)
C      LOGICAL KFLAG
C      REAL KW,LH(20),LUH(20),LCL(20),LCU3(20),LHC03(20),LEN(20),KSP,KPH,
C      $IS,ISK(20),KCL,KWA25
C      EXTERNAL PHAMOD,CONMOD
C      COMMON LH,LUH,LCU3,LHC03,LEN,LCL,PH,PCL,COND,TR,G,KSP,EJ,RB1X25,
C      $RB2X25,RKX25,EREF,ALFA,ENN,ISK,ALK,ECL,EPH,ECZ0,GGG,GGGG,B1A25,
C      $B2A25,KWA25

```

```

C
      INTEGER TITLE(10)
      DATA Z/20*0.0/
      TOL = .4

C
C      READ CONTROL CARD AND COEFFICIENT VECTOR #THETA# AS THP AND THC
      READ (5,27) (STP(1,I),I=1,7)
      READ (5,27) (STP(2,I),I=1,7)
      1 READ (5,26) NRX,NTHPH,NTHCU,NITER
C      EXIT IF NRX IS 0.0
      IF (NRX.EQ.0) GO TO 25

C
C      READ DATA MATRICES IN
      READ (5,47) (TITLE(L),L=1,10)
      DO 2 NX=1,NRX
      2 READ (5,28) EPH(NX),ECL(NX),COND(NX),T(NX)

C
C      PRINT OUT INPUT MATRIX #A#
      WRITE (6,30) (TITLE(N),N=1,10)
      WRITE (6,32)
      WRITE (6,33)
      DO 3 NX=1,NRX
      3 WRITE (6,31) EPH(NX),ECL(NX),COND(NX),T(NX)
C      BEGIN INTERPRETATION OF NEW DATA HERE
C
C      ADJUST CONSTANTS FOR IN SITU TEMPERATURE, SET UP MATRIX B
      WRITE (6,30) (TITLE(N),N=1,10)
      WRITE (6,39)
      WRITE (6,38)
      DO 4 NX=1,NRX
      TR(NX) = (273.16+T(NX))/(298.16)
      TQ = 1.-1./TR(NX)
      TD = T(NX)-25.0
      EREF = -0.0591*TR(1)*ALOG10(.0798+.00006*(T(1)-25.))
      KSP = 10.**(.1896-9.096/TR(1))
      RB1A25(NX) = 10.**(-2.83*TQ)
      RB2A25(NX) = 10.**(-5.38*TQ)
      RKWA25(NX) = 10.**(-9.693*TQ)

```

```

C
      LH(NX) = 349.8*EXP(.014*TD)
      LOH(NX) = 198.*EXP(.018*TD)
      LCL(NX) = 76.35*EXP(.02*TD)
      LCO3(NX) = 69.0*EXP(.02*TD)
      LHC03(NX) = 45.*EXP(.02*TD)
      LEN(NX) = 50.0*EXP(.02*TD)
      WRITE (6,37) NX,TR(NX),RKWX25(NX),RB1X25(NX),RB2X25(NX),LH(NX),
$      LOH(NX),LCL(NX),LCO3(NX),LHC03(NX),LEN(NX),EREF,KSP
4      CONTINUE
      KwA25 = 10.**(-14.0003)
      H1A25 = 10.**(+10.319)
      H2A25 = 10.**(+10.718)
      IROUTE = 0
      KFLAG = .FALSE.
      CSD = 2.
      PSD = .5
      GO TO 6
C ***** BAD DATA RECOVERY POINT *****
5      WRITE (6,44)
      IF (KFLAG) GO TO 1
      KFLAG = .TRUE.
C      COMPUTE INTERM VARIABLE MATRIX #Y#
6      DO 7 I=1,20
          G(I) = .96
7      EJ(I) = .08
      DO 8 I=1,8
          THP(I) = SIP(1,I)
8      THC(1) = SIP(2,1)
C      IROUTE CONTROLS PROGRAM THROUGH STAGE 1 AND STAGE 2
      IROUTE = 0
      DO 23 ICOUN=1,NITER
9          IROUTE = IROUTE+1
          DO 10 I=1,8
              ST(1,I) = THP(I)
10         ST(2,1) = THC(1)
C      NORMALIZE COEFFICIENTS
          C1 = THP(1)
          PH1 = THP(2)

```

C

```

PCL1 = THP(3)
EPZ = THP(4)
ECZ = THC(3)
ENN = THC(1)
CELK = THC(5)
WRITE (6,30) (TITLE(N),N=1,10)
WRITE (6,40)
DO 14 NX=1,NRA
  GGGG(NX) = GGG(NX)*G(NX)
  GGG(NX) = G(NX)**(3/2)
  B2 = B2A25*RB2X25(NX)*GGGG(NX)
  B1 = B1A25*RB1X25(NX)*GGG(NX)
  KW = KWA25*KKWA25(NX)
  KPH = THP(5)*TK(NX)
  KCL = THC(4)*TK(NX)
  ACL1 = 10.**(-PCL1)
  ACL1 = ACL1-KSP/ACL1
  IF(ACL1.LT.2.E-06)ACL1 = 2.E-06
  DO 11 NT=1,5
    EJG = EJ(NX)
    PH(NX) = (EREF-EPH(NX)+EJG+EPZ)/KPH
    AH = 10.**(-PH(NX))
    CH = AH/G(NX)
    COH = K*/AH/G(NX)
    PCL(NX) = (EREF+ECL(NX)-EJG-ECZ)/KCL
    ACL = 10.**(-PCL(NX))
    ACL = ACL-KSP/ACL
    IF(ACL.LT.2.E-06)ACL = 2.E-06
    CCL = ACL/G(NX)
    ALFA(NX) = 1.-(ACL/G(NX)-ACL1/G(1))/0.1
    CT = THP(1)*ALFA(NX)
    D = 1.+(B1+B2*AH)*AH
    CC03 = CT/D
    CHC03 = CC03*B1*AH
  11 CONTINUE
14 CONTINUE
C
C COMPUTE IONIC STRENGTH
IS = .5*(AH+ACL+K*/AH+4.*CC03+CHC03+ABS(ENN))
ISR(NX) = SQRT(IS)

```

```

C
C***** CHECK TO SEE IF IS IS OUT OF RANGE *****
          IF (IS.LT.1.E-07.OR.IS.GT.0.3) GO TO 5
C
C      COMPUTE ACTIVITY COEFFICIENT FROM DEBYE-HUCKEL RELATION
          G(NX) = (((-.509+.00068*(T(NX)-25.))*ISR(NX)/(1.+1.5*ISR
$          (NX)))+.25*IS
          G(NA) = 10.**G(NA)
          CD = COND(NX)*CEK
C      COMPUTE LIQUID JUNCTION POTENTIAL BY HENDERSON EQUATION
          EJGN = LH(NX)*CH
          EJGN = EJGN-LCL(NX)*CCL
          EJGN = -LOH(NX)*COH+EJGN
          EJGN = -LCO3(NX)*CCO3+EJGN
          EJGN = -LHCO3(NA)*CHCO3+EJGN
          EJGN = LEN(NX)*ENN+EJGN
          EJGN = EJGN-.0918*(LH(1)-LCL(1))
          EJGD = CD*1000.0
          EJGD = EJGD-.0918*(LH(1)+LCL(1))
          EJ(NX) = ALOG10(CD*1000.0/(.09182*(LH(1)+LCL(1))))
          EJ(NX) = -EJGN/EJGD*.0591*TR(NX)*EJ(NX)
          IF (ABS(EJ(NX)-EJG).LT.0.0005) GO TO 12
11      CONTINUE
12      CONTINUE
C      SAVE INITIAL COMPUTED CONDITIONS
          IF (NX.GT.1) GO TO 13
          AH = 10.**(-PH1)
          D = 1.+(B1+B2*AH)*AH
          CCO3 = CT/D
          CHCO3 = CCO3*B1*AH
          CH = AH/G(NA)
          COH = Kw/AH/G(NX)
          ALK = 2.*CCO3+CHCO3+COH-CH
          CTT = CT
          ECZO = ECZ
13      CONTINUE
C      PRINT OUT SCALED INTERM VARIABLES
          Y(1) = PH(NX)
          Y(2) = ACL*1.E+06

```

```

C
      Y(3) = (ACL/G(NX)-ACL1/G(1))*1E+06
      Y(4) = CC03*1.E+06
      Y(5) = CHC03*1.E+06
      Y(6) = CC03*B2*AH*AH*1.E+06
      Y(7) = ALFA(NX)
      Y(8) = EJ(NX)*1.E+03
      Y(9) = CD*1.E+06
      Y(10) = IS*1.E+06
      Y(11) = G(NX)
14      WRITE (6,43) NX,(Y(1),I=1,11)
      WRITE (6,46) (THP(1),I=1,5),(THC(1),I=1,5)
      WRITE (6,36) ALK,CTT
C
C      IF THERE ARE LESS THAN 6 DATA SETS, SKIP STAGE 2 INTERPRETATION
      IF(NRX.LT.6)IROUTE = 3+IROUTE
      GO TO (15,19,20,19,1,1,1,1), IROUTE
C
C      USE SIMPLE RELATIONS TO ESTIMATE INITIAL GUESSES
15      CONTINUE
C      FIND PHI AND PCL1
      THP(2) = PH(1)
      THP(3) = PCL(1)
C      FIND ALKALINITY BY LINEAR INTERPOLATION OF TITRATION CURVE
      DO 16 NX=1,NRX
        IF (PH(NX).LT.4.5) GO TO 17
16      CONTINUE
      WRITE (6,29)
      ALK = 0.001
      GO TO 18
17      ACL = 10.**(-PCL(NX))/G(NX)
      ACLX = 10.**(-PCL(NX-1))/G(NX-1)
      ALK = (4.5-PH(NX-1))*(ACL-ACLX)/(PH(NX)-PH(NX-1))+ACLX
      WRITE (6,34) ALK
18      KW = KWA25*RK*X25(1)
      B2 = B2A25*RB2X25(1)
      B1 = B1A25*RB1X25(1)
      AH = 10.**(-PH(1))
      CH = AH/G(1)

```

```

C
    COH = KW/AH/G(1)
    CF = (ALK-COH+CH)*(1.+AH*(B1+AH*B2))/(2.+AH*B1)
    THP(1) = CF
C
    FIND CA FROM CONDUCTIVITY DEFICITE
    THC(1) = ALK
    ENN = (COND(1)-CONMOD(1,THC,THP))*CELK*1000./LEN(1)
    THC(1) = THC(1)+ENN
C
    WRITE (6,35) THC(1)
    IF(THC(1).LT.10E-06)THC(1) = 10E-06
    GO TO 9
C
    BEGINNING OF STAGE 2
C
    CALL NON LINEAR REGRESSION WITH CONDUCTIVITY MODEL TO BETTER THC
19    CALL NLREG (COND,THP,3,NRX,THC,NTHCO,TOL,CONMOD,SDEV)
    THP(4) = THC(2)
C
    CHECK FOR GROSS DIVERGENCE
    IF (SDEV.GT.CSD*2.5) GO TO 24
    IF (SDEV.GT.CSD) GO TO 9
    CSD = SDEV
    GO TO 9
C
    CALL NON LINEAR REGRESSION WITH ALKALINITY CONSERVATION MODEL TO
C
    BETTER THP
20    CALL NLREG (Z,THC,3,NRX,THP,NTHPH,TOL,PHAMOD,SDEV)
    THC(2) = THP(4)
C
    CHECK FOR GROSS DIVERGENCE
    IF (SDEV.GT.PSD*1.2) GO TO 24
    IF (SDEV.GT.PSD) GO TO 21
    PSD = SDEV
C
C***** CHECK TO SEE IF COEFFICIENT VECTORS HAVE CONVERGED
21    DO 22 I=1,8
        U = ABS(ST(1,I)-THP(1))/ABS(THP(1)+.05)
        V = ABS(ST(2,I)-THC(1))/ABS(THC(1)+.05)
        IF (U.GT.0.002.OR.V.GT.0.002) GO TO 23
C
    COEFFICIENT VECTOR #THETA# STILL CONVERGING, PROCEED
22    CONTINUE
    WRITE (6,42) ICOUN
    IROUTE = 5

```

```

C
      GO TO 9
23  CONTINUE
C    COEFFICIENT VECTOR #THETA# DIVERGING, ABORT
      WRITE (6,41) NITER,U,V
      IROUTE = 5
      GO TO 9
24  WRITE (6,45)
      GO TO 1
25  STOP
C
C
C
26  FORMAT (4I5)
27  FORMAT (8F10.5)
28  FORMAT (2F10.7,1A,F9.7,F8.2)
29  FORMAT (48H NO EQUIVALENCE POINT,ALK ASSUMED TO BE 0.001 M.,/)
30  FORMAT (1H1,///10X,10A4,/)
31  FORMAT (1H ,4X,2F9.5,F10.6,F8.2)
32  FORMAT (1H ,/ 13X,23H ***** INPUT DATA *****,/)
33  FORMAT (1H0,8X,3MEPH,6X,3MECL,6X,5HCOND.,4X,5HTEMP.,/7X,7H(VOLTS),
$2X,7H(VOLTS),3X,6H(MHUS),2X,9H(D. CEN.),/)
34  FORMAT (26H0 INTERPOLATED ALKALINITY=,F8.6)
35  FORMAT (23H ESTIMATED OTHER IONS =,F9.6,15H AS EQ. SODIUM )
36  FORMAT (34H0 EQUILIBRIUM COMPUTED ALKALINITY=,F8.6,19H FROM TOTAL
$CO2 OF ,F8.6)
37  FORMAT (1H ,I4,4F8.4,6F8.1,F8.5,E8.2)
38  FORMAT (100H  NX      TR      RKX25  RB1X25  RB2X25    LH      LOH
$  LCL      LC03      LHC03      LEN      EREF      KSP,/)
39  FORMAT (1H ,      /39H      MATRIX B  COMPENSATED COEFFICIENTS,/)
40  FORMAT (1H ,      /31H      MATRIX Y  MODEL OUTPUT,///105H  NU.
$  PH      ACL      C.AC10      AC03      AHC03      AH2CO3      ALFA
$  EJ      COND.      IS      GAMMA,/)
41  FORMAT (1H0,///45H COEFFICIENT VECTORS HAVE NOT CONVERGED AFTER,I4,
$11H ITERATIONS,/24H TYPICAL CHANGE IS STILL,2F8.4)
42  FORMAT (1H0,///43H COEFFICIENT VECTORS CONVERGED TO .2 PERCENT,/
$25H NUMBER OF ITERATIONS WAS,I4)
43  FORMAT (1H ,2X,I4,2X,10F7.2,F8.4)
44  FORMAT (25H01S DETECTED OUT OF RANGE)

```



C

```
45  FORMAT (21H0 DIVERGENCE DETECTED)
46  FORMAT (1H0,10X,9HNEW THETA,///12X,2HCT,F9.6,5H  PHI,F6.2,5H PCL1,F
    $6.2,5H EPZ,F9.5,5H  KPH,F9.5,///12X,2HCX,F9.6,6H  EPZ2,F9.5,5H  EC
    $Z,F9.5,5H  KCL,F9.5,6H  CELK,F8.6//)
47  FORMAT (1H0,10A4)
    END
```

```

      FUNCTION PHAMOD (L,THP,TRC)
C      THIS FUNCTION GENERATES AN ERROR QUANTITY #PHMAMOD# WHICH IS PRO-
C      PORTIONAL TO THE DIFFERENCE BETWEEN TOTAL ALKALINITY AND AN EQUIL-
C      IBRUM ALKALINITY LESS ACID ADDED.
      DIMENSION THC(3), THP(8), PH(20), PCL(20), COND(20), TR(20), EJ(20
$), Z(20), G(20), ALFA(20), OV(10), RB1X25(20), RB2X25(20), RKWX25
$(20), ECL(20), EPH(20), GGG(20), GGGG(20)
      REAL KW,KW1,LH(20),LOH(20),LCL(20),LCO3(20),LHCO3(20),LEN(20),KSP,
$KPH,ISR(20),KWA25
      COMMON LH,LOH,LCO3,LHCO3,LEN,LCL,PH,PCL,COND,TR,G,KSP,EJ,RB1X25,
$RB2X25,RKWX25,EREF,ALFA,ENN,ISR,ALK,ECL,EPH,ECZO,GGG,GGGG,B1A25,
$B2A25,KWA25
C***** DEFINE PARAMETERS
      CI = THP(1)
      PH1 = THP(2)
      PCL1 = THP(3)
      EPZ = THP(4)
      B1 = B1A25*RB1X25(L)*GGG(L)
      B2 = B2A25*RB2X25(L)*GGGG(L)
      KW = KWA25*RKWX25(L)
C***** COMPUTE HYDROGEN IONS ADDED
      ACL = 10.**(-PCL(L))
      ACL = ACL-KSP/ACL
      HAUD = ACL/G(L)
      ACLI = 10.**(-PCL1)
      CLI = ACLI/G(1)
      HAUD = HAUD-CLI*ALFA(L)
C
C***** COMPUTE PRESENT EQUILIBRIUM CONDITIONS
      KPH = THP(5)*TR(L)
      PHP = (EREF-EPH(L)+EJ(L)+EPZ)/KPH
      H = 10.**(-PHP)
      D = 1.+(B1+B2*H)*H
      CH = H/G(L)
      COH = KW/H/G(L)
      PALK = (2.+(B1*H)*CI*ALFA(L)/D+COH-CH)
C
C***** REVALUE INITIAL COEFFICIENTS AND HI

```

```

KW1 = KWA25*RWX25(L)
B11 = B1A25*RB1X25(L)*GGG(L)
B21 = B2A25*RB2X25(L)*GGGG(L)
H1 = 10.**(-PHI)
D = 1.+(B11+B21*H1)*H1
CUM = KW1/H1/G(1)
CH = H1/G(1)
TALK = (2.+B11*H1)*CT/D+CUM-CH
TALK = TALK*ALFA(L)

```

C

```

C***** COMPUTE ERROR
ERROR = (TALK-PALK-HADD)
ERROR = ERROR/(TALK+PALK+HADD)
PRAMOD = ERROR
RETURN
END

```

```

      FUNCTION CONMOD (L,THC,THP)
C      THIS FUNCTION GENERATES A THEORETICAL CONDUCTIVITY READING IN
C      MMHOS SCALED TO THE SAME FACTOR AS THE COND READINGS.
C
      DIMENSION THC(3), THP(8), PH(20), PCL(20), COND(20), TR(20), EJ(20
$), Z(20), G(20), ALFA(20), OV(10), RB1X25(20), RB2X25(20), RKWX25
$(20), ECL(20), EPH(20), GGG(20), GGGG(20)
      REAL KW,LH(20),LOH(20),LCL(20),LCU3(20),LHCU3(20),LEN(20),KSP,KPH,
$IS,ISR(20),KCL,LAMDA,KWA25
      COMMON LH,LOH,LCU3,LHCU3,LEN,LCL,PH,PCL,COND,TR,G,KSP,EJ,RB1X25,
$RB2X25,RKWX25,EREF,ALFA,ENN,ISR,ALK,ECL,EPH,ECZ0,GGG,GGGG,B1A25,
$B2A25,KWA25
C
C***** DEFINE PARAMETERS
      KW = KWA25*RKWX25(L)
      B1 = B1A25*RB1X25(L)*GGG(L)
      B2 = B2A25*RB2X25(L)*GGGG(L)
      ENN = THC(1)*ALFA(L)
      ECZ = THC(3)
      EPZ = THC(2)
      CELK = THC(5)
C***** COMPUTE CORRECTED PCL AND PH
      KCL = THC(4)*TR(L)
C
      ECZ = ECZ-1.4E-07/(CELK*COND(L))
      PCLP = (EREF+ECL(L)-EJ(L)-ECZ)/KCL
      ACL = 10.**(-PCLP)
      ACL = ACL-KSP/ACL
      IF (ACL.LT.2.E-06) ACL = 2.E-06
      KPH = THP(5)*TR(L)
      PHP = (EREF-EPH(L)+EJ(L)+EPZ)/KPH
      H = 10.**(-PHP)
C***** COMPUTE CARBONATE EQUILIBRIUM
      D = 1.+(B1+B2*H)*H
      IF (L.NE.1) GO TO 1
      Q = D/(2.+B1*H)
1      CI = THP(1)*(1.+(ECZ-ECZ0)*2.3026/KCL)
      ALK = CI/Q

```

```

      CI = CI*ALFA(L)
      CC03 = CI/D
      CHC03 = CC03*H*B1
C
C***** COMPUTE THEORETICAL CONDUCTANCE
      CON = LH(L)*H
      CON = LOH(L)*KW/H+CON
      CON = LCL(L)*ACL+CON
      CON = LEN(L)*ABS(ENN)+CON/G(L)
      CON = LHC03(L)*CHC03+CON
      CON = LC03(L)*CC03*2.+CON
C***** COMPUTE USANGER EFFECT
      IS = ISR(L)*ISR(L)
      LAMDA = CON/IS
      LAMDA = LAMDA-(60.2+.229*LAMDA)*ISR(L)
      CONMOD = IS*LAMDA/1000./CELK
      RETURN
      END

```

```

SUBROUTINE PADSET (TH,PDM,FM,NRX,NRTH,MODEL,THS)
C
C THIS SUBROUTINE CALLS ON THE MODEL TO GENERATE A PARTIAL DERIVA-
C TIVE MATRIX, CALLED PDM. PARTIALS ARE ESTIMATED BY MAKING
C SMALL INCRIMENTS IN THETA, ONE ELEMENT AT A TIME.
C
  DIMENSION TH(8), PDM(20,8), FM(20), STH(8), THS(8)
  EXTERNAL MODEL
  REAL MODEL
  DO 1 L=1,8
1    STH(L) = TH(L)
    DO 2 L=1,NRX
      DO 2 M=1,NRTH
        DX = ABS(.01*STH(M))
        IF(DX.LT.4.E-05)DX = 6.E-05
        STH(M) = TH(M)+DX
        PDM(L,M) = (MODEL(L,STH,THS)-FM(L))/DX
2      STH(M) = TH(M)
    RETURN
  END

```

```

SUBROUTINE MODSET (TH,FM,NRX,MODEL,THS)
C
C THIS SUBROUTINE CALLS ON THE MODEL TO GENERATE A SET OF VALUES
C FOR THE INPUT VECTOR VA, AND THE CURRENT COEFFICIENT VECTOR
C THETA. THE RESULTANT VECTOR IS RETURNED AS FM
C
  DIMENSION TH(8), FM(20), THS(8)
  EXTERNAL MODEL
  REAL MODEL
  DO 1 L=1,NRX
1    FM(L) = MODEL(L,TH,THS)
  RETURN
C
C
  END

```

```

SUBROUTINE NLREG (Y,X,NQAS,NRX,THETA,NRTH,TOL,F,SDEV)
C      THIS IS AN IBM LIBRARY SUBROUTINE FROM THEIR NUMERICAL SUBROU-
C      TINE PACKAGE.
C      IT IS MODIFIED TO CALLSMDSET TO COMPUTE THE MODEL VECTOR #FM#
C      SPADSET TO COMPUTE THE PARTIAL DERIVA-
C      TIVE MATRIX #PDM#
C
      DIMENSION X(20,3), Y(20), FI(20), YMF0(20), D(10), THETA(10), FM
      $(20), PDM(20,8), A(10,11)
      EXTERNAL F
      DATA KSPACE/2H /
      NRTHP1 = NRTH+1
      CALL MUDSET (THEIA,FM,NRX,F,X)
      Q0 = 0.0
      DO 1 IH=1,NRX
          T = Y(IH)-FM(IH)
          YMF0(IH) = T
1      Q0 = Q0+T*T
          IIER = 0
2      IIER = IIER+1
      WRITE (6,16) IIER,Q0
      CALL PADSET (THEIA,PDM,FM,NRX,NRTH,F,X)
      DO 7 I=1,NRTH
          DO 3 IH=1,NRX
3          FI(IH) = PDM(IH,I)
          DO 5 J=1,NRTH
              T = 0.0
              DO 4 IH=1,NRX
4                  T = T+FI(IH)*PDM(IH,J)
                  A(J,I) = T
5          A(I,J) = T
              T = 0.0
              DO 6 IH=1,NRX
6                  T = T+YMF0(IH)*FI(IH)
7          A(I,NRTHP1) = T
      N = NRTH
      NP1 = N-1
      NP1 = N+1

```



```

      DO 8 I=1,NM1
        XII = 1.0/A(1,1)
        IP1 = I+1
        DO 8 J=IP1,NP1
          XR = A(1,J)*XII
          A(1,J) = XR
          DO 8 I2=IP1,N
8      A(I2,J) = A(I2,J)-XR*A(I2,1)
        XR = A(N,NP1)/A(N,N)
        DO 10 J=2,NRTH
          D(N) = XR
          DO 9 I=1,NM1
9      A(1,N) = A(1,NP1)-XR*A(1,N)
        NP1 = N
        N = NM1
        NM1 = NM1-1
10     XR = A(N,NP1)
        D(1) = XR
        DO 11 I=1,NRTH
          F1(I) = THETA(I)
11     THETA(I) = THETA(I)+0.5*D(I)
        CALL MODSET (THETA,FM,NRX,F,X)
        QVMIN = 0.0
        DO 12 IH=1,NRX
          T = Y(IH)-FM(IH)
          YMFU(IH) = T
12     QVMIN = QVMIN+T*T
        IF (ABS(QVMIN-Q0)-TOL*QVMIN) 14,14,13
13     Q0 = QVMIN
        GO TO 2
14     WRITE (6,17) QVMIN
        WRITE (6,18) ((KSPACE,I),I=1,NRTH)
        DO 15 IH=1,NRX
          ERR = Y(IH)-FM(IH)
15     WRITE (6,19) IH,Y(IH),FM(IH),ERR,(PDM(IH,I),I=1,NRTH)
        SDEV = SQRT(QVMIN/NRX)
        WRITE (6,20) SDEV
        RETURN

```

C

C

```
16  FORMAT (15H ITERATION NR. 12,7X,7HQ(0) = E14.8)
17  FORMAT (16H FINAL Q(VMIN) =E12.5)
18  FORMAT (1H0,/,33H6NX      Y      MODEL Y      ERROR      ,7(A2,7HDY/DTH(,
    $I1,1H)))
19  FORMAT (1H ,13,3F10.6,7(2X,E9.3))
20  FORMAT (14H0R.M.S. ERROR=,E9.3)
    END
```

## APPENDIX E

Example Data and Program Printout

From INTERPRETER

# TITRATION OF .002NA2CO3 AT 150 PSIG F10

\*\*\*\*\* INPUT DATA \*\*\*\*\*

FPH (VOLTS)	FCL (VOLTS)	COND. (MHOS)	TEMP. (D. CEN.)
-0.42092	0.27727	0.388265	24.03
-0.41049	0.26518	0.408632	24.37
-0.24883	0.21066	0.412430	24.67
-0.20481	0.19276	0.450343	24.84
-0.15009	0.18566	0.489294	24.96
-0.07124	0.17450	0.687945	25.05
-0.05588	0.16590	0.936459	25.12
-0.04958	0.15997	1.133570	25.18
-0.04691	0.15672	1.268700	25.24
-0.04491	0.15352	1.394200	25.29
-0.04345	0.15090	1.500600	25.34
-0.04245	0.14951	1.585300	25.39
-0.04151	0.14800	1.653000	25.42

# TITRATION OF .002NA2CO3 AT 150 PSIG F10

## MATRIX R COMPENSATED COEFFICIENTS

NX	TR	RKWX25	RB1X25	RB2X25	LH	LOH	LCL	LC03	LHC03	LEN	EREF	KSP
1	0.9967	0.9297	1.0215	1.0413	345.1	194.6	74.9	67.7	44.1	49.0	0.06470	.12E-08
2	0.9979	0.9538	1.0139	1.0266	346.7	195.8	75.4	68.1	44.4	49.4	0.06470	.12E-08
3	0.9989	0.9756	1.0072	1.0138	348.2	196.8	75.8	68.5	44.7	49.7	0.06470	.12E-08
4	0.9995	0.9881	1.0035	1.0067	349.0	197.4	76.1	68.8	44.9	49.8	0.06470	.12E-08
5	0.9999	0.9970	1.0009	1.0017	349.6	197.9	76.3	68.9	45.0	50.0	0.06470	.12E-08
6	1.0002	1.0037	0.9989	0.9979	350.0	198.2	76.4	69.1	45.0	50.1	0.06470	.12E-08
7	1.0004	1.0090	0.9974	0.9950	350.4	198.4	76.5	69.2	45.1	50.1	0.06470	.12E-08
8	1.0006	1.0136	0.9961	0.9926	350.7	198.6	76.6	69.2	45.2	50.2	0.06470	.12E-08
9	1.0008	1.0181	0.9948	0.9901	351.0	198.9	76.7	69.3	45.2	50.2	0.06470	.12E-08
10	1.0010	1.0219	0.9937	0.9880	351.2	199.0	76.8	69.4	45.3	50.3	0.06470	.12E-08
11	1.0011	1.0257	0.9926	0.9860	351.5	199.2	76.9	69.5	45.3	50.3	0.06470	.12E-08
12	1.0013	1.0296	0.9915	0.9839	351.7	199.4	76.9	69.5	45.4	50.4	0.06470	.12E-08
13	1.0014	1.0319	0.9909	0.9827	351.9	199.5	77.0	69.6	45.4	50.4	0.06470	.12E-08

# TITRATION OF .002NA2CO3 AT 150 PSIG F10

## MATRIX Y MODEL OUTPUT

NO.	PH	ACL	C.ACID	AC03	AHC03	AH2C03	ALFA	EJ	COND.	IS	GAMMA
1	9.71	21.64	-0.17	278.08	1340.33	0.78	1.00	87.25	197.24	2362.95	0.9495
2	9.51	55.57	38.63	223.55	1393.96	1.04	1.00	86.51	207.59	2218.08	0.9509
3	6.76	661.91	670.96	0.33	1137.43	470.56	0.99	86.50	209.51	1929.79	0.9539
4	5.99	1293.83	1333.11	0.02	466.13	1131.45	0.99	85.20	228.77	1909.88	0.9541
5	5.05	1637.17	1692.52	0.00	70.72	1521.06	0.98	83.92	248.56	1887.79	0.9544
6	3.62	2047.95	2129.64	0.00	2.76	1581.95	0.98	78.31	349.48	2175.04	0.9514
7	3.27	2357.12	2462.04	0.00	1.24	1578.08	0.98	73.19	475.72	2475.94	0.9485
8	3.11	2635.05	2761.75	0.00	0.86	1573.61	0.97	70.02	575.85	2734.29	0.9463
9	3.03	2789.50	2928.96	0.00	0.72	1571.04	0.97	68.16	644.50	2886.65	0.9450
10	2.97	2982.71	3137.91	0.00	0.63	1567.75	0.97	66.61	708.25	3052.06	0.9436
11	2.93	3159.38	3329.21	0.00	0.57	1564.72	0.97	65.41	762.30	3198.71	0.9425
12	2.90	3224.42	3400.41	0.00	0.53	1563.60	0.97	64.51	805.33	3277.48	0.9419
13	2.87	3333.59	3519.04	0.00	0.49	1561.72	0.96	63.81	839.72	3373.83	0.9412

## NEW THETA

CT 0.001619 PHI 9.62 PCL1 4.33 EPZ 0.00000 KPH 0.05920

CX 0.002059 EPZ2 0.00000 ECZ 0.00600 KCL 0.05760 CELK0.000508

EQUILIBRIUM COMPUTED ALKALINITY=0.001938 FROM TOTAL CO2 OF 0.001619

## APPENDIX F

### Preparation of Solutions and Electrodes

## APPENDIX F

Preparation of Solutions and ElectrodesF.1 Electrodes

F.1.1 Glass electrodes were Broadly-James type 9003, general purpose electrodes with extra strength, 12 mm diameter, pH glass bulbs. These electrodes were then sealed with epoxy glue into the Delron body of the electrode assembly shown in Figure 12.

F.1.2 The silver-silver chloride electrodes were made by electrolyzing a 3/4" segment of number 14 silver wire for 30 minutes at a current density of 1 ma per cm<sup>2</sup> in a 0.1 Molar solution of HCl. The silver wire was first silver soldered to the central conductor of a coaxial cable. The wire and connection were cast in epoxy cement into a plug shape, a 1/4 inch diameter and 3/4 inch long. The plug was set into the Delron body of the electrode assembly with Silastic (see Figure 12). Before electrolyzing, the 3/16" tip of silver wire which protruded beyond from the plug was cleaned and sanded with clean strips of fine emery paper, then washed in dilute nitric acid and distilled water. Two hours after deposition of the silver chloride coating the electrodes were observed to have an offset potential of 1.25 millivolts in 0.1 N HCl and 2.5 millivolts in a 0.001 M HCl solution.



F.1.3 The auxiliary electrode was an inch long piece of silver wire formed into an open helix. The silver wire was soldered to a copper wire and the connection cast with epoxy cement, into a plug shape similar to that for the silver-silver chloride electrodes. The thermistor bead was also cast into this same plug so that the actual bead extended about 3/16 inch beyond the plug into the center of silver wire helix. The plug was cemented into the Delron electrode assembly with Silastic.

F.1.4 The gold working electrode was constructed in much the same fashion as the chloride electrodes, only 1 mm gold wire was used. The exposed portion of the gold wire was ground so that it was flush with the epoxy plug and the Delron electrode assembly, leaving a flat, gold button about 0.79 square millimeters.

## F.2 Test Solutions

F.2.1 Sodium Carbonate 0.02 N (standard) - 1.059 gms of reagent grade  $\text{Na}_2\text{CO}_3$ , dried at  $104^\circ\text{C}$  for two hours, was dissolved in one litre of deionized, distilled water. The solution was kept in a stoppered volumetric flask.

F.2.2 Hydrochloric acid, 0.1 N (reference solution). A solution of about 0.1 N plus was made from diluting reagent grade HCl. This was standardized against the sodium carbonate solution by

titration of a diluted 5 ml aliquot of acid to pH 4.5 with 0.02 N

$\text{Na}_2\text{CO}_3$  as the titrant.

F.2.3 All other test solutions were made by volumetric dilution of these solutions with distilled water.

## APPENDIX G

### Temperature Adjustment of Coefficients

## APPENDIX G

Temperature Adjustment of Coefficients

The solubility and equilibrium coefficients used in this model were adjusted to the in situ temperature using the general relationship;

$$K_T = K_{298^\circ K} \cdot r(T)$$

where;  $K_T$  = a general equilibrium coefficient adjusted to the in situ temperature,

$K_{298^\circ K}$  = the same equilibrium coefficient reported at 25°C,

$r(T)$  = a ratio function of absolute temperatures,  $298/T$ .

The basis for this relation is the integral form of the van't Hoff equation, usually expressed as:

$$- \log_{10} \left\{ K_T \right\} = \frac{\Delta H}{2.303 RT} + \text{constant}$$

By treating  $\Delta H$ , the heat of reaction at constant pressure, to be essentially constant over the small pressure range, 15 to 150 psia, the relation can be written the form;

$$K_T = 10^{- \left\{ A \cdot T/298 + B \right\}}$$

where A and B are taken as constants for a given equilibrium. By definition, then

$$K_{298} = 10^{-\{A + B\}}$$

and by substituting this into the above relation produces

$$K_T = K_{298} \cdot 10^{-\{A(1 - 298/T)\}}$$

Expressing the in situ adjusted equilibrium coefficients by this relation permits the standard coefficients (i. e. at 25°C) to be entered into the interpreting program. In so far as A is a small fraction of the term (A + B), and the temperature excursion about 25°C is small, then this first order adjustment method provides useful compensation. Appendix Table I summarizes the coefficient values used in the model program along with their respective A factors as determined by curve fitting tabulated data from references.

Hence the ratio function,

$$r(t) = 10^{-\{A(1 - 298/T)\}}$$

is a simple function of the factor A for each equilibrium.

Appendix Table 1. Equilibrium coefficients and their temperature compensation.

Coefficient	A	$K_{298^\circ\text{K}}$	$\text{p}K_{298^\circ\text{K}}$	Reference
$K_w$	-9.693	$1.008 \times 10^{-14}$	13.999	<u>1</u> /
$K_1$	-2.55	$4.30 \times 10^{-7}$	6.36	
$K_2$	-2.83	$5.61 \times 10^{-11}$	10.25	
$\beta_1 = 1/K_2$	2.83	$1.783 \times 10^{+10}$	-10.25	
$\beta_2 = 1/K_1 \cdot K_2$	5.38	$4.145 \times 10^{+16}$	-16.62	
$K_{\text{SP}}(\text{AgCl}/\text{Ag}^+\text{Cl}^-)$	-9.096	$1.24 \times 10^{-9}$	8.906	

The equivalent conductances were also adjusted to the in situ temperature using the relation,

$$\lambda_T = \lambda_{298^\circ\text{K}} \exp \{q \cdot (T-298)\}$$

where  $\lambda_{298^\circ\text{K}}$  and the temperature coefficient,  $q$ , were taken from Table 5-11, Handbook Analytical Chemistry, page 5-30.

1/ Handbook of Analytical Chemistry, Table 1-12.

The electrode sensitivity factors  $K_{\text{pH}}$  and  $K_{\text{Cl}}$  were treated in a like manner. The adjusting relationship in this case is

$$K_{\text{electrode}} @ T = K_{\text{electrode}} @ 298^{\circ}\text{K} \times T/298$$

The effective reference potential developed in the reference solution is also a function of the in situ temperature. A direct relation is assumed with the activity of a 0.1 N HCl solution as reported in Gladstone and Lewis, pp. 509. The expression used to compute the reference potential for both the pH and chloride electrode sets was:

$$E_R = -0.0591 \cdot \frac{T}{298^{\circ}\text{K}} \cdot \log_{10} \left\{ a_{\text{H}^+, \text{Cl}^-} + \frac{T - 298^{\circ}\text{K}}{17000} \right\}$$

where,  $a_{\text{H}^+, \text{Cl}^-}$  = the mean activity of  $\text{H}^+$  and  $\text{Cl}^-$  in at 0.1 N concentration and  $25^{\circ}\text{C}$  ( $a_{\text{H}^+, \text{Cl}^-} = 0.0798$ ).

This is an empirical relationship closely approximating the real situation, used with the understanding that slight errors would be absorbed into the best fit values of  $E_{\text{PZ}}$  and  $E_{\text{CZ}}$ .