CONTINUOUS PHYSICOCHEMICAL MONITORING AND MODELING OF AN AQUATIC ECOSYSTEM

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CONTINUOUS PHYSICOCHEMICAL MONITORING AND MODELING OF AN AQUATIC ECOSYSTEM

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PREFACE

The objectives of this study were to develop a method for continuously monitoring physical and chemical parameters for research in aquatic ecosystems. An effort was made to evaluate the resulting instrument in a laboratory monitoring experiment and to acquire some chemical data on a real aquatic ecosystem.

The work described here should provide guidelines for future comprehensive data acquisition efforts and will hopefully contribute to the advancement of the science of environmental monitoring.

This study was made possible by Dr. L. P. Varga who served as major adviser. Drs. H. A. Mottola, T. E. Moore, and T. C. Dorris served on the advisory committee. A special thanks is due to Dr. Dorris for his interest and support of this project since its conception. The generous assistance with instrument design of Jerry Waughtal and Joe Zinn of the Oklahoma State University Electronics Laboratory is gratefully acknowledged. Mr. R. F. Buck, Director of the Oklahoma State University Electronics Laboratory, provided consultation during the initial stages of this project and generously provided facilities and equipment during most of the electronic development. Special gratitude is extended to Ronald Morrison for his conscientious assistance with electronic design and construction and

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CHAPTER I

INTRODUCTION

Determination of chemical constituents in natural water systems tends to be done on a basis of grab sampling with subsequent laboratory analysis. As more detailed information about a water system is desired, short term variations, such as diurnal cycles, must be measured. In order to assemble a complete description of a water system, the short term variations must be measured over extended periods of time. The large number of analyses which must be performed dictates automated methods of analysis and automatic sampling techniques. Sample transport mechanics and time between sampling and analysis can be minimized by locating the point of analysis near the point of sampling.

On-site physicochemical monitors are commercially available and are widely used in natural water systems to record water quality parameters. Many of these commercial instruments have physical limitations or are excessively costly for use where numerous locations must be monitored.

The primary objective of this research was to develop a reservoir continuous monitoring system suitable for use in biogeochemical

research. The monitoring system was to measure the response of a number of ion-selective electrodes and other sensors. Measurements were to be recorded on a computer compatible medium. The monitoring system, to be housed on a floating instrument platform, was to be capable of unattended operation for periods of at least one week. Measurements were to be made on water samples from multiple depths. And the entire monitoring system hardware should be producible at moderate cost.

Coincident with the monitoring system development was the formation of an interdisciplinary research, education, and demonstration effort known as the Lake Carl Blackwell Ecosystem Analysis Program. The interdisciplinary nature of natural water research had been recognized and an effort was made to correlate the development of the continuous monitor with efforts to obtain ecological data on Lake Carl Blackwell. The study area was chosen partially because of its size, proximity to the main campus, and importance as a municipal water supply.

The aquatic division of the Lake Carl Blackwell study group proposed a fifteen compartment model of the Lake Carl Blackwell aquatic ecosystem. A simplified portion of that model is reproduced in Figure 1. The compartments, or blocks, in Figure 1 represent mass of the components. The k's are transfer coefficients which represent rates of mass transport among the compartments along the pathways designated by arrows. For example, k_{3-11} is the coefficient for the

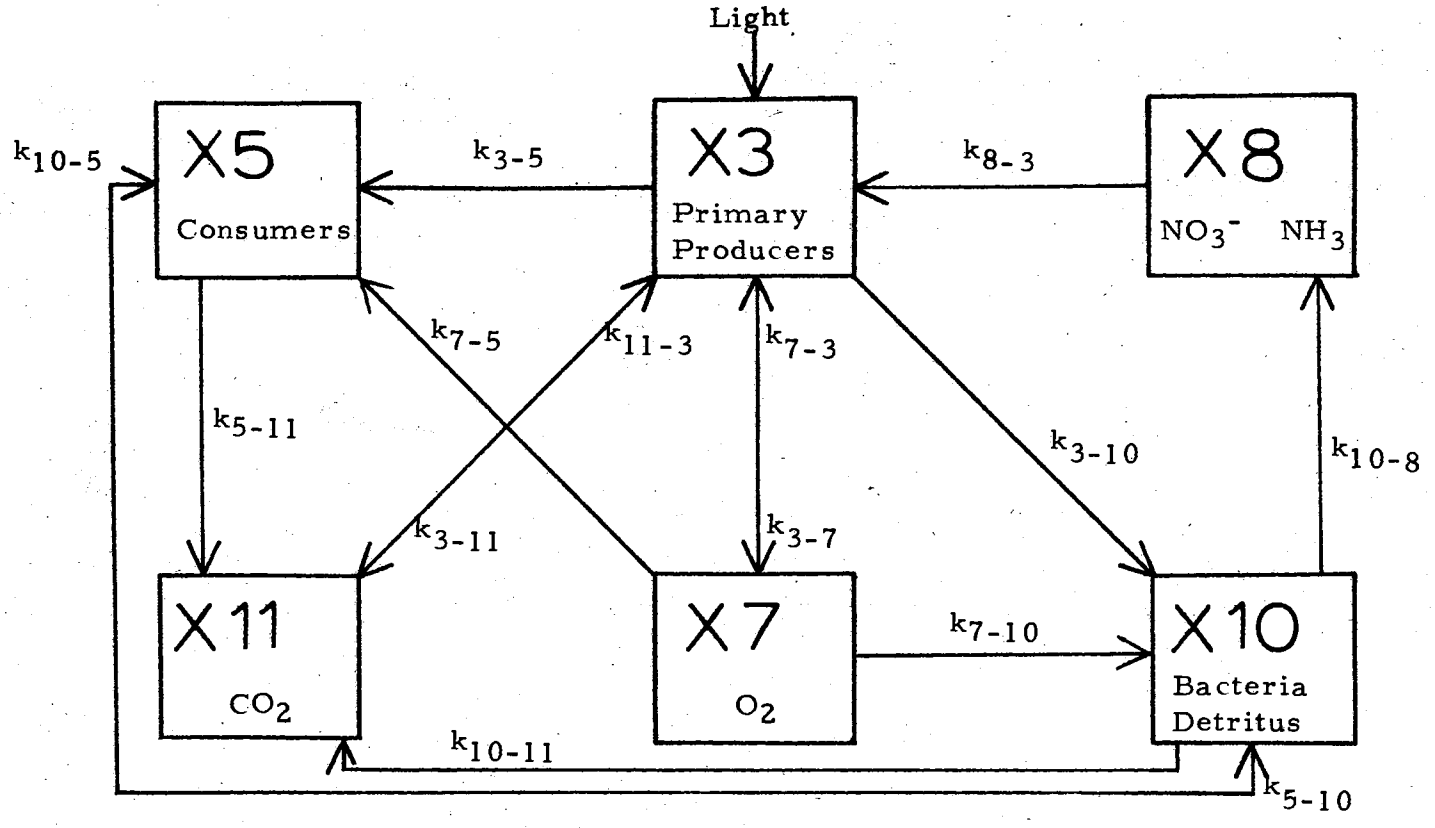

Figure 1. Simplified Model of the Lake Carl Blackwell Aquatic Ecosystem

transfer of mass from primary producers to the CO_2 compartment; this might correspond to a coefficient of respiration for phytoplankton.

The CO_2 compartment represents all of the inorganic carbonate forms in Lake Carl Blackwell. Since continuous monitoring would lend itself readily to measuring fluxes within compartment X11, the CO_2 compartment was chosen as the chemical system to be analyzed. Carbonate system data was not available from the study area; therefore, a grab sampling program was initiated to provide background data while monitor development continued. The aqueous carbonate system would also be emphasized during laboratory checkout of the instrument and procedures.

Lake Carl Blackwell is a chemically stable system in that major changes normally occur slowly. Thus, thoughout this study all dissolved chemical carbonate components were assumed to be in equilibrium at all times. Mass transport should occur mainly by wind induced currents. Currents were not quantified in this study, but spatial considerations were made by sampling multiple depths at six different locations on the lake.

The chemical concentration terms molality and molarity were considered equivalent in the aquatic systems studied. The small errors produced by this assumption were always within experimental variation.

The abbreviations used in this writing are consistent with common forms used in publications of the American Chemical Society.

The computer programs listed in Appendices A and B are written in Fortran IV and may contain some IBM S/360 Fortran IV language extensions. These programs were executed on an IBM S/360/65 computer, G level compiler.

CHAPTER II

THEORY AND APPLICATION OF CONTINUOUS MONITORING FOR CHEMICAL RESEARCH IN NATURAL WATER SYSTEMS

Monitoring

Natural water monitoring can be divided by objectives into two main categories: 1) pollution detection and 2) research. Pollution monitoring measures parameters that can be used to determine water quality (1). Monitoring for research collects data useful for determining the composition and nature of a water system. Equipment and procedures are similar for both classifications, but parameters measured, data handling, and data interpretation differ in line with different objectives. Research monitoring implicitly requires highly accurate measurements, while approximate measurement in pollution monitoring is sufficient to indicate if undesirable conditions are present, especially since pollution indices are somewhat arbitrary.

Recent government and industrial interest in pollution monitoring has brought about the development and commercialization of several automated water quality monitoring systems. A typical system is described by Keyser (2). Monitoring equipment for research is not

as well developed for two main reasons: national interest has inspired little effort and minimal financing for development, and accuracy required is difficult to maintain under field conditions. Some automated water monitoring for research has been done in the oceans, using specially designed instruments and adapted commercial equipment to measure only a few of the desired parameters. Pollution monitoring instrument methods suggest techniques for monitoring water for research, and field experience with pollution monitors will dictate design of future research monitoring systems.

Continuous Monitoring

Continuous monitoring strictly means that a continuous (with respect to time) analog record is produced. When data is digitized (electronically or manually), the continuum is lost, and the measured parameter is represented by points at intervals in time. If digital data is recorded in such a manner that a continuum is approximated within a specified error bound, that data can be considered continuous with a precision within that error bound. Therefore, a continuous monitor may be any monitoring device that produces data from which continuous data can be inferred.

When continuous monitoring is used to collect data reflecting short time-interval changes, measurements of multiple parameters may be required at time intervals of a few hours or less, continuously for months or longer. Generation of this type of data dictates

automation. Continuous monitoring in natural water systems requires that methods for measuring the necessary parameters be instrumented and then automated in a manner that produces continuous (or nearly continuous) data accurately for extended periods of time. This premise is the basis of the following development.

Parameters of Interest in Natural Waters

Parameters to be monitored are determined by the type of study being made. The equations in Table I were determined by Falls (3) to account for more than 99% of the total dissolved solids in a natural freshwater system. These same equations also define more than 99% of the dissolved constituents in seawater (4). Table I, then, represents the major inorganic mass balance for almost any natural water system in the world. If one term in each of the equations in Table I can be measured, the stability constants in Table II can be used to solve for all other terms, thus defining the major inorganic chemical system for the measured water mass at the time of measurement. The braces { } denote activities.

Note that mass balance equations in Table I contain concentration terms and that thermodynamic equilibria constants are expressed by activity terms. Concentration, C, is related to activity, a, by the activity coefficient, y.

$$a = y\,C \qquad (1)$$

TABLE I

INORGANIC MASS BALANCE EQUATIONS

	Equation Number
$[\text{Total Ca}] = [Ca^{++}] + [CaSO_4^{o}] + [CaCO_3^{o}] + [CaHCO_3^{-}]$	(2)
$[\text{Total Mg}] = [Mg^{++}] + [MgSO_4^{o}] + [MgCO_3^{o}] + [MgHCO_3^{-}] + [MgF^{+}]$	(3)
$[\text{Total Na}] = [Na^{+}] + [NaSO_4^{-}] + [NaCO_3^{-}] + [NaHCO_3^{o}]$	(4)
$[\text{Total K}] = [K^{+}] + [KSO_4^{-}]$	(5)
$[\text{Total } HCO_3] = [HCO_3^{-}] + [CaHCO_3^{+}] + [MgHCO_3^{+}] + [NaHCO_3^{o}]$	(6)
$[\text{Total } CO_3] = [CO_3^{--}] + [CaCO_3^{o}] + [MgCO_3^{o}] + [NaCO_3^{-}]$	(7)
$[\text{Total } SO_4] = [SO_4^{--}] + [CaSO_4^{o}] + [MgSO_4^{o}] + [NaSO_4^{-}] + [KSO_4^{-}]$	(8)
$[\text{Total Si}] = [H_4SiO_4] + [H_3SiO_4^{-}]$	(9)
$[\text{Total F}] = [F^{-}] + [MgF^{+}]$	(10)
$[\text{Total Sulfide}] = [H_2S] + [HS^{-}] + [S^{--}]$	(11)

(From Reference 3)

TABLE II

EQUILIBRIUM REACTIONS AND STABILITY CONSTANTS INVOLVING THE DISSOLVED COMPONENTS

Reaction	Stability Constant, K =	Log K	Equation Number
$CO_2 + H_2O = H_2CO_3^{\#}$	$\{H_2CO_3^{\#}\}/\{CO_2\}$	$-540.0/T - 0.777$	(12)
$HCO_3^- + H^+ = H_2CO_3^o$	$\{H_2CO_3\}/\{H^+\}\{HCO_3^-\}$	$+630.0/T + 4.238$	(13)
$CO_3^{--} + H^+ = HCO_3^-$	$\{HCO_3^-\}/\{H^+\}\{CO_3^{--}\}$	$+860.0/T + 7.447$	(14)
$Ca^{++} + HCO_3^- = CaHCO_3^+$	$\{CaHCO_3^+\}/\{Ca^{++}\}\{HCO_3^-\}$	+1.26	(15)
$Ca^{++} + CO_3^{--} = CaCO_3^o$	$\{CaCO_3^o\}/\{Ca^{++}\}\{CO_3^{--}\}$	+3.20	(16)
$Mg^{++} + HCO_3^- = MgHCO_3^+$	$\{MgHCO_3^+\}/\{Mg^{++}\}\{HCO_3^-\}$	+1.16	(17)
$Mg^{++} + CO_3^{--} = MgCO_3^o$	$\{MgCO_3^o\}/\{Mg^{++}\}\{CO_3^{--}\}$	+3.40	(18)
$Na^+ + HCO_3^- = NaHCO_3^o$	$\{NaHCO_3^o\}/\{Na^+\}\{HCO_3^-\}$	-0.25	(19)
$Na^+ + CO_3^{--} = NaCO_3^-$	$\{NaCO_3^-\}/\{Na^+\}\{CO_3^{--}\}$	+1.27	(20)
$Ca^{++} + SO_4^{--} = CaSO_4^o$	$\{CaSO_4^o\}/\{Ca^{++}\}\{SO_4^{--}\}$	$-292.7/T + 3.288$	(21)
$Mg^{++} + SO_4^{--} = MgSO_4^o$	$\{MgSO_4^o\}/\{Mg^{++}\}\{SO_4^{--}\}$	$-1190.5/T + 6.350$	(22)
$Na^+ + SO_4^{--} = NaSO_4^-$	$\{NaSO_4^-\}/\{Na^+\}\{SO_4^{--}\}$	+0.72	(23)
$K^+ + SO_4^{--} = KSO_4^-$	$\{KSO_4^-\}/\{K^+\}\{SO_4^{--}\}$	$-673.6/T + 3.106$	(24)
$H^+ + HS^- = H_2S$	$\{H_2S\}/\{H^+\}\{HS^-\}$	$+1500.0/T + 1.932$	(25)
$H^+ + S^{--} = HS^-$	$\{HS^-\}/\{H^+\}\{S^{--}\}$	$+1470.0/T + 7.911$	(26)
$H^+ + H_3SiO_4^- = H_4SiO_4^o$	$\{H_4SiO_4^o\}/\{H_3SiO_4^-\}\{H^+\}$	+9.7	(27)
$Mg^{++} + F^- = MgF^+$	$\{MgF^+\}/\{Mg^{++}\}\{F^-\}$	+1.82	(28)

$H_2CO_3^{\#}$ = true H_2CO_3; $H_2CO_3 = CO_2 + H_2CO_3^{\#}$

(From Reference 3)

Determination of activity coefficients is necessary when activities and concentrations must be related. Activity coefficients may be calculated by the Debye-Hückel equation which for single ions is:

$$- \log f = \frac{A z^2 \sqrt{I}}{1 + B\mathring{a}\sqrt{I}} \tag{29}$$

Where f is the rational activity coefficient (nearly equal to y in dilute solutions), z is the charge on the ion, I is the ionic strength, A and B are constants, and $\mathring{a}$ is an empirical constant defined as the effective diameter of the hydrated ion. Values of $\mathring{a}$ are tabulated. A and B can be calculated for water as functions of temperature only. I is a measure of the total ions in solution.

The Davies equation, Equation (30), seems to offer a better fit to experimental data at 25° (5).

$$- \log f = 0.5\, z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30\, I \right) \tag{30}$$

This empirical equation has been shown to successfully calculate activity coefficients for a large number of 1-1 and 1-2 electrolytes at 0.1 M. Fairly good fit is obtained as ionic strength varies over a small range. The Davies equation may be useful at temperatures other than 25° by substituting a temperature dependent parameter similar to the Debye-Hückel A for 0.5.

Besides no experimental verification of calculated single ion

activity coefficients, other uncertainties are intrinsic in the use of the Debye-Hückel or Davies equations. Lack of accurate mean activity measurements at temperatures other than 25° prevents verification that successful calculation of mean activity coefficients is possible over a range of temperatures. The Debye-Hückel and Davies equations are empirically based on results of pure systems under laboratory conditions; the application to natural water systems is questionable.

Other calculations of activity coefficients can be made, but results are inconclusive. For example, Garrels and Thompson (6) calculate an activity coefficient for Mg^{++} in seawater of 0.36. Pytkowicz and Duedall (7) found a value of 0.17 under similar conditions.

Ion association and stability constants in natural waters were critically reviewed by Wigley (8). Wigley found that ion pair stability constant discrepancies appear in the literature due to assumptions about particular chemical systems and variations occur because of different methods of determination. There is also controversy about the existance of some ion pairs in natural waters such as $CaCO_3$ and $CaHCO_3^+$. Geochemical solution models are greatly dependent on concepts of ion pair formation and association stability constants. Ultimate success of these models awaits resolution of the predominant chemical equilibria in natural waters and consequent determination of associated stability constants (or, more correctly, stability functions of temperature). Research is currently underway to determine

association constants from 0^{o} to 100^{o} of ion pairs thought to be important in natural water systems (9).

Water research of biological significance may require monitoring of some minor components (less than 1% of total dissolved solids) and dissolved gases. CO_2 and O_2 concentrations are important in biological systems. Nutrients, such as various forms of nitrates and phosphates, may largely determine growth characteristics of phytoplankton. Various trace elements may significantly influence the system being investigated. Some of known importance are Fe, Mo, Mn, and B.

Pollution monitors typically emphasize physical parameters because they are easiest to monitor. Some physical measurements are required for chemical research. Water temperature is almost always necessary. Many analytical techniques are temperature dependent, and the temperature dependence on equilibrium constants is illustrated in Table II. Ionic strength can be correlated with conductivity. Turbidity, atmospheric temperature, solar radiation, and light attenuation may also be monitored when important.

Biological Influence

Studies are frequently made on effects of the chemical system on aquatic organisms, but less consideration is given to biological influence on chemical equilibria. Lee and Hoadley have written a good discussion on this subject (10). An obvious interaction is biological CO_2

production and uptake influence on the carbonate system, and subsequent variation in all pH-dependent equilibria. Other interactions include chemoautotrophic organisms which obtain energy by oxidizing inorganic substances.

Turnover rates by the biological system may determine availability of elements to the chemical system. Some substances, such as phosphates, have a relatively fast turnover rate. Others, such as Ca, carbonates, and silicates, may be involved in insoluble skeletal structures and turnover time will be very long.

Biological activity in water greatly influences O_2 concentration. Gaseous oxygen can oxidize Mn^{2+} and Fe^{2+} to products that are generally insoluble, but reduction can occur in anoxic waters via the following reaction:

$$MnO_2 + 4H^+ \rightarrow Mn^{2+} + 2H_2O - 2e^- \quad E^o = +1.28V \qquad (31)$$

Reducing conditions in natural waters are largely established by biological mechanism. A theory suggesting direct biological reduction of MnO_2 has been questioned (11). However, biological control of both Fe and Mn chemistry is often neglected in water chemistry when their very existance in solution depends on certain biological conditions. Another aspect of biological-organic interaction with inorganic equilibria has recently been discovered. The carbonate-seawater system is not usually at equilibrium (4). Microscopic examination of suspended carbonate particles revealed that each is covered with an organic

coating which inhibits solution in seawater. Further work is needed to prove what effects such protective coatings have on solubility equilibria in general.

The biological and chemical systems are inseparable. Biological influence on chemical equilibria is very real and very important, but unfortunately, very complicated. Biological processes are difficult to represent mathematically, and significant progress in this area has been made only recently. It is probable that many other biological components of importance will be discovered in the future, further complicating the problem. In the meantime, models based on pure chemical thermodynamics may agree better with field observations if corrections are made for the important biological parameters, especially those based on known biochemical mechanisms.

Kinetic Factors

The validity of extrapolation of laboratory solution concepts to natural waters is debatable. Tyree (12) questions how many true equilibrium constants are known and whether or not solutions in natural waters are at equilibrium. Mass transport phenomena in natural waters (advection, convection, and diffusion) introduce spatial factors into ion concentration terms. This movement of chemical species through the solvent changes their environment which may change equilibrium conditions. Whether or not an equilibrium model will adequately describe chemistry of natural waters depends on how closely steady

state conditions are approached. If residence time (the time an ion is subject to particular conditions) is sufficiently large relative to reaction half-time, steady state conditions are approached (13). If a system is not at equilibrium, kinetic factors based on reaction rates and mass transport have to be considered.

Methods of Measuring Chemical Parameters

After the parameters to be monitored are determined, automated methods of measurement must be found. Measurement techniques may be derived from pollution monitoring methods, industrial process control (14, 15), and also from laboratory procedures developed for analyzing natural waters (16). Almost any laboratory technique can be automated, but past difficulties encountered with mechanizing particular methods (14, 15) form a basis for designating some techniques as less suitable for automation than others. Of all analytical methods two are most commonly adapted for continuous monitoring in natural waters: colorimetry and potentiometry.

Automated colorimetric analysis methods are well developed and well documented. Almost all require wet chemical methods. A good introduction with theory of operation is given by Sheen and Serfass (17). An example of a popular commercial automatic colorimetric analyzer is the Technicon AutoAnalyzer[1]. The sample handling and processing

[1] Technicon Corporation, Tarrytown, New York.

echniques of the Technicon instrument are similar to those used in nost commercial automated colorimetric equipment. Sample and reagents are proportioned before mixing by a peristaltic pump. Usually ll liquids are handled by the same pump so that mixing is in phase nd ratios are determined by cross section areas of the pump tubes. 'roperly proportioned liquids are combined and flow into a coil of ıbing which serves as a mixing chamber. Various optional components are available to dialyze, filter, digest, distill, or heat as required for a particular analysis. Reagents can be added and mixed before or after any of these operations. The detector is usually a colorneter, similar to laboratory units with flow-through cells. Strip hart recorders are often used to present data for pollution or industrial process monitoring, but means are provided to record on more omputer compatible media.

Technicon's CSM6 system is of special interest because it is specially designed for continuous monitoring of natural and waste water ystems. It will analyze up to six parameters simultaneously. Reagent onsumption has been minimized to allow unattended operation for up) one week. There is also a unit that prefilters sample water through 0.45μm filter.

A simpler method of reagent addition has been developed which implifies the processing apparatus. Reagent is contained in a solid od that is immersed in the sample stream where proportioning is

controlled by surface area of the reagent rod and sample flow rate (18). Once a sample stream is provided, an analyzer of this type can be built without any moving parts or valves.

Potentiometric methods provide a more direct measurement for many ions. The operation and application of ion-selective electrodes has been well documented; especially good descriptions are given by Durst (19) and Rechnitz (20). Ion-selective electrodes are suited for use in natural water systems (21, 22, 23) and have been used in automatic analyzers (24). When mounted in flow-through cells, these electrodes can be used for continuous monitoring. Many ions are measured directly by ion-selective electrodes which make the measuring part of a continuous monitoring system relatively simple and inexpensive.

Fluoride is determined by direct potentiometric measurement in an industrial fluoride monitor (25). A Ag-AgCl electrode is used for direct potentiometric determination of Cl^- in a commercial water quality monitoring instrument (26). A sophisticated continuous monitoring system records NO_3^- electrode data on magnetic tape (27). Water quality monitors are available which can be specially equipped with a variety of ion-selective electrodes. The electrodes may be housed in individual sample chambers (28), or in submersible sensor assemblies (28, 29). One of these instruments can record a maximum of twelve parameters (28), but none of them can automatically sample multiple

depths.

Ion-selective electrodes can also be used as indicators for titration reactions and this method usually gives more sensitivity than direct potentiometric measurement. Endpoints can be detected by monitoring either the ion of interest or another ion in the titration reaction. Indirect methods, where an electrode measures a different ion from the ion of interest, can be used to determine some ions for which electrodes are not available. When interfering ions are present, known addition techniques (19, 30) can be used to avoid corrections for high background potential or complexing agents. Of course, these later potentiometric methods (other than direct measurement) require reagent mixing and special handling of the data which complicate continuous monitoring processes.

Other methods of analysis are less often used for monitoring, but may have utility in special applications. The colorimetric detector of a wet chemical analyzer may be replaced by a flame photometer (26, 27), fluorometer, spectrophotometer, or atomic fluorometer. Simplified and ruggedized versions of these laboratory instruments, perhaps designed specifically for one type of analysis only, will be necessary before they are suited for continuous operation in the field

Some separation techniques could be automated. Instruments are commercially available that automatically perform gas-liquid chromatography. Automated solvent extraction and distillation methods have

been used with industrial effluent monitors (33). No doubt other separations could be automated if a need should arise that would justify development.

Remote sensing has also been used in studying natural waters (34). Aerial and satellite photography using special color sensitive film and filters is the most common technique. Water movements (using a tracer dye), general pollution detection, oil pollution detection, and kelp inventory have been determined with some success by remote sensing. Application of this method to continuous monitoring in chemical research may be best effected from low orbiting satellites carrying high resolution television cameras equipped with special filters and image-converter tubes. Application of satellite photography in the near future will be limited to gross measurements in large water masses, but could be quite valuable when supplemented by in situ monitoring

Critique of Methods

Before methods can be selected for a particular analysis, the suitability for continuous monitoring under field conditions has to be evaluated. The wet chemical--colorimetric method has been evaluated under conditions of continuously monitoring river water (35). Results were not encouraging and indicate problems that might arise with any similar monitoring system. This system was run for one year and no

valid analytical data was obtained. The equipment was not rugged enough to operate reliably even with daily attention of a trained operator. Valves malfunctioned and plastic tubing to glass connections frequently failed. There was no way to compensate for interfering color or suspended matter. A dual beam colorimeter with a sample water blank might help this problem. Baseline drift could also be decreased by using a dual beam detector, but organic slime and algae growth inside the sample tubes and colorimeter cells will have to be controlled for long term stability.

Ion-selective electrodes can be used for water analysis (36) and are used in some commercial pollution monitoring instruments with good results. They have not been evaluated, however, with respect to long term stability of precision measurement in natural waters. Some general advantages and disadvantages of electrode methods given by Ross (37) are applicable. Electrode measurements are rapid and nondestructive, usually no sample pretreatment is required, and colored or turbid water can be measured directly. Electrodes are especially well suited for monitoring because equipment for direct measurement is relatively inexpensive, power consumption of instruments can be quite small, and simplicity allows compact and rugged design. Electrodes are not highly accurate because of drift. Under field conditions a precision of 4 mV is typical. This is an uncertainty of 15% in monovalent ion measurements and 30% for divalent ions. Much better

precision is obtained by using the electrode as an endpoint detector in a potentiometric titration. Electrode response is logarithmic; therefore, trace ions can be determined with as much precision as ions in more concentrated solutions. Equation 32 gives the potential response to cations in solution.

$$E = E_o + \frac{RT}{nF} \ln a \qquad (32)$$

E_o = potential due to standard reduction potential, reference potentials, reference junctions, etc.
R = molar gas constant
T = absolute temperature
n = charge on the ion
F = faraday constant
a = chemical activity of ion being measured

Since electrodes respond to ion activity, they are especially well suited for chemical research monitoring because activity terms are used in equilibria expressions. There are, however, uncertainties in determining activities of calibration solutions (38). This has prompted work now underway at the National Bureau of Standards to develop activity standards for ion-selective electrodes (38). Activity coefficient determination is especially important when electrode measurements have to be related to total ion concentration.

Chemical interferences occur with electrode response to ions other than the ions being measured. Overall electrode response to an ion of activity, a, is described by a form of the Nernst equation empirically determined by Ross (39).

$$E = E_o + \frac{RT}{nF} \ln (a + \sum_i K_i a_i^{n/x}) \qquad (33)$$

K_i = selectivity constant of i th ion
a_i = chemical activity of i th interfering ion
x = charge on i th ion

Typical K_i values range for 10^{-4} to 10^2, so the $K_i a_i$ terms are negligible in some cases. Approximate values of K_i are tabulated by electrode manufacturers for use in obtaining some idea about what interferences to expect. Selectivity values vary with solution composition. A method based on selectivity has not yet been devised that will resolve an electrode potential into its component contributions from various ions. The measuring electrode--reference electrode pair constitutes an electrochemical cell with very high internal impedance. Glass electrodes typically have resistances of 10^7 ohms. In order to obtain accurate potential measurements, high impedance input electrometers must be used. Extreme care has to be taken that all measuring leads are well insulated from ground and shielded against electrostatic noise. This could present some problems in the field with typically high humidity.

In situ monitoring requires operation of electrodes at varying temperature. Electrode response variation with temperature is given by taking the temperature differential of Equation 32 (40).

$$\frac{dE}{dT} = \frac{dE_o}{dT} + \frac{0.19841}{n} \log a + \frac{0.19841T}{n} \frac{d \log a}{dT} \qquad (34)$$

The first term is characteristic of a particular ion-selective electrode and its reference electrode. The second term is the temperature coefficient slope term of the Nernst equation. This is the only term that is usually corrected by manual or automatic temperature compensation during measurement. The last part is the solution temperature coefficient term. Evaluation of this expression is complicated by the ionic activity being temperature dependent also. Theoretical evaluation of these terms has been attempted, and agreement with experiment is within experimental variation for some systems (41).

Specific Methods

Suppose that all of the concentration terms in Table I are to be determined. If thermodynamic equilibrium is assumed, the stability constants in Table II can be used to calculate some of the terms in Table I so that not all of them have to be measured directly.

If ionic activity is within the dynamic range of an electrode specific for that ion, direct measurement is possible. Electrodes are commercially available that are specific for H^+, Ca^{++}, Na^+, K^+, F^-, and S^{--} activities normally present in natural waters (23, 42, 43). Mg^{++} measurement in synthetic seawater has been demonstrated by means of a divalent cation electrode (44) that is approximately equal in response to Ca^{++} and Mg^{++}.

A SO_4^{--} electrode has been built (45), but its selectivity over

other anions is poor. SO_4^{--} can be titrated by Pb^{++} which can be monitored by a Pb^{++} electrode. Since $PbSO_4$ is only slightly soluble in water, a continuous monitoring technique (46) may be used to indirectly monitor SO_4^{--} with a Pb^{++} electrode. A reagent stream containing a known concentration of Pb^{++} is proportionally mixed into the sample stream. $PbSO_4$ precipitates and the concentration of Pb^{++} remaining is monitored by a Pb^{++} electrode. Since the concentration of Pb^{++} in the reagent stream and the ratio of reagent to sample is constant and known, the amount of Pb^{++} combined with SO_4^{--} is calculable. This method of sulfate monitoring is not as simple as direct measurement, but only one reagent is required so plumbing is kept to a minimum, and use of a colorimetric detector with its associated problems is avoided.

A recently developed pressed-crystal membrane electrode may be useful for monitoring SO_4^{--} (47). At the time of this writing, insufficient data had been published on this electrode to evaluate its usefulness in natural water systems. The preliminary data that is available, however, does indicate good selectivity for SO_4^{--} over other anions.

HCO_3^- and CO_3^{--} can be determined from pH if CO_2 can be measured (Equations 13, 14, and 15). An electrode commonly used for determining dissolved CO_2 in blood (48) may be applicable to natural waters. Direct measurement of CO_2 by an electrode assembly is most desirable because other CO_2 determination methods are complex (49) and would be difficult to automate.

At the present time there is no suitable potentiometric method to determine silicates in natural waters. In this case good colorimetric procedures are available (50) and have been automated (51).

Measurement of the above parameters and temperature is sufficient to calculate all of the concentration terms in Table I which describe the major dissolved species in natural waters. With the exception of silicates, all activities required for calculation of stability constant terms in Table II can be determined by potentiometric techniques. Conversion from activities to the concentration terms in Table I requires individual ion activity coefficients which may be calculated by Equation 29 or Equation 30.

If biological interactions are to be considered, some biologically important chemical parameters can also be monitored. Dissolved O_2 is easily monitored by a number of commercially available galvanic electrodes or by one of the newer potentiometric techniques (52, 53). Total carbon analysis has been automated (54), and commercial instruments are available. Indirect measures of organic content such as chemical oxygen demand (55) and biological oxygen demand (56) have been automated. Automated colorimetric methods have been developed for monitoring inorganic nutrients and associated species such as NH_3, NO_3^-, NO_2^-, PO_4^{3-}, etc. (57). A newly developed oxidation titration for NH_3 (58) may yield a simpler way of monitoring that component. Many of these methods involve complex procedures, so the problems

encountered with the automatic colorimetric analyzer could be expected to plague continuous measurement of these parameters also.

Recording, Data Processing, and Display

Many commercial monitoring instruments contain analog circuits that convert detector response to appropriate units (ppm, C^o, etc.) and record on strip charts. Strip charts are good visual displays; but if any calculations are to be made using the data, interpolation from graphs soon becomes tedious. Since equilibria determinations involve a large number of mathematical steps, calculations are usually done by a digital computer. Data translation problems are avoided if the monitoring system records directly on machine readable media. Punched paper tape or magnetic tape are frequently used; the choice between them is based mainly on amount of data to be recorded before retrieval. Direct transmission of data to a computer is possible via wire or radio when immediate data reduction is desired (59).

Large numbers of calculations are quickly done on high speed digital machines so that it is convenient to use successive iteration techniques for data reduction. Activity coefficients are calculated from ionic strength, I, which is not measured directly, but can be calculated from concentration of the ions.

$$I = \frac{1}{2} \sum_i C_i Z_i^2 \qquad (35)$$

C_i = concentration of the ion, i
Z_i = charge on the ion

All of the ionic concentrations necessary for calculation of I are usually not measured directly. Using the monitoring procedures outlined above, individual activities of each of the ions are measured or calculated, and I can be calculated by assuming concentration and activity are equal (activity coefficient assumed equal to 1). Activity coefficients are calculated and used to calculate a new set of concentrations. These concentrations then determine another value for I which gives a new estimate for the activity coefficients. This iteration can continue until the data is self-consistant within a specified error bound.

Continuous data would normally be taken in order to study some particular chemical processes in a water body. But display of concentrations or activity data is often useful to obtain a physical concept of these parameters. Tabulation of selected data will often show gross correlations. Isopleths on horizontal (60) or vertical (61) cross sections of the water body can be produced by computer (62) and are useful for observing spatial distributions. Three dimensional isopleths are difficult to construct and not often used, but by using computer generation and CRT display, they might be worth-while. Master variable diagrams of particular chemical systems are beneficial for visualizing which components could be expected to predominate under given conditions (63).

Sampling Frequency and Location

A parameter should be measured with enough frequency that the data accurately depicts any variations. One sample per day may be sufficient for deep ocean water while measurements may be taken each minute in a flowing stream. Sampling frequency of a shallow lake depends on the parameter and time of day, but would probably require between 0.1 and 10 samples per hour. If too many measurements are recorded, data reduction becomes formidable. For example, if 11 parameters at each of 10 depths, twice per hour, and at five separate locations in a reservoir are monitored to determine all chemical species in Table I, over 360,000 data points per week will be generated. Some data quality may be sacrificed if quantity has to be decreased.

Location of monitoring points depends on the type of study and the nature of the water body. A sizeable section of a turbulent stream may be well represented by measurements made at one location and one depth. A stratified lake may require continuous monitoring of one meter increments at multiple locations. Again, volume of data has to be considered along with cost per monitoring system if multiple fixed stations are used. Monitoring locations should be selected so that the data is representative of the largest possible water mass.

CHAPTER III

CONTINUOUS MONITORING SYSTEM

A continuous monitoring system (Figure 2) was developed and constructed during 1968 and operated from July, 1968, through November, 1968, near the dam of Keystone Reservoir, Oklahoma. The instruments diagramed in Figure 2 were housed in a floating instrument platform which was anchored in water approximately 20 meters deep located about 100 meters upstream from Keystone Dam. One-hundred ten volt AC power was supplied to the floating platform from the dam via an underwater cable. Water from each of the five depths was pumped through a plastic pipe and solenoid actuated valve to a sampling chamber containing a thermistor and a galvanic O_2 electrode. As the programmed controller actuated each valve for 9 minutes in sequence, O_2 and temperature data was recorded on strip chart. When data from each depth had been recorded, the controller started the entire sampling sequence again. This method of periodic sampling and measurement is adequate for continuous monitoring if the data variance with time is small in the sampling period.

The Keystone monitoring system demonstrated the feasibility and general principles of multiple depth continuous monitoring in a

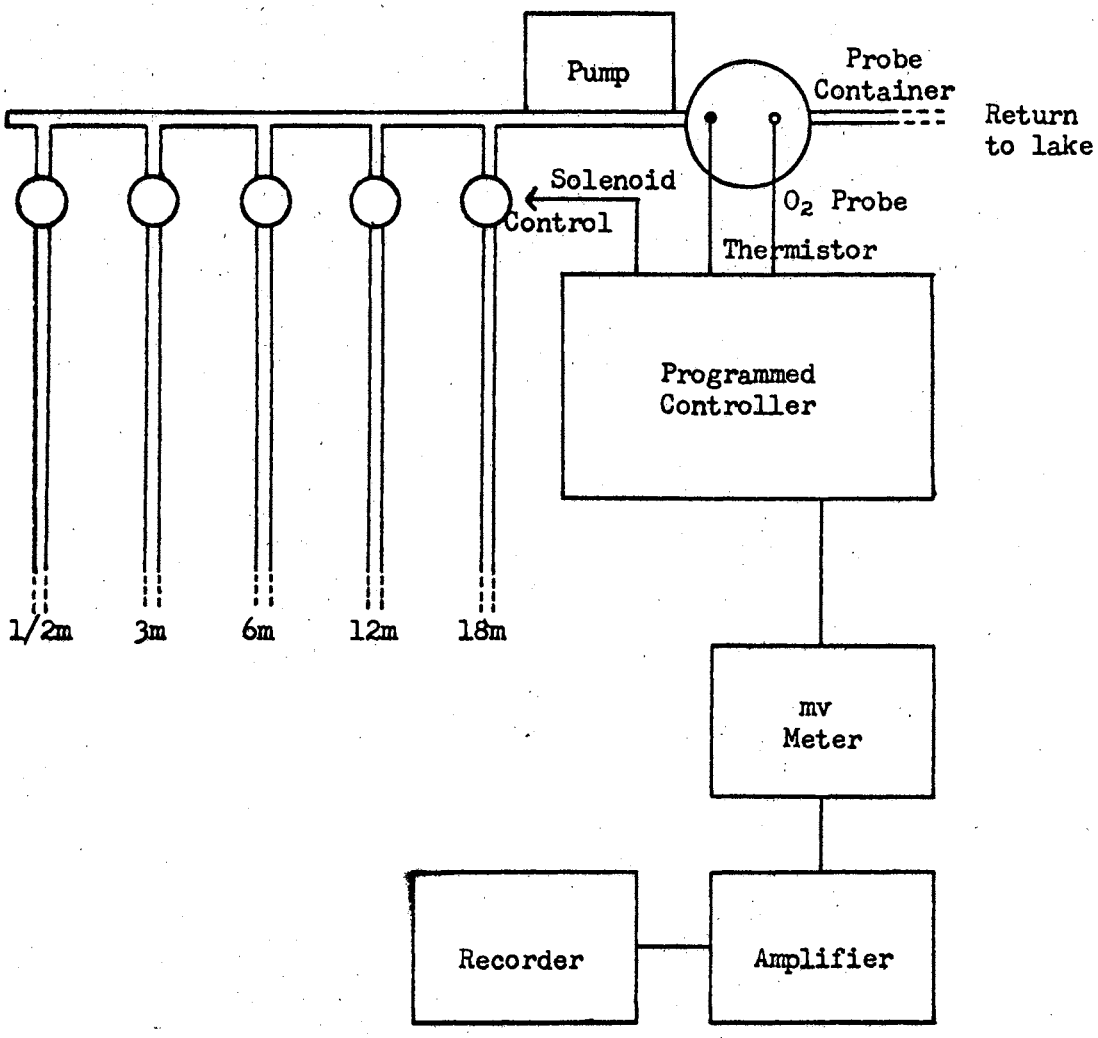

Figure 2. Continuous Monitoring System Used on Keystone Reservoir

reservoir. The strip chart data from this study was computer analyzed and used to evaluate multiple depth continuous monitoring as a method for measuring primary production in a reservoir (64).

Once the principles of multiple depth continuous monitoring were established, a more sophisticated system with larger sample and electrode capacity, more versatility, and a computer compatible recording medium could be designed. Much of the design of the final monitoring system was dictated by the experience with the earlier Keystone system.

A monitoring system has been developed for continuous automatic data acquisition of measurements on natural waters (Figure 3). Since a detailed description of the monitoring system hardware is available elsewhere (65), only a brief explanation of the monitoring system function is presented here. The monitoring system is designed particularly to record data from ion-selective electrodes which are electrical transducers of chemical activity in aqueous solutions. Water from selected depths is pumped into a sampling chamber allowing one set of electrodes to analyze samples from multiple depths. Data is recorded on punched paper tape which was chosen as the recording medium because of its computer compatibility and economy.

An electrode switching device, multiplexer, makes multiple electrode measurements possible with the single input mV meter. The multiplexer allows selection of any one of 5 (expandable to 24) sensor inputs by means of a high-impedance switching circuit. Accuracy of

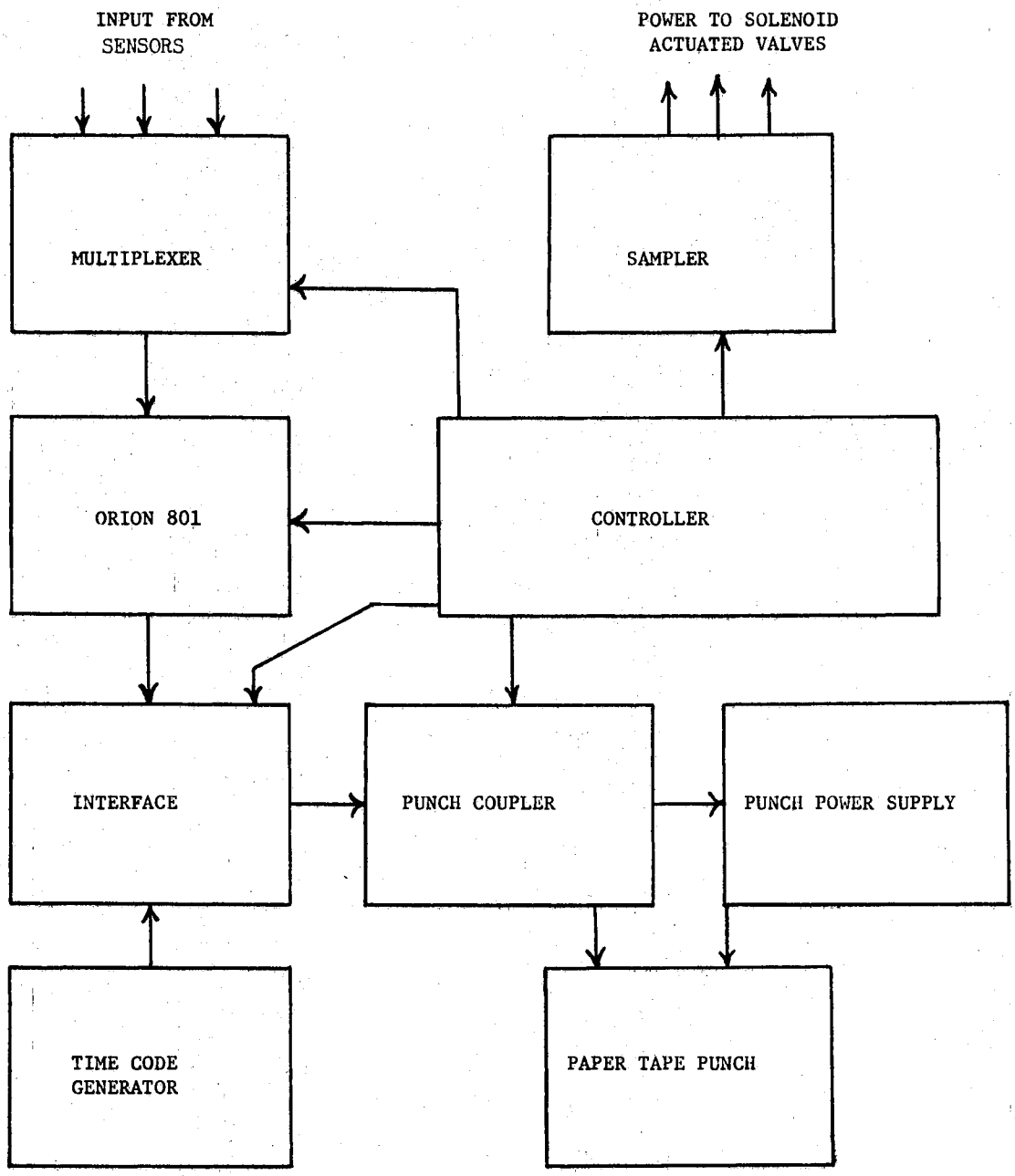

Figure 3. Block Diagram of Reservoir Monitoring System. Arrows indicate general directions of information flow.

electrode potential is maintained by 19 of these inputs being isolated from ground and from each other through an impedance on the order of 10^{14} ohms. Special input jacks and reed switches maintain this circuit isolation from electrode input, through the multiplexer, and to the mV meter. The multiplexer also has 2 (expandable to 15) tip jack inputs to switch reference half-cell electrodes or other inputs which do not require especially high impedance isolation. All 15 tip jack inputs can be individually switched to the reference input of the mV meter. Six of the tip jack inputs can be individually switched into the high impedance bus for sensing-circuit input to the mV meter. Similarly, 3 of the 19 high-impedance multiplexer inputs can be switched to the reference circuit for special measurements.

The multiplexer design is an example of a theme of great flexibility and ease of change evident throughout the entire monitoring system. Flexible capabilities are necessary in prototype design to allow adjustment to obtain optimum performance under a variety of operating conditions and to increase utility in a multifaceted research program. For example, the multiplexer switching functions can be manually controlled by means of front panel control or put under full or partial program control of the controller. Patchboards in the multiplexer allow programming its switching function in automatic mode. The multiplexer function can be programmed to measure its inputs in any selected order, an input can be read numerous times at any place

or several places in a measuring sequence, and any reference input may be selected for any measurement. The last capability allows one or a few reference electrodes to serve with a large number of measuring electrodes, and measurements can be repeated with different references for comparison purposes. Any of six tip jack inputs or any of three high-impedance inputs may be switched to the reference or the measuring inputs of the mV meter at any time during a measuring sequence.

Electrical response of the sensors is measured by an Orion[1] model 801 digital millivolt meter. The function of the Orion mV meter within the monitoring system is one of a high-impedance precision analog-to-digital converter. The four decimal digits of absolute mV data generated by the mV meter are displayed on its front panel and available in parallel binary coded decimal format from a rear connector tab. This digital output is relatively easy to record for direct computer reduction of the data.

The interface translates logic levels of the mV meter data and controller generated identification data into logic required for the punch coupler. Since the mV meter is to make measurements in an earth grounded solution, the mV meter measuring circuit has to be isolated from earth ground. This requires that all digital output lines from the mV meter be electrically isolated from the rest of the

[1]Orion Research Incorporated, Cambridge, Massachusetts.

monitoring system. The interface provides this electrical isolation by opto-electronically coupling each logic line from the mV meter. When time code data is to be punched, the interface translates logic and switches approximately 40 logic lines of time code data into the punch coupler in place of mV data and controller generated identification code. A Hewlett-Packard[2] model 2545A tape punch coupler receives ten decimal digits in parallel binary coded decimal format from the interface. The punch coupler stores the data in a shift register which serves as a parallel-to-serial converter during the punching operation. Parity and end-of-word codes for paper tape are generated. The punch coupler completely controls operation of the paper tape punch. Front panel controls allow manual or automatic modes of operation and manual asynchronous punching of tape feed code to make tape "leaders" and "trailers".

Power for the punch solenoids is furnished to the punch coupler by a Hewlett-Packard model 2545B punch power supply.

The ten decimal digits of data from the punch coupler are serially punched on one-inch wide eight-level paper tape by a Teletype model BRPE 11 paper tape punch under punch coupler control. The punch is capable of punching 110 characters per second which far surpasses any foreseeable requirements of the monitoring system. Each data record occupies 1.1 inch of tape, therefore a supply reel

[2]Hewlett-Packard Company, Palo Alto, California.

capacity of 1000 feet of tape should allow unattended operation of at least two weeks for most monitoring applications.

The punched tape is rewound by a Cycle Tape Minder[3] which has a take-up reel capacity of 1000 feet of punched tape.

The controller, as its name implies, performs a function of time sequenced control and coordination of the components in the monitoring system. The controller contains an adjustable timing system which initiates an electrode recording sequence. When operating in automatic mode, the multiplexer switches sensors on controller command. During data recording, controller generated signals give the mV meter a hold command, a signal commands the interface to switch either mV meter data or time code data to the punch coupler, and punching is initiated by a punch signal from controller to punch coupler.

An adjustable time interval of a few seconds between electrode readings allows stabilization of the measuring circuitry before recording. Time is allowed between recording sequences to permit thorough flushing of the electrode chamber by a new sample and chemical and thermal equilibrium between sample and sensors.

Controller action is programmable, and the controller can, to some extent, override the program in the multiplexer, further increasing the utility of the system. The controller program could be changed automatically if that need should ever arise. This capability

[3]Cycle Equipment Company, Los Gratos, California.

was designed especially to provide automatic selection of depths sampled in case the instrument is required to monitor water systems with widely fluctuating depths such as flowing streams.

The controller generates two decimal digits each of sample and sensor identification data in parallel binary coded decimal format. This data is translated by the interface and punched with mV data to identify the sensor and sample data being recorded.

At the end of each recording sequence, the controller advances the sampler to start flushing the next sample. The sampler is a programmable switching device with manual override capability which powers and controls solenoid actuated valves on the sample intake manifold.

The time code generator supplies coded output for recording time of day to the nearest minute and day of the year. The time code is recorded at periodic intervals to provide a time reference for sensor measurements. Sufficient accuracy of the time code should be obtained to allow correlation of data with that of other monitoring systems and weather stations, determination of diurnal cycles, etc.

A typical monitoring operation will be described with all instruments set in automatic mode and time punch set to auto. The following initial conditions are assumed: Sample has been flushing through the electrode chamber. The controller has signalled the multiplexer to switch the first sensor with its appropriate reference to the mV meter.

All sensors are at equilibrium with the water sample, and the first sensor reading has stabilized on the mV meter.

The controller initiates a recording operation. The mV meter, on command from the controller, stores and holds the mV data. A controller generated command to the interface switches time code data to the punch coupler. A punch signal to the punch coupler initiates a punching operation which punches time code data on paper tape (Table III).

After time code data is punched, the interface switches mV and controller identification data to the punch coupler along with another punch signal. The mV and identification data is punched (Table IV), the mV meter hold is released, and the controller signals the multiplexer to switch the next electrode set to the mV meter. An adjustable time interval (usually 10 to 20 seconds) is allowed for stabilization of the measuring circuitry. The mV reading is held while mV and identifying data is punched on paper tape. The mV meter hold is released and the controller signals the multiplexer to switch to the next electrode set. This process is repeated until all of the programmed sensor data is recorded.

After the last sensor reading is recorded, the multiplexer is recycled to the first electrode set in its program, the sampler starts flushing the next sample through the electrode chamber, and another time code is punched. The entire monitoring system then waits until

TABLE III

PAPER TAPE RECORD FORMAT, TIME DATA

Character Position	Valid Characters	Interpretation
1	2	record contains time code data
2	0	no significance
3	0	no significance
4	0-9	day hundreds digit
5	0-9	day tens digit
6	0-9	day units digit
7	0-2	hour tens digit
8	0-9	hour units digit
9	0-5	minute tens digit
10	0-9	minute units digit
11	EOW	end of word

TABLE IV

PAPER TAPE RECORD FORMAT, SENSOR DATA

Character Position	Valid Characters	Interpretation
1	1	record contains mV data
2	3 or 4[4]	mV<0 if 3, mV≥0 if 4
3	0-9	mV hundreds digit
4	0-9	mV tens digit
5	0-9	mV units digit
6	0-9	mV tenths digit
7	0-2	sensor ID tens digit
8	0-9	sensor ID units digit
9	0-2	sample ID tens digit
10	0-9	sample ID units digit
11	EOW	end of word

[4]When mV data is positive, the punched mV data is the nines complement of its actual value.

the end of the flushing period when the time code and the first sensor mV data is recorded. The sensor reading and recording program is repeated for each sample until data for all samples has been recorded. At the end of the sampling sequence the sampler is recycled to the first of its program and the entire cycle is repeated automatically with all sensor measurements in the multiplexer program being recorded for each sample. Time code data is recorded immediately before the first sensor record and immediately after the last sensor record for each sample.

The entire monitoring program can be automatically repeated continuously to effectively monitor a water system.

CHAPTER IV

ION-SELECTIVE ELECTRODES AS CHEMICAL SENSORS IN NATURAL WATER SYSTEMS

Reference Electrode

The "other electrode" (66) used in potentiometric measurements is as important as the sensing electrode. Attention should be given to the reference electrode function and to possible sources of error that may occur from it. Reference electrodes and their properties have been extensively reviewed (67) and more recently have been reviewed with respect to applications with ion-selective electrodes (66).

The most common types of reference electrodes used for general laboratory and field applications are the calomel and Ag-AgCl types. Of these, the Ag-AgCl reference electrode is preferable for field monitoring applications. Next to the H_2 gas electrode, the Ag-AgCl electrode is probably the most reproducible electrode available, and is the most reliable reference electrode (66). Internal reference elements inside ion-selective electrodes are usually Ag-AgCl, therefore use of a Ag-AgCl external reference provides some self-compensation of systematic errors. The calomel electrode, less reproducible than

Ag-AgCl, has the serious disadvantage of a marked temperature hysteresis attributed to mercuric complexes formed at higher temperatures.

The half-cell potentials of both the calomel and Ag-AgCl electrodes depend on Cl^- activity in the electrolyte solutions. When the sample to be measured has varying and unknown Cl^- activity, a stable reference potential is maintained by reference electrode immersion in an electrolyte of constant Cl^- concentration. Contact between the internal reference electrolyte solution and the sample can produce a liquid junction potential which has been reviewed briefly by Covington (66).

Liquid junction potentials arise when the reference filling solution contains positive and negative ions which diffuse into the sample at different rates. Different rates of total charge migration lead to a potential difference across the liquid junction. The requirements of good reference electrode filling solutions, including equitransference, are discussed in Reference 68. An electrolyte solution will be approximately equitransferent if

$$\Sigma Z_+ C_+ \lambda_+ = \Sigma Z_- C_- \lambda_- \qquad (36)$$

where Z is the charge on the ion; C, the ionic concentration and λ is the equivalent conductivity (mho cm^2/eq).

The Orion Research Incorporated model 90-01 single junction

reference electrode used in this study has a Ag-AgCl internal element. It has very little junction potential in dilute solutions when used with Orion number 90-00-01 filling solution. The electrolyte filling solution contains a mixture of K^+, Na^+, NO_3^-, and Cl^- in the appropriate ratios to satisfy Equation 36. The rugged plastic body and easily flushed sleeve-type liquid junction make this kind of reference electrode well suited for field applications.

Standard Solutions

Cation standard solutions (except H^+ standards) were prepared from the respective chloride salts as suggested by Bates and Alfenaar (38). All salts used in standard preparation meet A. C. S. specifications and were used without further purification.

Standard stock solution of approximately 5×10^{-2} M NaCl was prepared from a measured weight of oven dried NaCl. Approximate 3×10^{-2} M stock solutions of $CaCl_2$ and $MgCl_2$ were prepared. A solution of 5×10^{-2} M $AgNO_3$ was standardized by titration with the standard NaCl. The titration endpoint was detected potentiometrically by a Ag-AgCl electrode vs calomel reference electrode assembly. The Ca^{++} and Mg^{++} solutions were then standardized by potentiometric titration with standard $AgNO_3$ solution. All standard solutions were stored in polyethylene bottles

Electrode calibration solutions were prepared by dilution of the

appropriate stock solution. Chemical activity of each calibration solution was determined from concentration by Equations 1 and 29. A least squares curve fit to mV vs activity data for each electrode provided a linear calibration equation with the form of Equation 32.

Hydrogen Ion Electrode

The H^+ electrodes used in this study were glass membrane general purpose electrodes, Beckman[1] numbers 41263 and 39000. According to the manufacturer, Na^+ interference should be negligible in samples where pH $<$ 9 and $[Na^+] < 10^{-2}$ M (69).

All H^+ calibrations were done in pHydrion[2] buffer solutions at 25°. Millivolt readings were taken at several $[H^+]$ values, and a least squares fit of the data yielded calibration equations with the form of Equation 32. H^+ activity was assumed equal to concentration for $[H^+] < 10^{-5}$ M.

After approximately one week of monitoring a laboratory culture of 120 mg/l Dactylococcopsis at pH 8.5, H^+ electrode response became very unstable. Electrode response was neither stable nor reproducible in buffer calibration solutions. After wiping the H^+ sensitive membrane clean and soaking overnight in 0.1 M HCl, stability was restored and the electrode could be recalibrated.

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[1]Beckman Instruments, Incorporated, Fullerton, California.

[2]Micro Essential Laboratories, Brooklyn, New Jersey.

Sodium Ion Electrode

Na^+ activity was determined by a glass membrane electrode, Beckman number 39278. The manufacturer reports that this electrode responds to H^+, K^+, and Ag^+ in addition to Na^+ (70). Sensitivity data indicates there is no interference with Na^+ measurement if $[Na^+] > 10^4 [H^+]$, $[Na^+] > 10 [K^+]$, and $[Na^+] > 10^{-4} [Ag^+]$(70). If all three of these conditions are not met, the actual selectivity of the electrode should be determined to quantify the amount of interference to expect.

Na^+ electrode response degradation was observed in the Dactylococcopsis culture similar to that of the H^+ electrode. The condition was corrected by wiping the membrane clean and soaking overnight in 0.1 M NaCl solution.

Calcium Ion Electrode

An Orion model 92-20 liquid junction Ca^{++} electrode was used for potentiometric determination of Ca^{++} activity. The manufacturer's list of approximate selectivities for other divalent cations indicates that no appreciable ionic interference should be expected in most oxygenated natural freshwater systems where $[H^+] < 10^{-7}$, $[Ca^{++}] > 1.5 [Mg^{++}]$, and $[Ca^{++}] > 1.5 [Sr^{++}]$(71). If these conditions are not met by the sample, the possibility of interference must be considered.

Laboratory experience with this electrode indicated that with about four weeks use, the Ca^{++} electrode response time increased, drift became more pronounced, and the calibration slope decreased. When this occurs, the electrode must be disassembled, cleaned, refilled with new solutions, and recalibrated.

Divalent Cation Electrode

There is no commercially available electrode specific for Mg^{++} in aqueous solutions. A part of this study was to evaluate the Orion model 92-32 divalent cation electrode as a sensor for determining Mg^{++} in the presence of Ca^{++}. The electrode responds approximately equally to Mg^{++} and Ca^{++} in aqueous solutions and interference from Sr^{++} may occur unless $[Mg^{++}] + [Ca^{++}] > 50\ [Sr^{++}]$(72).

Since this electrode responds to both Ca^{++} and Mg^{++}, it would seem possible that Mg^{++} activity could be determined if Ca^{++} activity is known. In order to predict electrode response to Mg^{++} in the presence of Ca^{++}, it is necessary to examine the nature of electrode selectivity.

A membrane potential theory for liquid ion exchanger membrane electrodes has been developed by Sandblom, Eisenman, and Walker (73) and re-presented by Eisenman (74). An experimental examination by Eisenman (75) of the selectivity of Na^{+} and H^{+} in di-2-ethylhexyl phosphoric acid in wet n-amyl alcohol supports the validity of

theoretical prediction of liquid membrane selectivity. Their model (Figure 4) of two counterion species in an organic exchanger where counterions and sites are strongly associated most nearly corresponds to the Orion divalent cation electrode.

Sandblom, Eisenman, and Walker (73) have shown that for two counterions, the steady-state membrane potential is given by Equation 37.

$$E = \frac{RT}{nF} \left\{ (1-\tau) \ln \frac{(a_1)_e + \frac{u_2 + u_s}{u_1 + u_s} \frac{k_2}{k_1} (a_2)_e}{(a_1)_i + \frac{u_2 + u_s}{u_1 + u_s} \frac{k_2}{k_1} (a_2)_i} + \right.$$

$$\left. \tau \ln \frac{(a_1)_e + \frac{u_{2s}}{u_{1s}} \frac{k_2 K_{2s}}{k_1 K_{1s}} (a_2)_e}{(a_1)_i + \frac{u_{2s}}{u_{1s}} \frac{k_2 K_{2s}}{k_1 K_{1s}} (a_2)_i} \right\} \qquad (37)$$

Where τ, given by Equation 38, is in the range $0 \leq \tau \leq 1$ (65).

$$\tau = \frac{u_s (u_{2s} K_{2s} - u_{1s} K_{1s})}{(u_1 + u_s) u_{2s} K_{2s} - (u_2 + u_s) u_{1s} K_{1s}} \qquad (38)$$

This theory assumes that ion pairs is the highest order complex formed in the membrane. K_{1s} is the association constant for the formation of the neutral ion pair $(M_1)s$ in the organic phase. The u's represent mobilities of ions or ion pairs in the membrane phase, and

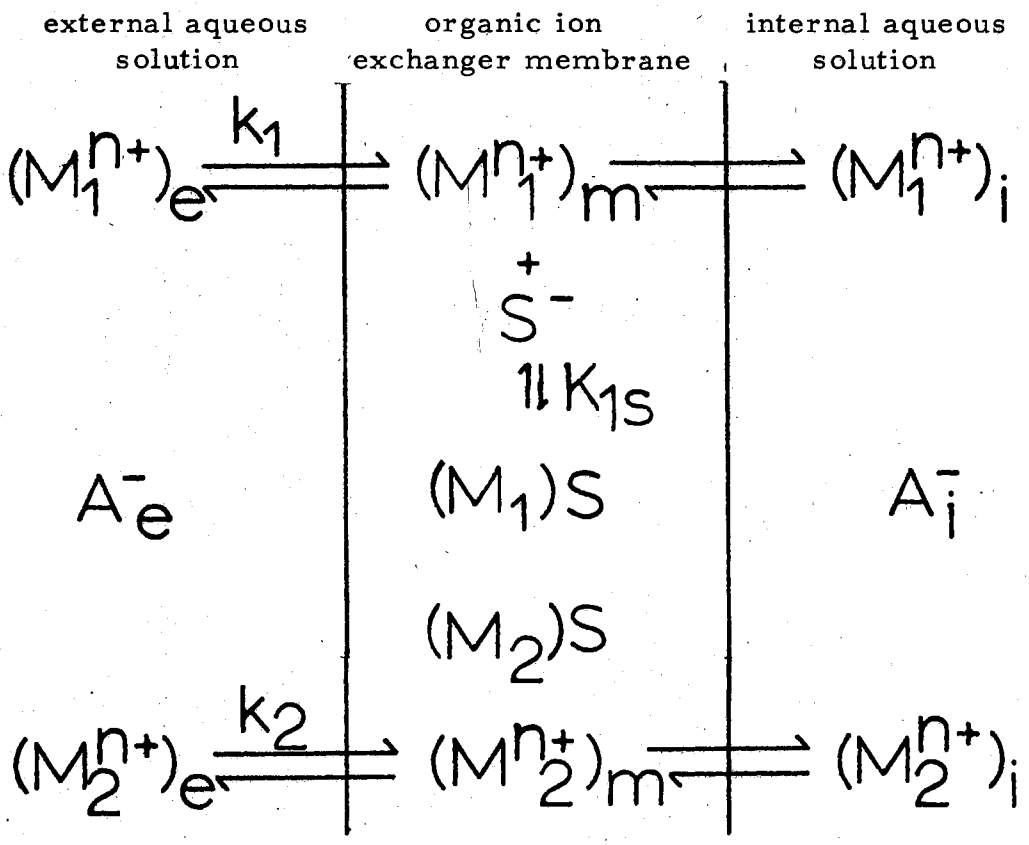

Figure 4. Diagram of a Water-Immiscible Liquid Cation Exchange Membrane. This diagram was modified from Reference 67. Phase boundaries are freely permeable to counterion M_1^+ and M_2^+. Co-ions, A^-, and exchange sites, S^-, remain in the respective phases.

k_1 is the partition coefficient of M_1^{n+} between aqueous and organic phases. All of the terms in the denominator of each logarithm except $(a_1)_i$ and $(a_2)_i$ are constant for a given membrane. The internal solution activities are fixed by constant composition of the internal electrolyte solution; therefore the log denominator terms in Equation 37 are constant. Under these conditions, the membrane potential is given by Equation 39 where e subscripts have been dropped from the external solution terms.

$$E = \text{const} + \frac{RT}{nF}\{(1-\tau)\ln\left[a_1 + \frac{u_2 + u_s}{u_1 + u_s}\frac{k_2}{k_1}a_2\right] + \tau \ln\left[a_1 + \frac{u_{2s}}{u_{1s}}K_{12}a_2\right]\} \quad (39)$$

$$K_{12} = \frac{k_2 K_{2s}}{k_1 K_{1s}} \quad (40)$$

K_{12} represents ion exchange selectivity of the reaction:

$$(M_2^+)_e + (M_1)\ S \overset{K_{12}}{\rightleftharpoons} (M_1^+)_e + (M_2)\ S \quad (41)$$

As has been pointed out by Srinivasan and Rechnitz (76), K_{12} is not the equilibrium constant for Reaction 41 because the constants in Equation 37 are defined in terms of concentration instead of activity.

The value of τ depends only on properties of the ion exchanger

and the membrane solvent, and for some systems τ is near 0 or 1. In these cases Equation 39 reduces to Equation 42 which has the same form as the empirical Equation 33.

$$E = \text{const} + \frac{RT}{nF} \ln (a_1 + Ka_2) \qquad (42)$$

Membrane selectivity in Equation 42 depends only on the single constant K. Also, Sandblom, Eisenman, and Walker (73) have shown that for any single value of τ, Equation 39 is closely approximated by Equation 42 where K represents an average ionic selectivity.

At this point, the assumption is made that within the exactness of Equation 39 in representing the mathematical function of the divalent cation membrane potential, Equation 42 should closely approximate the functional form for divalent cation electrode selectivity. Equation 43, then, represents the observed potential vs a reference electrode, of a cation electrode responding to only two ions in solution.

$$E = E_o + \frac{RT}{nF} \ln (a_1 + Ka_2) \qquad (43)$$

E_o includes the usual potential contributions described in relation to Equation 32 plus the const term in Equation 42.

If a_1 and a_2 in Equation 43 are changed by Δa_1 and Δa_2 respectively, the electrode produces a new potential E'.

$$a_1' = a_1 + \Delta a_1 \tag{44}$$

$$a_2' = a_2 + \Delta a_2 \tag{45}$$

$$E' = E_o + \frac{RT}{nF} \ln (a_1' + Ka_2') \tag{46}$$

Equation 47 results from subtracting Equation 43 from Equation 46.

$$\Delta E = E' - E = \frac{RT}{nF} \ln \left(\frac{a_1' + Ka_2'}{a_1 + Ka_2}\right) \tag{47}$$

The change in potential, ΔE in Equation 20, can be positive or negative, depending on whether Δa_1 and Δa_2 are positive or negative. Equation 47 can be rearranged to give Equation 48 which is the cation analogy of the anion selectivity equation derived by Srinivasan and Rechnitz (76).

$$a_1 \left(\exp \left(\frac{nF\Delta E}{RT}\right) - 1\right) + \Delta a_1 = K \left(\Delta a_2 + a_2 \left(1 - \exp \left(\frac{nF\Delta E}{RT}\right)\right)\right) \tag{48}$$

This equation can be solved explicitly for K, or the left hand side of Equation 48 can be plotted vs the right hand part within parentheses and a value for K determined by the slope of a least squares fit of the data.

Equation 43 can be used to describe the divalent cation electrode response to Ca^{++} and Mg^{++}.

$$E = E_o + \frac{RT}{nF} \ln (\{Ca^{++}\} + K \{Mg^{++}\}) \qquad (49)$$

The slope and intercept of Equation 49 can be determined from electrode calibration. Ca^{++} activity can be determined by a Ca^{++}electrode. Then if K is known, Mg^{++} activity can be determined from the electrode potential response and Equation 49. Since the divalent cation electrode was designed to give equal response to both Ca^{++} and Mg^{++}, K should be equal to one. An exact value for electrode selectivity must be determined in order to solve Equation 49 for Mg^{++} activity.

The Nernstian slope term required for the solution of Equation 48 was obtained by calibrating the divalent cation electrode in standard Ca^{++} solutions. Solutions of known Ca^{++} concentration were made in the range from approximately 2×10^{-5} M to 5×10^{-3} M Ca^{++}. Five increments of standard Mg^{++} solution were added to each Ca^{++} solution. Mg^{++} concentrations ranged from 10% to 100% of each Ca^{++} concentration. The activities of each ion were calculated by Equations 1 and 29. A selectivity plot of the four electrode potential changes based on Equation 48 was prepared by computer. A least squares determination of the slope of the selectivity plot gave a value for K. A selectivity coefficient was determined for each Ca^{++} solution. The results are plotted in Figure 5.

Obviously the selectivity coefficient, K, is not a constant. The variations in K in Figure 5 indicate that Mg^{++} activity can be

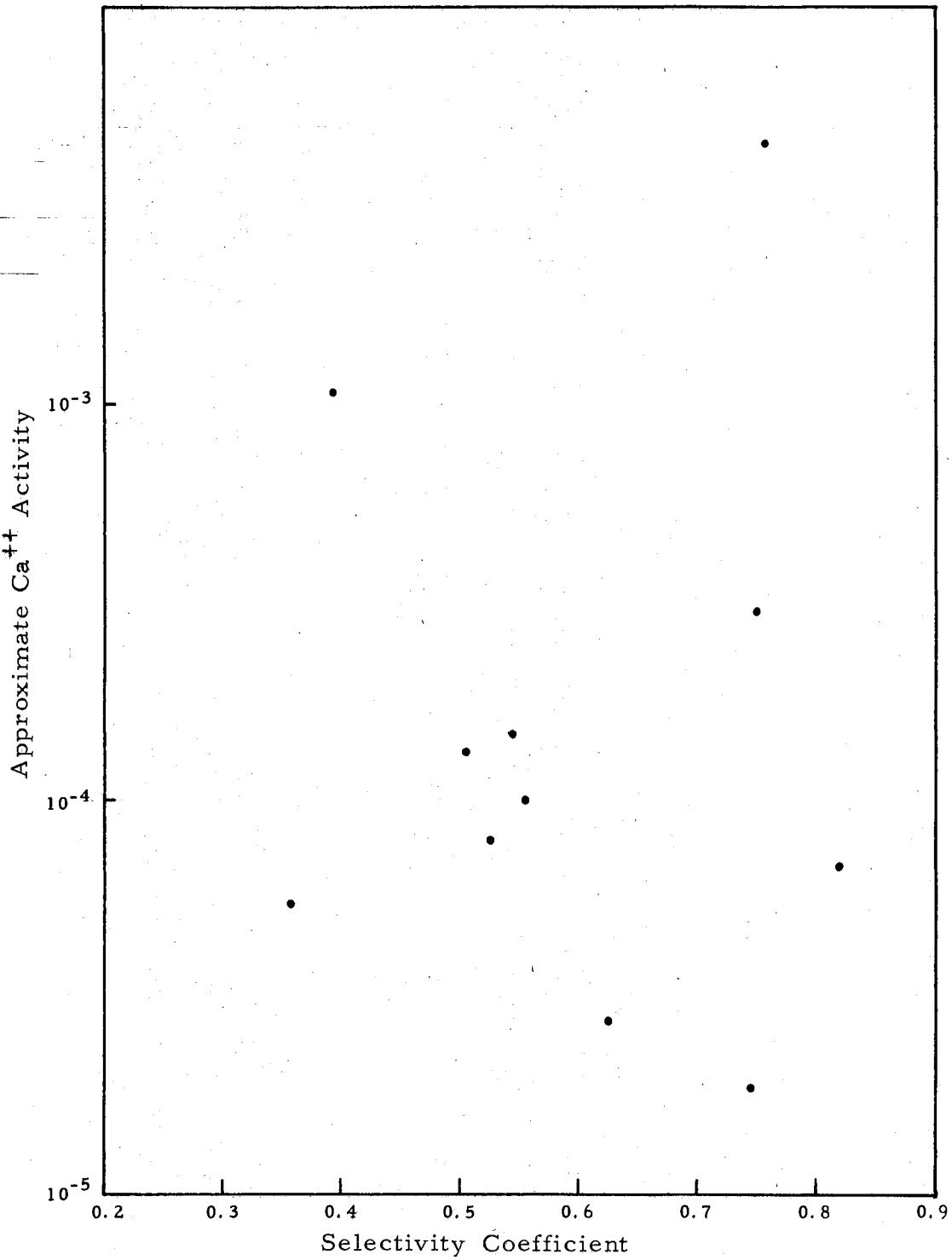

Figure 5. Selectivity of the Divalent Cation Electrode

determined only to within an order of magnitude by this method.

Precision Mg^{++} measurements will require that another method for the determination of Mg^{++} be used. The direct method described above may prove useful in the future if a functional form to describe the variations in K can be found. Some experimental evidence was obtained during this study to indicate that these values of K may be nearly reproducible. However, a mathematical description of the data in Figure 5 is not available at this time.

Electrode Drift

The accuracy of monitoring by direct potentiometric measurement depends on long term stability of the sensing electrodes. All electrodes drift with time. In most cases, the drift is noncumulative.

Three of the ion-selective electrodes were recalibrated daily while they were being used to monitor a laboratory culture of Dactylococcopsis (2×10^6 cells/ml, algae biomass 77 mg/l). Table V shows the deviation in Nernstian slope and intercept of daily calibration of Na^+, H^+, and Ca^{++} electrodes. The actual daily mV response to a particular standard solution represents actual potential variation which might occur while monitoring a water sample.

The % deviation of activity was calculated by assuming a hypothetical monitoring situation. A hypothetical calibration equation for the week was assumed to ideally predict the arithmetic average of all

TABLE V

DAILY VARIATION OF ELECTRODE RESPONSE

day	slope	E_o	mV of 8.504 X 10^{-4} M	% deviation calc. activity
		Na^+		
1	48.2	241.7	+88.7	+77.2
2	42.9	187.8	+55.4	-56.0
3	40.7	197.8	+73.8	+17.6
4	35.3	168.3	+59.8	-38.4
			$\bar{x}$ = +69.4	
		H^+		
day	slope	E_o	mV of pH = 8.2 buffer	% deviation calc. activity
1	54.4	382.1	-65.7	+0.8
2	50.1	343.5	-66.9	+5.6
3	51.9	357.8	-65.9	+1.6
4	54.6	382.2	-65.7	+0.8
5	49.6	341.3	-64.0	-6.0
7	54.7	384.0	-64.9	-2.4
			$\bar{x}$ = -65.5	
		Ca^{++}		
day	slope	E_o	mV of 6.420 X 10^{-4} M	% deviation calc. activity
1	28.3	97.4	+4.5	+24.0
2	30.9	103.9	+3.0	+12.0
3	30.5	101.6	+3.3	+14.4
4	30.5	99.9	-0.5	-16.0
5	30.6	100.7	+0.0	-12.0
7	27.8	90.1	-1.1	-20.8
			$\bar{x}$ = +1.5	

daily potentials. The deviation of each daily potential from the mean represents a mV error in the hypothetical calibration equation. The % deviations were calculated from mV error by assuming an activity deviation of 4% per mV for monovalent cations and 8% per mV for divalent cations. The % deviation in calculated activity column gives an idea of how much error to expect from daily drift when using direct potentiometric monitoring.

The very high biological activity in the laboratory culture may represent an extreme condition relative to natural systems which may have contributed to drift, especially the large deviations observed for the Na^+ electrode. Also, the electrodes in the laboratory were subjected to only minor temperature perturbations compared with that expected in field monitoring situations. Therefore, the drift exhibited in Table V should be regarded as only a very crude estimate of precision to expect from field data.

Carbon Dioxide Electrode

An electrode for measuring partial pressure of CO_2 dissolved in blood has been developed by Severinghaus and Bradley (77). A similar electrode was used in this study to measure dissolved CO_2 in natural waters.

Figure 6 is a schematic diagram of the electrode assembly used. CO_2 gas in the sample diffuses through the silicone rubber membrane

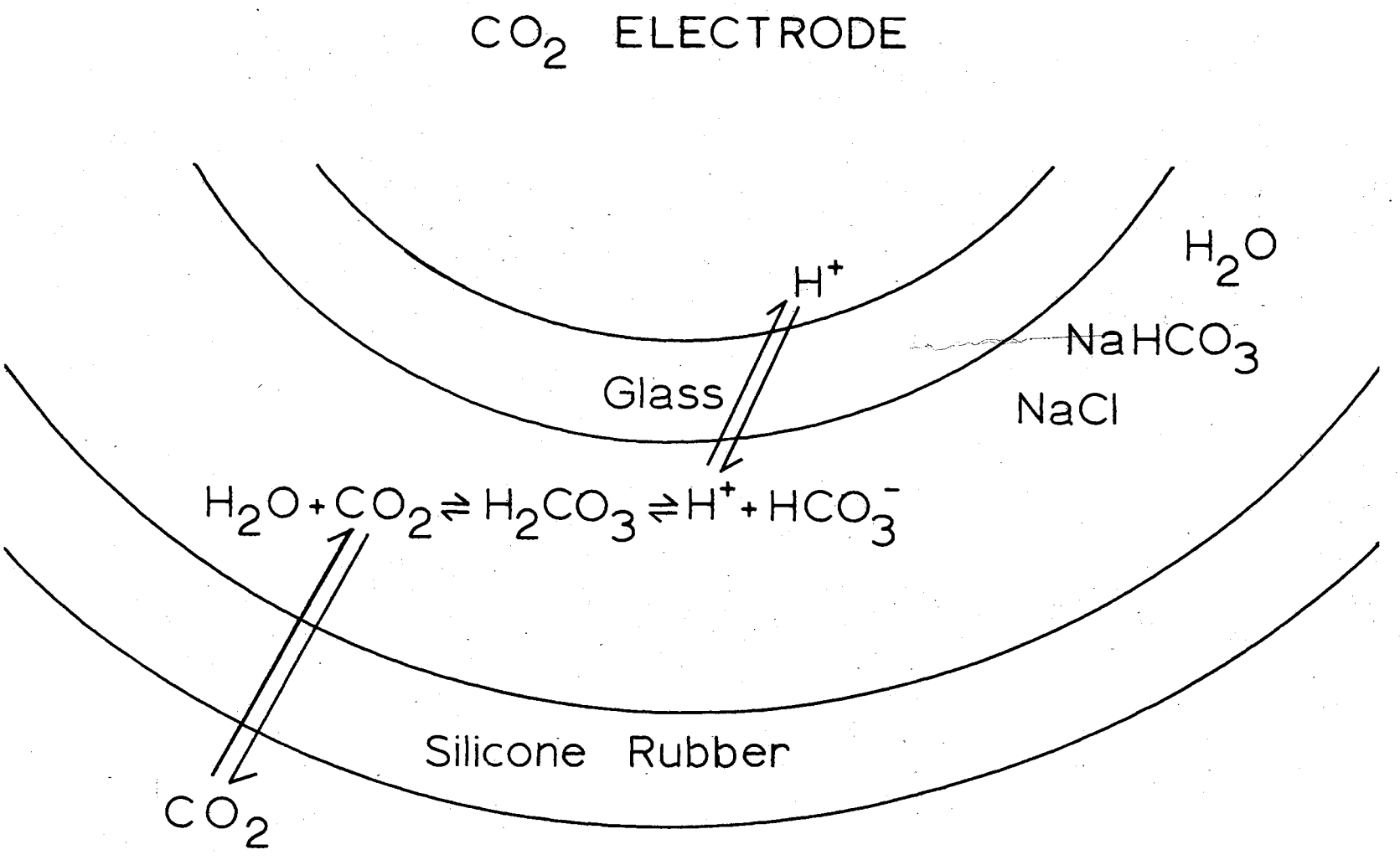

Figure 6. Schematic Cross Section of CO_2 Electrode Assembly. A Ag-AgCl reference electrode in the electrolyte solution is not shown.

where the H^+ activity change in an electrolyte solution is sensed by a glass membrane electrode.

Materials of choice for the CO_2 permeable membrane include Teflon[3] and Silastic[4] (silicone elastomer). Silastic 372[5], a medical grade silicone elastomer, was used because it is about 80 times more permeable to CO_2 than Teflon of the same thickness (78).

The membrane was supplied in 5 mil thick sheets. After stretching over the H^+ sensitive end of a Beckman 41263 electrode, the membrane thickness was estimated to be 2 to 3 mils. Thinner membranes could be produced to increase permeability by calendering before stretching in the electrode assembly.

The electrolyte solution contained 0.1 M NaCl and 0.001 M $NaHCO_3$ in water. The NaCl provided a constant Cl^- activity for the Ag-AgCl reference electrode and helped maintain a constant ionic strength. $NaHCO_3$ increased the electrode sensitivity to CO_2. Equations 13, 14, and 50 can be combined with the charge balance Equations to give Equation 52.

$$[H^+]\,[OH^-] = K_w \qquad (50)$$

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[3]Du Pont Corporation.

[4]Dow Corning Corporation.

[5]Supplied by Center for Aid to Medical Research, Dow Corning Corporation.

$$[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^=] + [OH^-] \quad (51)$$

$$[CO_2] \approx [H_2CO_3] = \frac{[H^+]^2 + [H^+][Na^+] - K_w}{K_1 \left(1 + \frac{2K_2}{[H^+]}\right)} \quad (52)$$

The electrode sensitivity has been defined as expressed in Equation 53 (75).

$$S \equiv \frac{\Delta pH}{\Delta \log [CO_2]} \quad (53)$$

In electrolyte solutions without $NaHCO_3$, Equation 52 reduces to Equation 54.

$$[CO_2] = \frac{[H^+]^2}{K_1}, \quad S = 0.5 \quad (54)$$

Experimental verification has shown that electrode sensitivity to CO_2 is increased to a maximum when the electrolyte contains 10^{-3} M $NaHCO_3$ (77). In this case, the second term in Equation 52 predominates and electrode response is given by Equation 55.

$$[CO_2] = \frac{[H^+][Na^+]}{K_1}, \quad S = 1.0 \quad (55)$$

The CO_2 electrode was calibrated in a solution made by bubbling CO_2 into a solution of 0.01 M NaCl. At approximately pH 5 the bubbling was stopped and the response of the CO_2 electrode and a H^+

electrode in the solution were monitored for about six hours. The stirred solution, thermostated at 25.0° ± 0.1°, was open to the atmosphere. The CO_2 concentration changed from approximately 10^{-2} M to 10^{-5} M during the monitored period. The monitoring system described in Chapter III was used to record electrode response, usually every six minutes.

The CO_2 concentration can be calculated from $[H^+]$ at each recorded time by means of Equation 58. Equation 58 is derived from combining Equation 13, 14, and 50 with the mass balance Equation 56 and proton balance Equation 57.

$$C_{H_2CO_3} = [H_2CO_3] + [HCO_3^-] + [CO_3^=] \tag{56}$$

$$[H^+] = [HCO_3^-] + 2[CO_3^=] + [OH^-] \tag{57}$$

$$[H_2CO_3] = \frac{[H^+]^4 + K_1[H^+]^3 + (K_1K_2 - K_w)[H^+]^2 - K_1K_w[H^+] - K_1K_2K_w}{K_1([H^+]^2 + 2K_1K_2[H^+] + 3K_1K_2 + 2K_1K_2^2[H^+]^{-1})} \tag{58}$$

A computer program for performing the calibration calculations is listed in Appendix A. The program first calibrates the H^+ electrode from pH buffer data by the method described previously. Paper tape data is then read and punched tape code is converted to mV data for both the H^+ and CO_2 electrodes. H^+ activity is calculated from mV data and the internally generated H^+ calibration equation. H^+ activity for each recording sequence gives a value of $[H_2CO_3]$ by means of

Equation 58. $[CO_2]$ in nearly equal to $[H_2CO_3]$; nevertheless the program applies the small correction defined by Equation 12.

The data is tabulated and plotted, log $[CO_2]$ vs mV, by an internal plotting routine. A CO_2 calibration equation results from a linear least squares fit to the plotted data.

Calibrating an electrode in terms of CO_2 activity (a_{CO_2}) when electrode response is to partial pressure (P_{CO_2}), perhaps deserves some comment. The H^+ electrode inside the CO_2 electrode assembly actually responds linearly to H^+ activity. Since in the pH range of the internal electrolyte solution, H_2CO_3 dissociates according to the reaction associated with Equation 13, a_{CO_2} is proportional to a_{H^+} in the internal solution. Therefore, the equation for CO_2 electrode response could be written as Equation 59.

$$E = \text{const} + \frac{RT}{F} \ln a_{CO_2} \tag{59}$$

In this case, a_{CO_2} is CO_2 activity in the internal electrolyte solution. Assuming a CO_2 activity coefficient of one, $a_{CO_2} = \underline{m}_{CO_2}$ ($\underline{m}$ = molality). Molality is related to partial pressure by Henry's law. Both inside the electrode

$$(\underline{m}_{CO_2})_{int} = k_{int} (P_{CO_2})_{int} \tag{60}$$

and outside the electrode

$$(\underline{m}_{CO_2})_{ext} = k_{ext} (P_{CO_2})_{ext} \tag{61}$$

The Henry's law constant, $\underline{k}$, is dependent upon temperature and solution composition. At equilibrium

$$P_{ext} = P_{int}; \tag{62}$$

therefore

$$(\underline{m}_{CO_2})_{int} = (\underline{m}_{CO_2})_{ext} \frac{k_{int}}{k_{ext}} . \tag{63}$$

Equation 59 can now be rewritten in terms of $(\underline{m}_{CO_2})_{ext}$, the quantity to be measured by the electrode.

$$E = \text{const} + \frac{RT}{F} \ln \left[(\underline{m}_{CO_2})_{ext} \frac{k_{int}}{k_{ext}}\right] \tag{64}$$

The Henry's law constants ratio can be included with the const term and concentration again equated with activity.

$$E = \text{const}' + \frac{RT}{F} \ln a_{CO_2} \tag{65}$$

Equation 65 is similar to Equation 59, but in Equation 65, electrode response is described in terms of a_{CO_2} of the external solution, i.e., the sample. Equation 65 should be valid for any ionic strength of internal or external electrolyte since any changes in $\underline{k}$ will be

incorporated in const'. The same value for k_{ext} is required, however, in both sample and calibration solution. A tabulation of Henry's law constants by Harned and Davis (79), indicates that deviation in the const' term will be small if both sample and calibration solutions have ionic strengths of the same order of magnitude and less than 10^{-1} M.

Carbon Dioxide Electrode Response Time

Two solutions of CO_2 in water were prepared. A low CO_2 concentration solution gave a mV response approximating 10^{-6} M. The solution of higher concentration was approximately 10^{-3} M. The response of the electrode was manually recorded after it was transferred from one stirred solution to the other. The experiment was then repeated with 1 mg/ml of carbonic anhydrase[6] added to the CO_2 electrode internal electrolyte solution. The results are plotted in Figure 7.

Without the enzyme, the low to high response was faster than for high to low which took approximately 10 min for 90% response. When monitoring lake water from multiple depths, a faster response time may be desirable. The enzyme carbonic anhydrase which catalyzes the hydration and dehydration reactions of CO_2 substantially decreased the response time for both increasing and decreasing CO_2. The low to high and high to low response times were more nearly

[6]Sigma Chemical Company, St. Louis, Missouri.

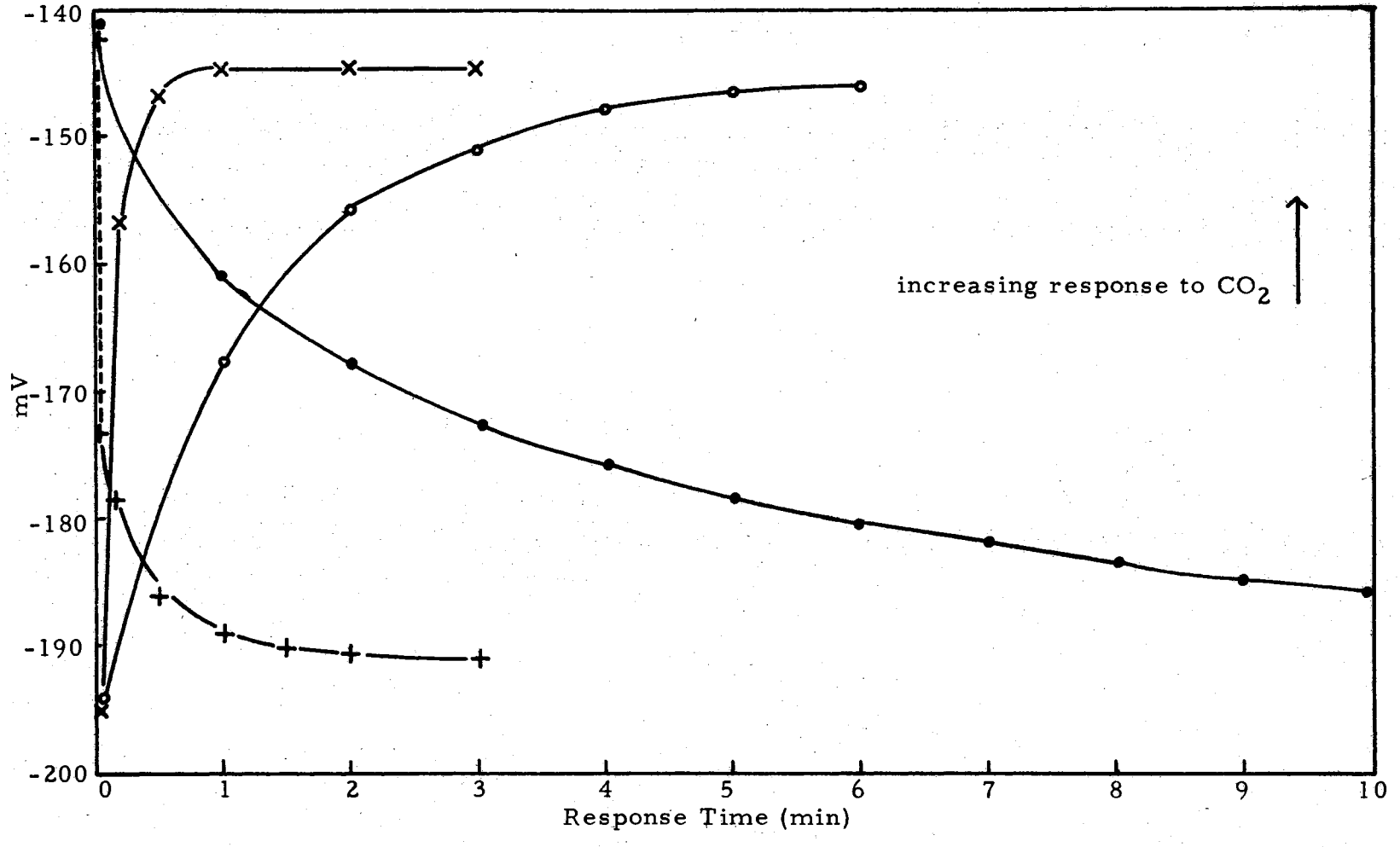

Figure 7. Carbon Dioxide Electrode Response Time. Closed circles represent a change from high to low CO_2 without enzyme. Open circles are low to high without enzyme. + = high to low response with carbonic anhydrase. X = low to high with the enzyme.

equal with the enzyme. High to low response time was decreased to approximately 30 sec for 90% response.

CHAPTER V

DETERMINATION OF CARBONATE COMPONENTS IN LAKE CARL BLACKWELL

In order to obtain some preliminary information about the chemical system in Lake Carl Blackwell, a grab sampling program was begun in Summer, 1971. The field sampling and laboratory analyses were designed to give information similar to that expected from an in situ monitoring system. The data would also provide carbonate system data for an ecosystem modeling project which was initiated late in 1970 as a part of the Lake Carl Blackwell Ecosystem Analysis Program.

Description of Lake Carl Blackwell

Lake Carl Blackwell (Figure 8) located in north-central Oklahoma was completed in 1938 and first attained spillway level (283.2 m m.s.l.) in 1945. The lake has a maximum surface area at spillway elevation of approximately 3700 acres. During the study period, July, 1971, to January, 1972, the lake elevation was about 279 m m.s.l., and the lake surface area was less than 2500 acres (80). The main inflow to the lake is Stillwater Creek. Almost all of the water

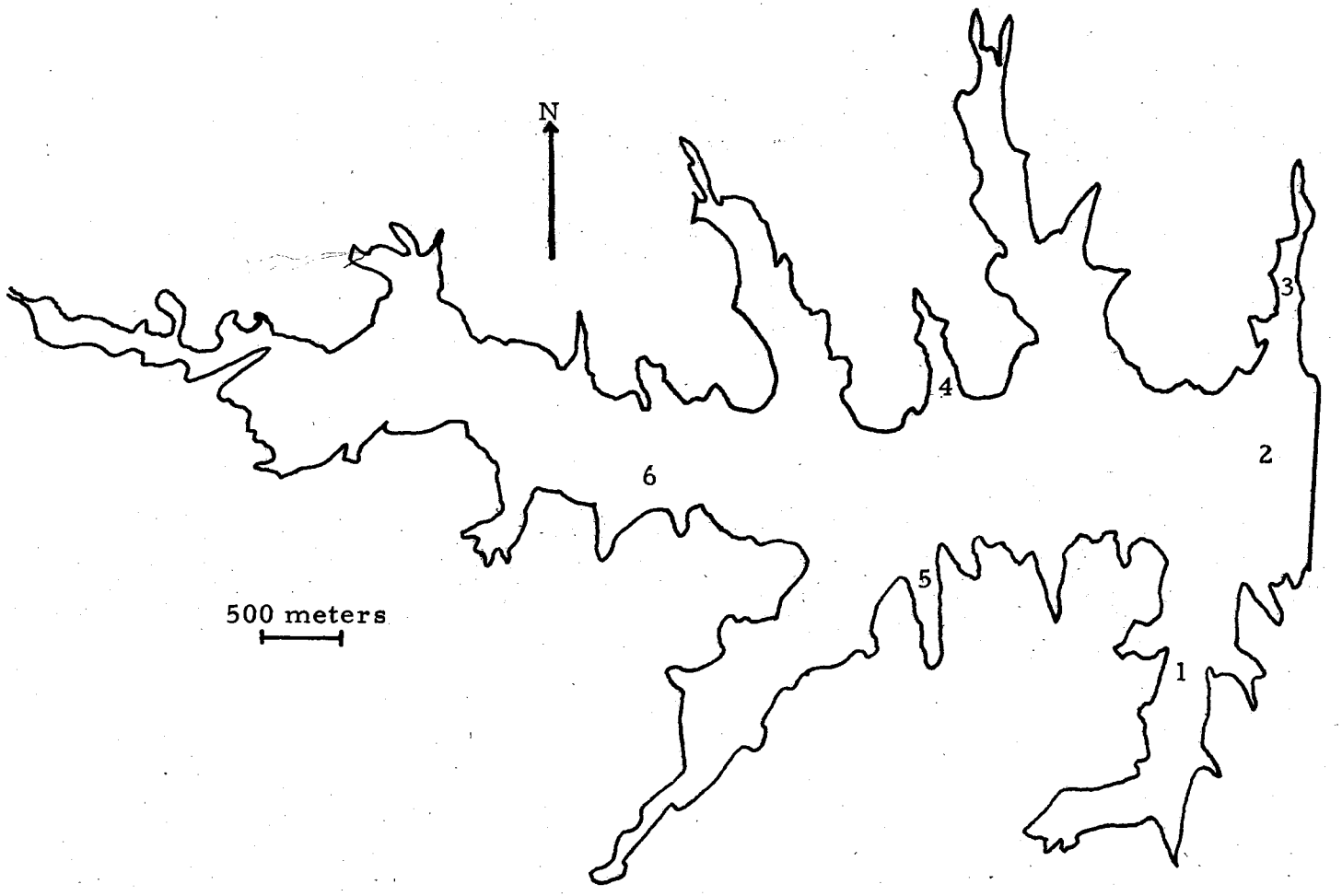

Figure 8. Shoreline Map of Lake Carl Blackwell. Numbers identify sampling stations.

flowing into the lake is from runoff. The main outflow during the time of this study was the water intake pipe to the water supply for the City of Stillwater. The drainage basin consists mainly of pastured grassland and wheat farmland. The lake stratifies in early summer, and turbidity and chemical distribution indicate the epilimnion is wind circulated.

The location of sampling stations used for this study are represented by numbers 1 through 6 in Figure 8. Each of the six sampling stations on the lake were marked by a permanent bouy to insure reproducibility of sampling location.

Samples at each station were taken at 0, 1, 2 and consecutively even numbered depths measured in meters from the surface. Table VI gives the depths sampled at each station. A total of 20 samples were taken from the lake on each day sampled.

TABLE VI

DEPTHS AND DEPTHS SAMPLED AT EACH OF SIX SAMPLING STATIONS ON LAKE CARL BLACKWELL

Station Number (see Figure 8)	Approximate Depth (m)	Depth Sampled (m from surface)
1	2.5	0, 1, 2
2	12	0, 1, 2, 4, 6, 8, 10
3	3.5	0, 1, 2
4	1.5	0, 1
5	1.5	0, 1
6	3	0, 1, 2

Sampling Procedure

Water samples were obtained at each station from a boat by means of a two-liter water sampling bottle[1], G M number 135WA142. The Van Dorn type bottle allowed only transparent butyrate plastic and rubber to contact the sample. Since all components being analyzed were well above trace amounts, contamination from the sampling bottle or line as discussed by Robertson (81) should not have been a problem.

Surface samples were obtained by holding the sampling bottle horizontally and releasing the end plugs just under the water surface. Deeper samples were obtained with the bottle in its normal vertical position. The center of the bottle was held at the exact depth to be sampled by a calibrated nylon rope, and the end plugs were closed by messenger activation.

Water was transferred to sample storage bottles with as little contact as possible with the atmosphere. One liter narrow-mouth polyethylene sample storage bottles with screw caps were chosen for chemical inertness (81, 82), and break resistance in the field.

Immediately after samples were taken and tightly capped, they were stored in ice or refrigerated at 4° until analysis. The cooling of samples was to inhibit biological activity and to increase the solubility of dissolved gases.

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[1] G M Manufacturing Company, New York.

Preceeding analysis in the laboratory, each sample was shaken to resuspend settled material. Then water was transfered from sample bottle via a polyethylene tube to a water jacketed beaker. There the sample was stirred and heated to 25.0°. After temperature equilibration, electrodes placed in the sample furnished mV analogs of activities of H^+, CO_2, Na^+, Ca^{++}, and Mg^{++}. In most cases, all samples were analyzed within 48 hours after collection.

Data Reduction

Data from the laboratory water analyses provided input for the computer program listed in Appendix B which calculated chemical activities in each sample. Electrode calibration equations expressing log (activity) as linear functions of mV were available from calibration data previously processed by computer programs.

The data reduction program (Appendix B) read all calibration equations along with each time of calibration and stored the calibration slopes and intercepts as time and electrode referenced array elements. All electrode mV data for each day was read in with identification codes representing time the sample was taken, station number, and depth. The sampling date was compared with calibration time codes, and the calibration equations were updated if necessary.

Using the proper calibration equation, electrode mV response for the day's data was converted to chemical activities of the five

measured species. (The selectivity coefficient in Equation 49 was assumed equal to one in order to approximate Mg^{++} activity.) Then all the other species listed in Table I were calculated for each sample by combining the five measured activities with the equilibrium equations in Table II.

The data for each day was tabulated and plotted vs depth for each station. Several components were plotted on each graph by scaling the data for each species according to a factor calculated from values for each species at zero depth. Plotting symbols are keyed with scale factors at the bottom of each graph. Asterisks form connecting line segments between alphabetic symbols. Activities tabulated by the program are in moles/l at 25°.

If more data than for one day was included with the input, the program repeated itself by automatically dividing the data into one-day segments until all input data was processed.

CHAPTER VI

CHEMICAL EQUILIBRIA IN LAKE CARL BLACKWELL

The waters of Lake Carl Blackwell have the usual chemical characteristics of a small wind mixed eutrophic lake. An ionic strength on the order of 10^{-2} M reflects a lack of contact of the inflowing water with major mineral deposits. Carbonates in solution average about 10^{-3} M and are present almost entirely as bicarbonate ion since the pH is usually between 7.8 and 8.5.

Carbonate Complexes in Solution

The carbonate ions, complexes and CO_2 in Table I were assumed to represent all of the carbonates in solution. It was further assumed that no cations other than those in Table I significantly affect the carbonate system. Complexes of higher order than ion pairs have not been demonstrated as significant in natural water systems and were not considered in this study.

Since the inorganic carbonate system in Lake Carl Blackwell is directly connected to biological activity through primary production, respiration, and decomposition, it is important when studying the inorganic carbonate system to consider its interrelations with the other

aquatic systems which affect it.

Samples of algae and bacteria were taken from Lake Carl Blackwell at the same times and locations that chemical samples were collected. The biological analyses were made by participants in an interdisciplinary effort of which this chemical study is a part.

Since only a part of the biological data was available at the time of this writing, data from a selected period, July 15, 1971, through August 5, 1971, which comprises four weekly sampling periods, will be discussed with some empirical observations. No general conclusions about the lake system behavior can be attempted until more data becomes available and a more detailed analysis of the data is made.

Surface total algae cell counts and bacteria counts for the water column at station two are plotted in Figure 9. Referring to Figure 9, a large algae bloom is evident on July 1. As algae from the bloom died, a very large bacteria peak occured which was falling off by July 15, the first complete chemical sampling date.

Dissolved O_2 and temperature data were obtained in situ at the same time water samples were collected. Dissolved O_2 and temperature in Figure 10 are plotted with the ordinate scale reversed from usual profile graphs to match the computer generated profile graphs which plot zero depth at the coordinate origin. Both O_2 and temperature profiles indicate lake stratification between 6 and 7 m depth. The chemical ion graph in Figure 11 for the same date reflects the

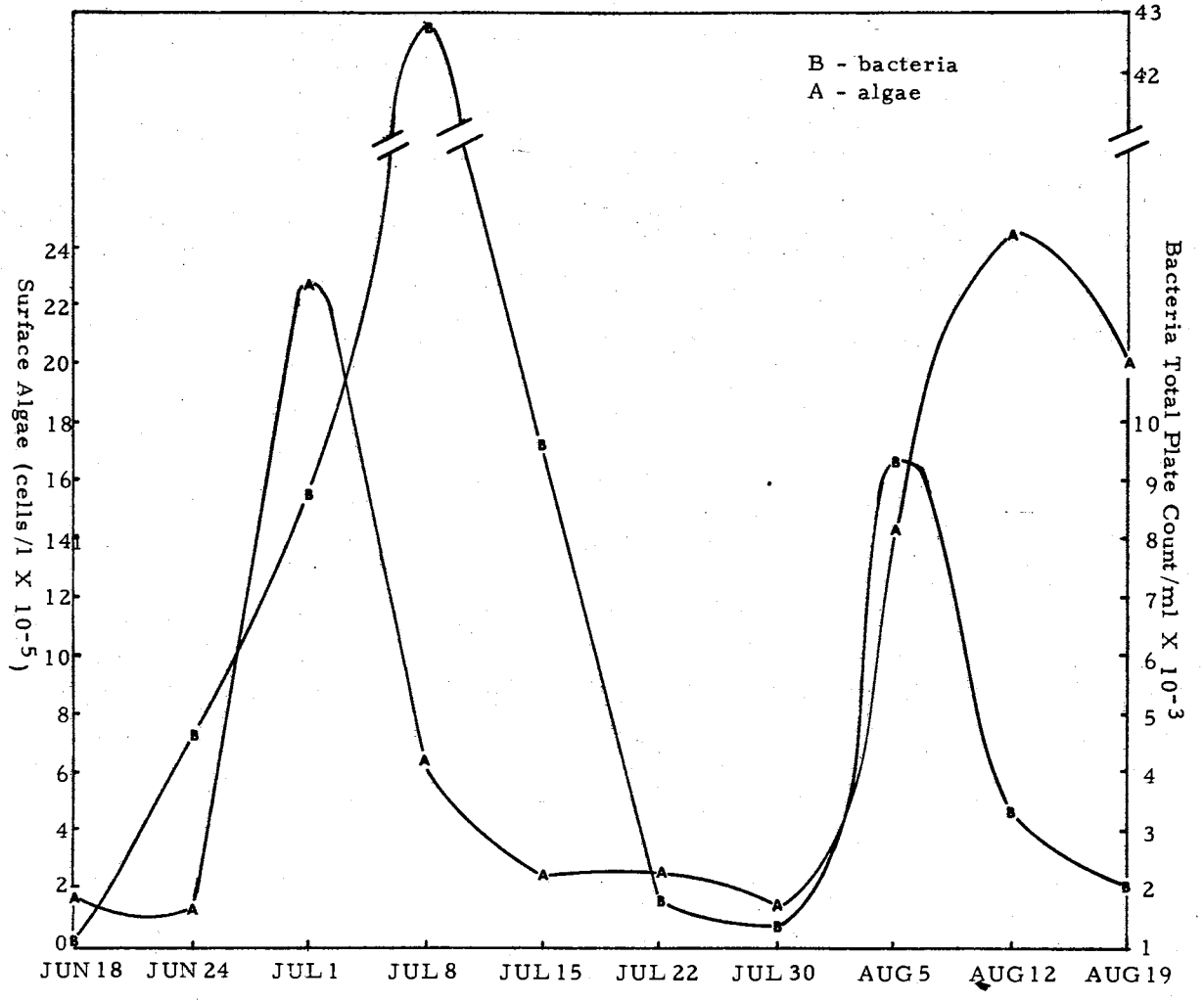

Figure 9. Algae and Bacteria Counts, Lake Carl Blackwell, Summer, 1971. Algae data is from Reference 83. Bacteria data is from Reference 84.

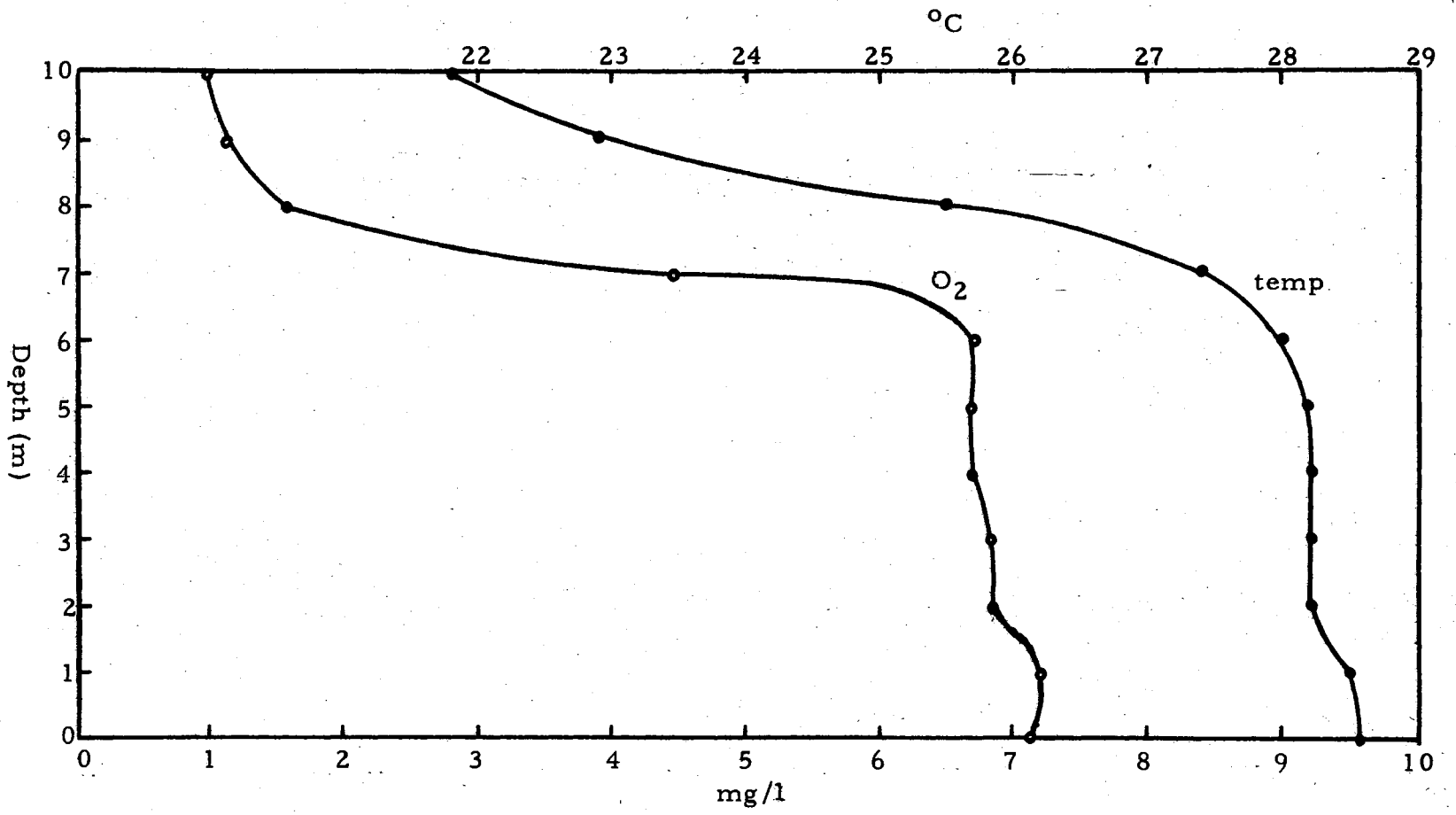

Figure 10. O_2 and Temperature Profiles of Lake Carl Blackwell, Station Two, July 15, 1971

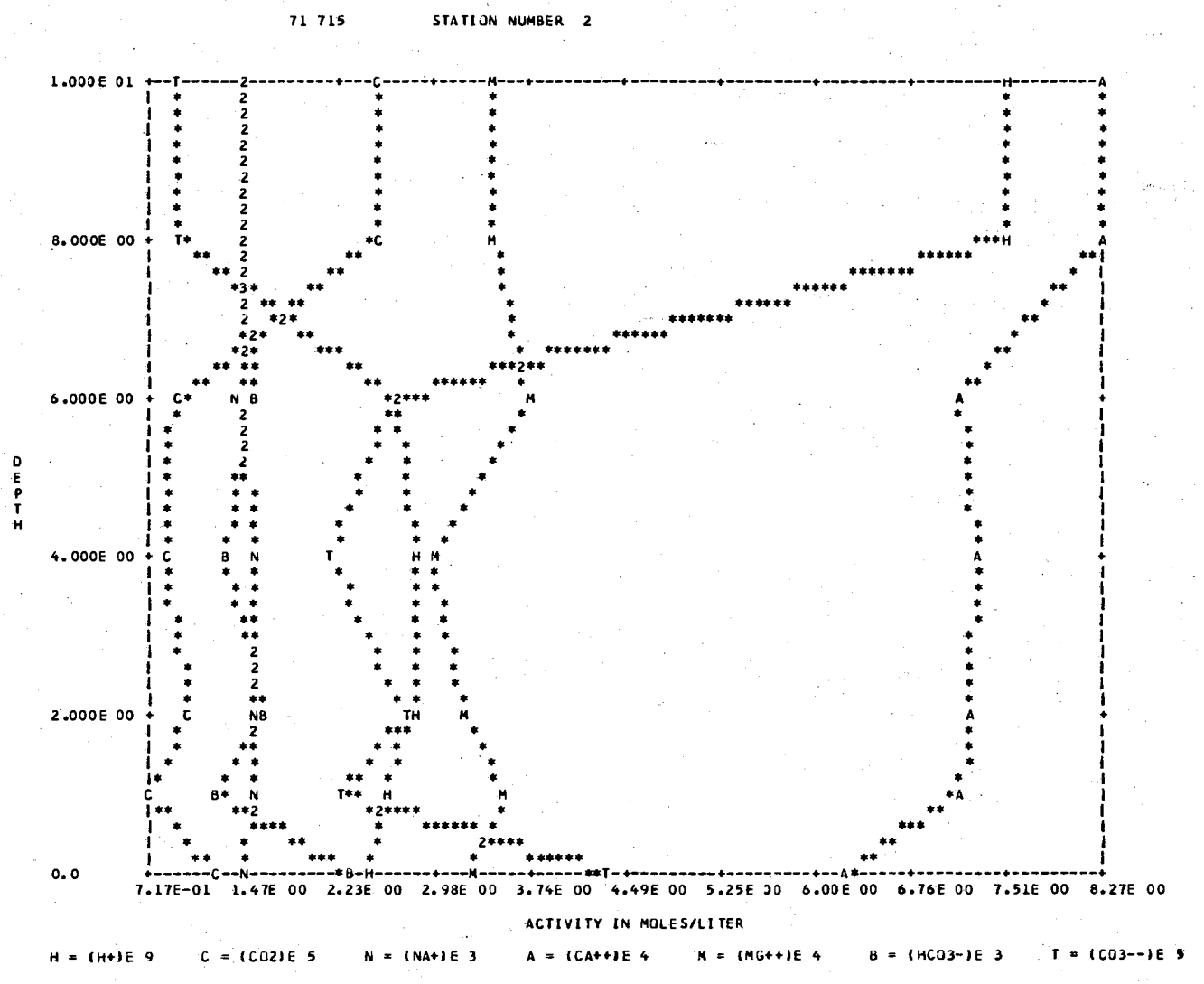

Figure 11. Chemical Profile of Lake Carl Blackwell, Station Two, July 15, 1971

observed stratification by increasing H^+ and CO_2 activities below 6 m. The $CO_3^=$ curve in Figure 11 resembles a mirror image of the CO_2 curve which simply indicates the shift in carbonate equilibria with the H^+ increase. HCO_3^- activity being nearly constant through the 6 m depth suggests no total carbonate system change due to stratification. The large H^+ increase below 6 m may be due to bacterial decomposition products from the algae bloom of July 1. This data does not show that CO_2 is a decomposition product but rather that the CO_2 increase is due to a shift in carbonate equilibria caused by the H^+ increase. There is no distinct chemocline for the metal ions; therefore stratification must be due to thermal differences only. The Ca^{++} increase below 6 m can be attributed to a $CO_3^=$ decrease and subsequent reduction in $CaCO_3$ complex. The simultaneous decrease in all free carbonate species at 1 m with very little change in H^+ indicates a region of HCO_3^- uptake, probably by photosynthesis since O_2 increases at 1 m in Figure 10.

By July 22, both bacteria and algae counts had decreased to a low level. Thermal stratification is still evident in Figure 12, but the temperature of mixed epilimnic water had decreased by 2.4° which in effect moved the thermocline downward to 8 m. A comparison of O_2 profiles in Figures 10 and 12 indicates water was mixing to the 8 m depth. The profiles of H^+, CO_2, and $CO_3^=$ in Figure 13 also show partial mixing to 8 m.

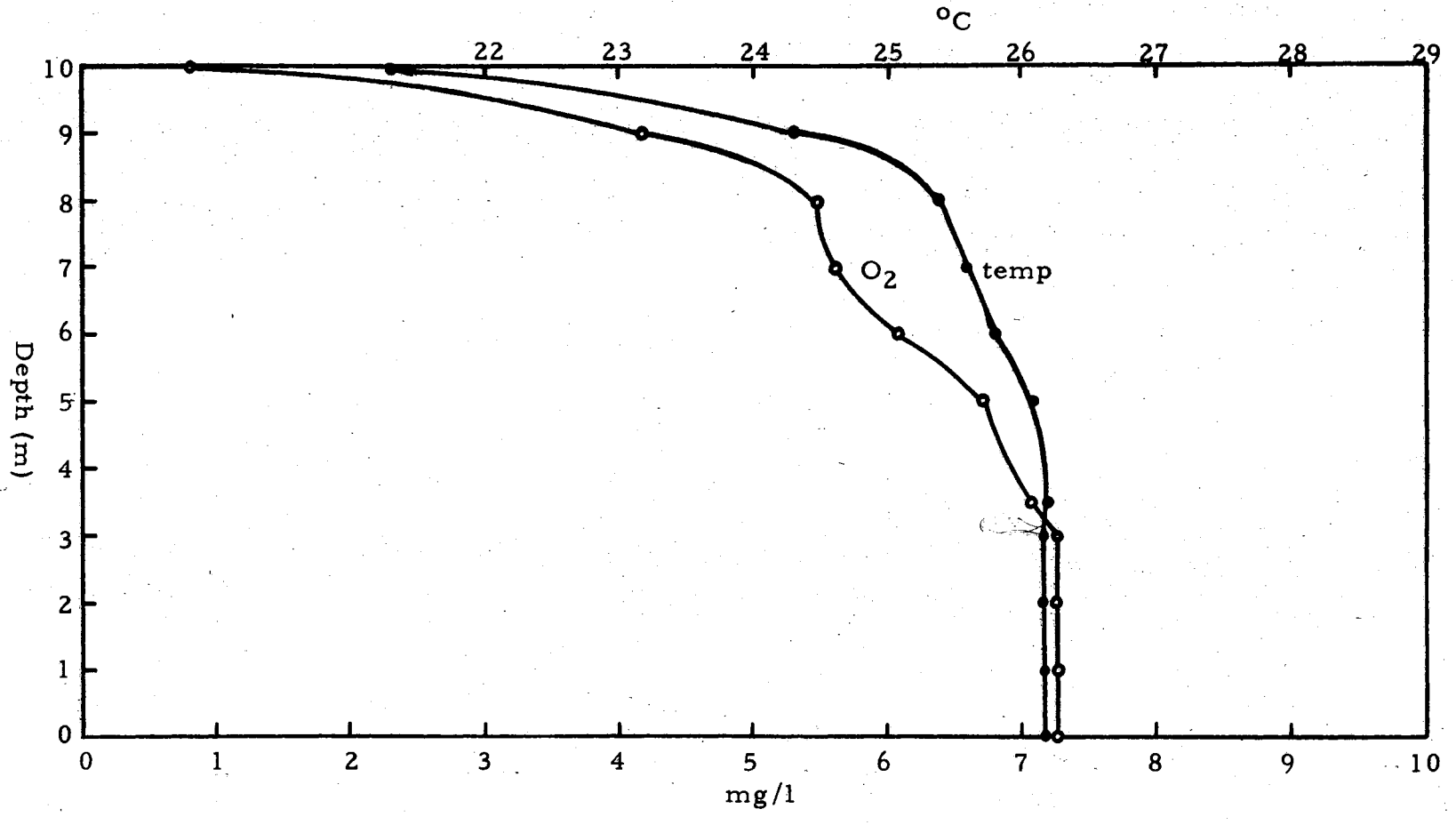

Figure 12. O_2 and Temperature Profiles of Lake Carl Blackwell, Station Two, July 22, 1971

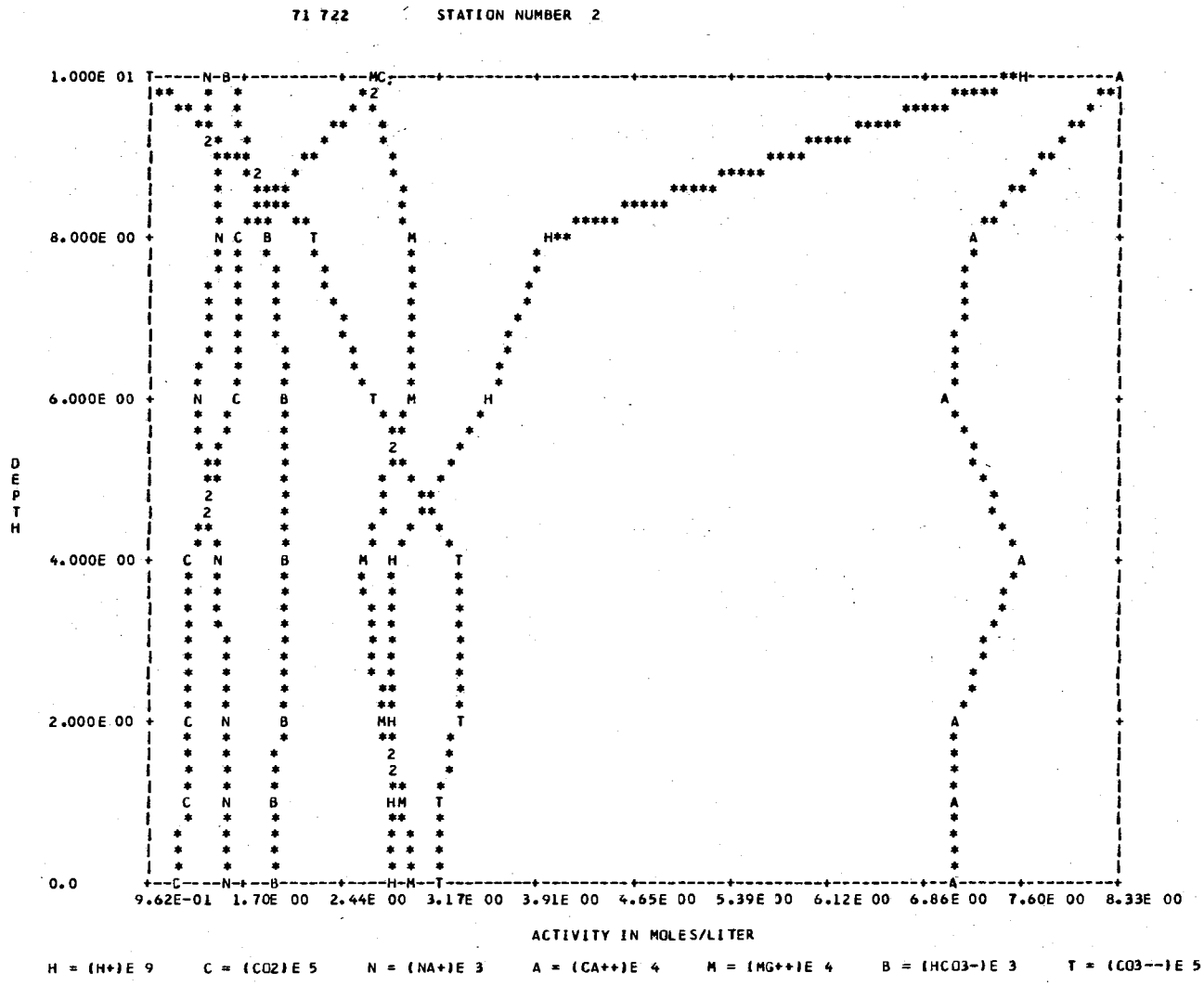

Figure 13. Chemical Profile of Lake Carl Blackwell, Station Two, July 22, 1971

On July 30, with both bacteria and algae still at low populations, the thermocline in Figure 14 moved to below 9 m. H^+ difference between 8 and 10 m is small in Figure 15. Figure 15 does show a highly variable but decreased HCO_3^- activity. The decrease could have been due to HCO_3^- uptake by algae. Notice the CO_2, HCO_3^-, and $CO_3^=$ curves are nearly parallel from 0 to 2 m. The large amount of change in the carbonates may indicate high biological activity at a time which turned out to be the start of another algae bloom.

Then on August 5, both bacteria and algae counts went up almost simultaneously. The station was thermally destratified according to Figure 16. The increasing H^+ with depth below 6 m may again be attributed to bacterial decomposition products since the bacteria count for this date was high. The CO_2 increase below 6 m in Figure 17 can again, be attributed to the change in H^+ activity at low depths. But a large decrease in O_2 is observed in Figure 16 below 6 m in unstratified water without a corresponding increase in CO_2 in Figure 17.

Insufficient evidence was obtained during this study to determine the mechanism of periodic algae blooms in Lake Carl Blackwell. The following explanation of the August 5 algae increase is offered as a conjecture based on a preliminary analysis of the available data. O_2 during the week before August 5 had been reduced in concentration by aerobic bacterial decomposition of dead algae. The decomposition products were organic acids which caused the rise in H^+ below 6 m.

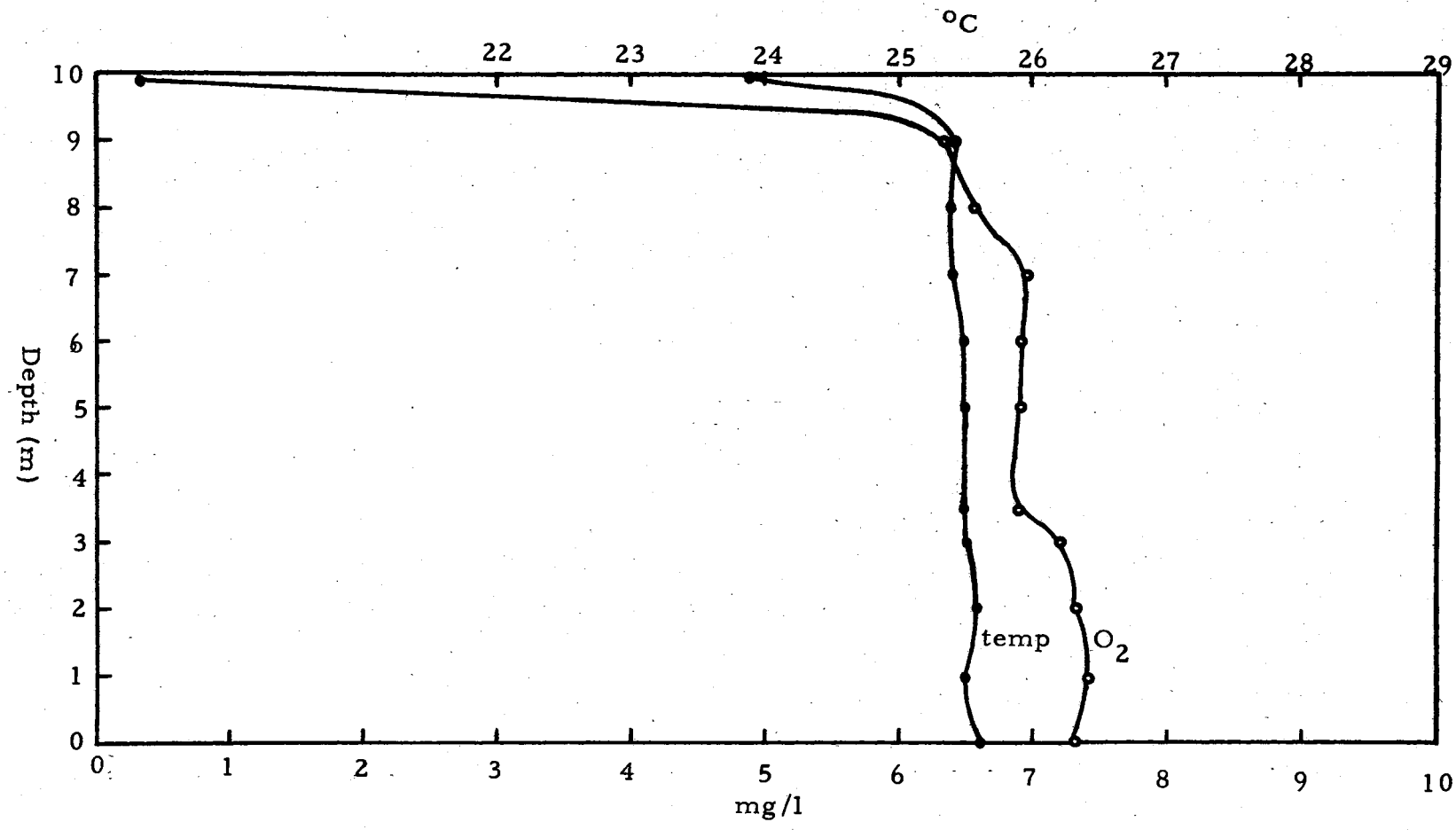

Figure 14. O_2 and Temperature Profiles of Lake Carl Blackwell, Station Two, July 30, 1971

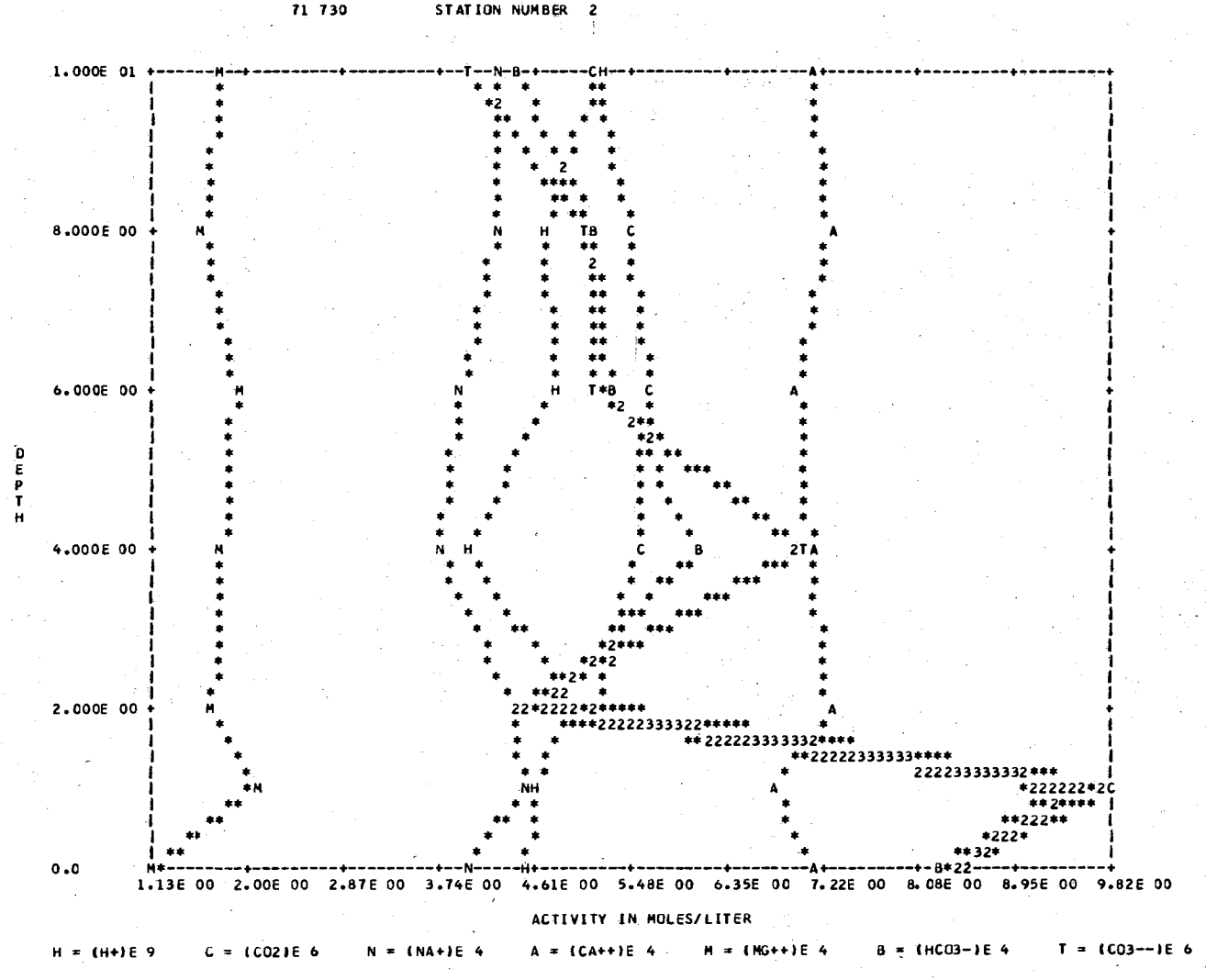

Figure 15. Chemical Profile of Lake Carl Blackwell, Station Two, July 30, 1971

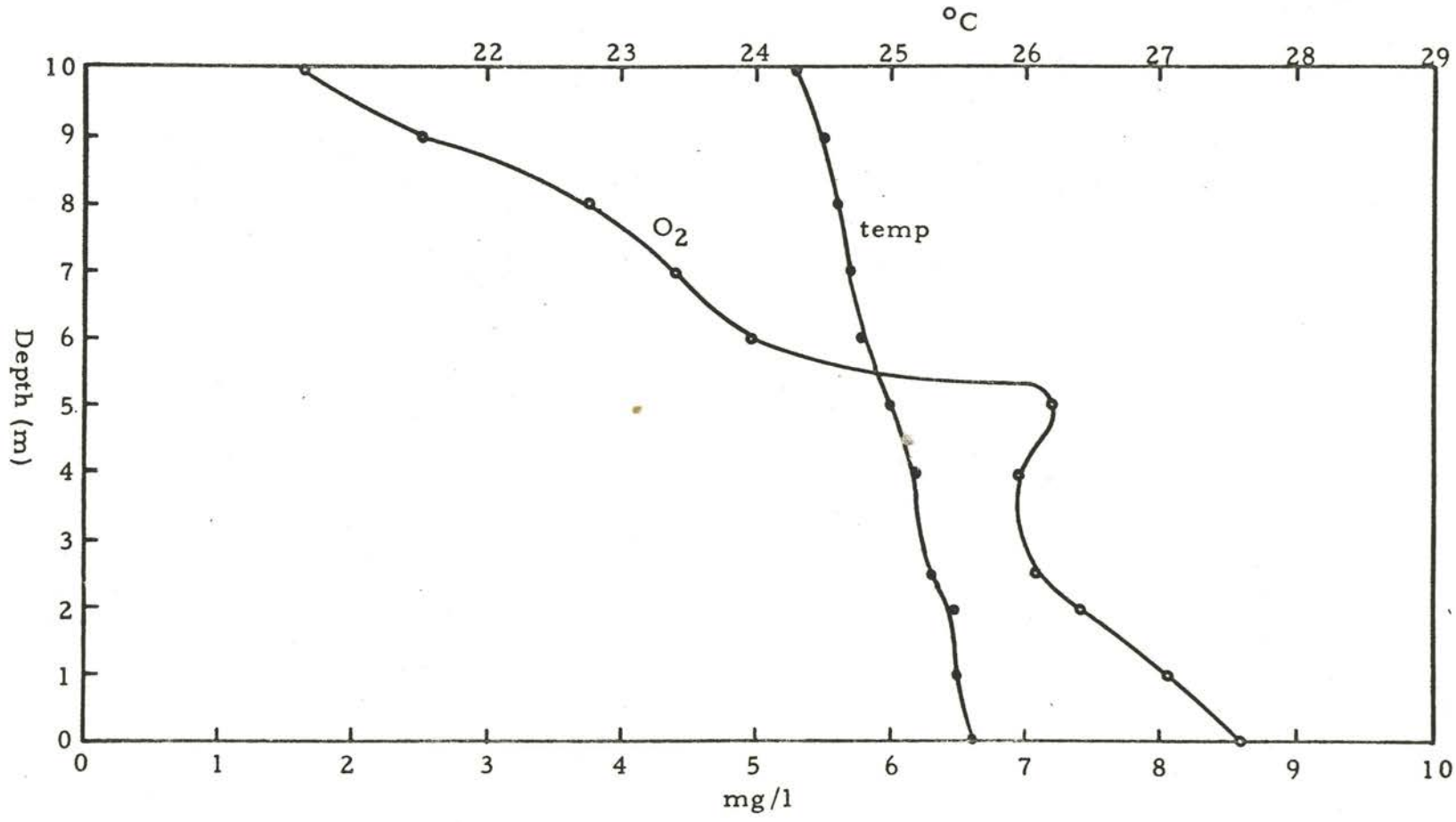

Figure 16. O_2 and Temperature Profiles of Lake Carl Blackwell, Station Two, August 5, 1971

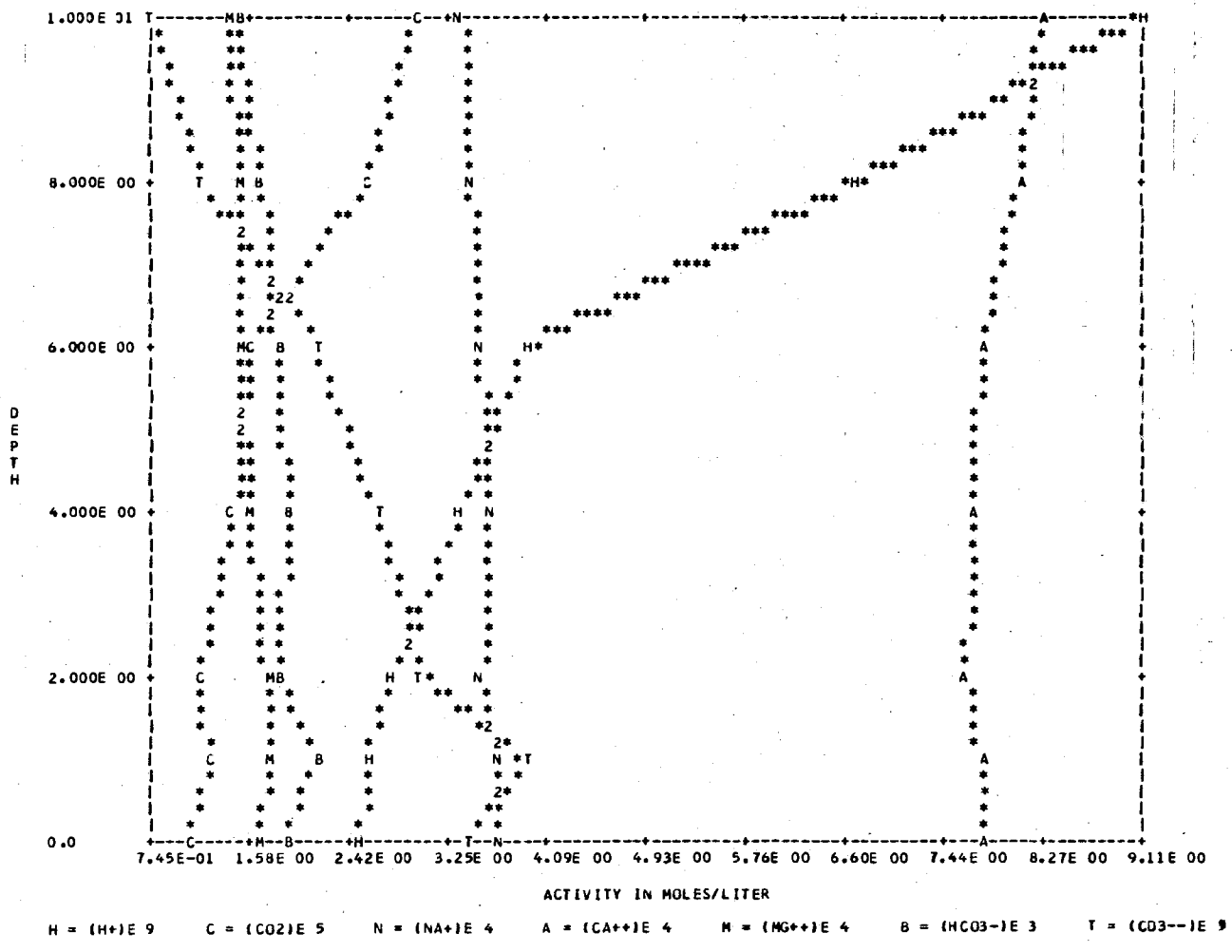

Figure 17. Chemical Profile of Lake Carl Blackwell, Station Two, August 5, 1971

As these organic acids were further decomposed to CO_2, the CO_2 produced was immediately taken up by algae, thus there was no net gain in HCO_3^-. The high O_2 concentration from 0 to 5 m measured at midday on August 5 was a product of photosynthesis by the large amount of algae present.

It is interesting to note that HCO_3^- which had undergone an overall decrease on July 30 had increased on August 5 to approximately the same value on July 22, before the bloom. Also, HCO_3^- activity was nearly the same from surface to bottom with only a small decrease below 6 m.

In Figure 17 Na^+, Ca^{++}, and Mg^{++} activities show little change from surface to 10 m. This may (but not necessarily) mean that analytical concentrations of these species were the same throughout the water column on August 5. The small decrease in activity of Na^+ and Mg^{++} may have resulted from temperature lowering as depth increased (Figure 16). The small increase in Ca^{++} activity, where a decrease would be expected because of temperature lowering, can be accounted for by corresponding decreases in $CaHCO_3^+$ and $CaCO_3^o$ complexes as shown in Figure 18. The changes in activity of the carbonate complexes follow patterns established by the respective free anion activities. Generally, in Figure 18 the $CO_3^=$ complexes show variable activities while HCO_3^- complexes reflect the usual HCO_3^- constancy with depth.

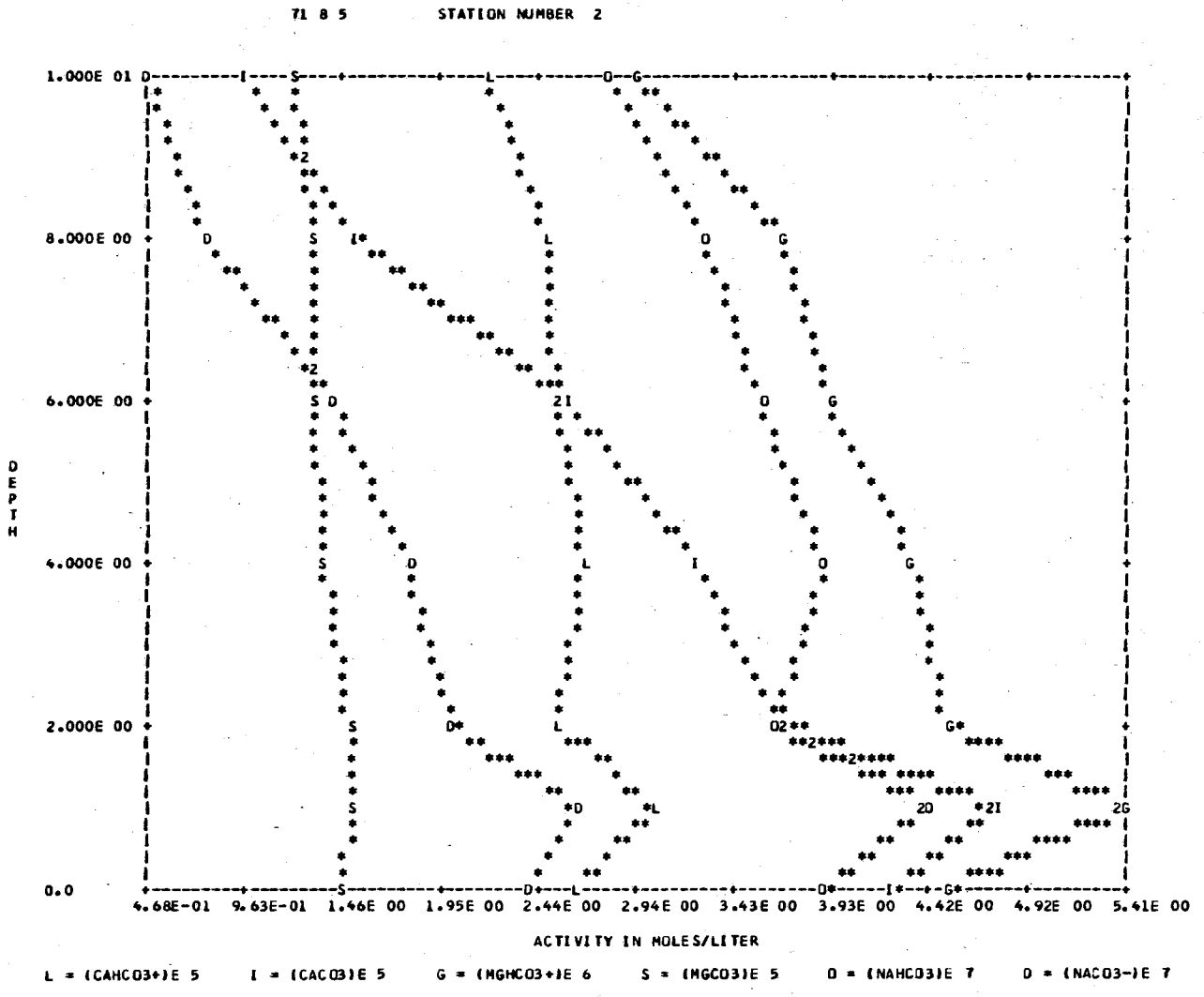

Figure 18. Profile of Carbonate Complexes in Lake Carl Blackwell, Station Two, August 5, 1971

Solubility Equilibria

Chemical activity data, such as that obtained for Lake Carl Blackwell, is also useful for solubility equilibria determinations. A lake is not a completely closed chemical system. Dissolved and suspended material are contained in inflowing water and some material is released with the outflow. Dissolved gases exchange with the atmosphere. When the ion products of certain dissolved species become greater than the solubility product constants, solids may precipitate. Precipitated solids may be suspended, redissolved, or fall out of the water phase and become part of the sediments. Solubility may be of biological importance when chemical species affecting growth are involved.

Carbon Dioxide Solubility

The exchange flux of CO_2 across the air-water interface depends upon the partial pressure difference between CO_2 in air and CO_2 in water. When $(P_{CO_2})_{atmosphere} = (P_{CO_2})_{water}$, there is no net exchange and the water is saturated with CO_2. Since P_{CO_2} is constant in the atmosphere at $10^{-3.48}$ atm, it is possible to calculate the molality of CO_2 required to saturate lake water at 25°. The relation between molality and partial pressure of CO_2 in water is expressed by Henry's law in Equation 61. A Henry's law constant of 0.0343 for 10^{-2} M NaCl at 25° was interpolated from data in Reference 79. Then,

by Henry's law the lake at 25° will be saturated with CO_2 at 1.10 X 10^{-5} m CO_2.

CO_2 data from the chemical analysis program for station two surface water is plotted in Figure 19. Comparing the data with the saturation line, high CO_2 production in summer along with warm water contribute to CO_2 saturation. Cold water in January contained a high CO_2 concentration which shows a saturated condition at 25°.

Carbonate Ion Solubility

$CO_3^=$ may precipitate from natural waters in the form of calcite, $CaCO_3$. The saturation line in Figure 20 was drawn based on a log K_{SO} of -8.35 for calcite (85). The plot of ion products in Figure 20 indicates a possibility of calcite precipitation in summer when $CO_3^=$ activity is high.

Another form of $CO_3^=$ precipitation could be dolomite, $CaMg(CO_3)_2$ with a log K_{SO} of -16.50 (86). That dolomite saturation in summer months is possible is evident from the ion products plotted in Figure 21.

Other minerals which may play secondary solubility roles under certain conditions are aragonite, another form of $CaCO_3$, and magnesite, $MgCO_3$. It is possible that HCO_3^- available for primary production may be limited by $CO_3^=$ precipitation at least part of the time.

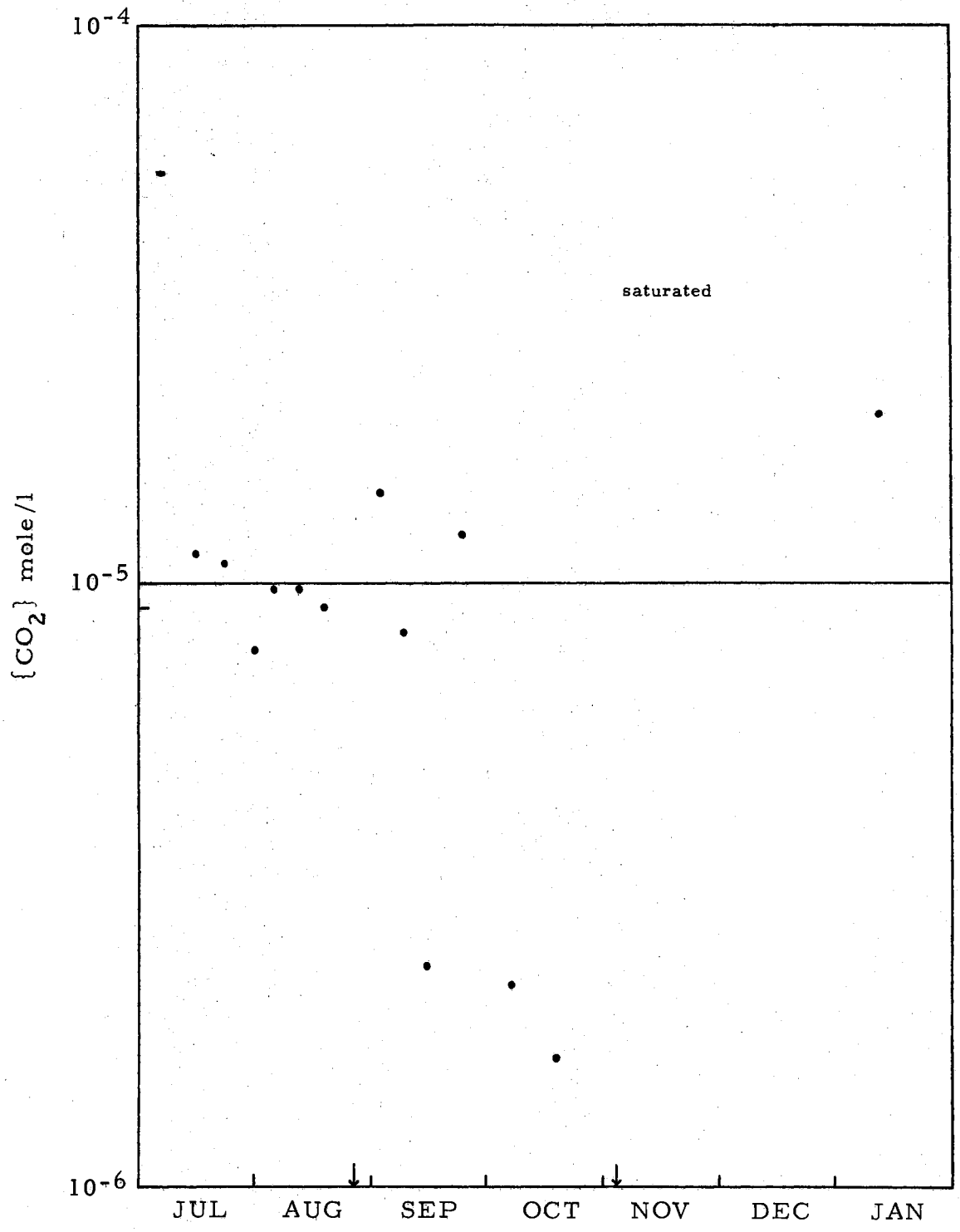

Figure 19. Carbon Dioxide Saturation of Lake Carl Blackwell, Station Two Surface Water at 25°. Arrows designate points off scale.

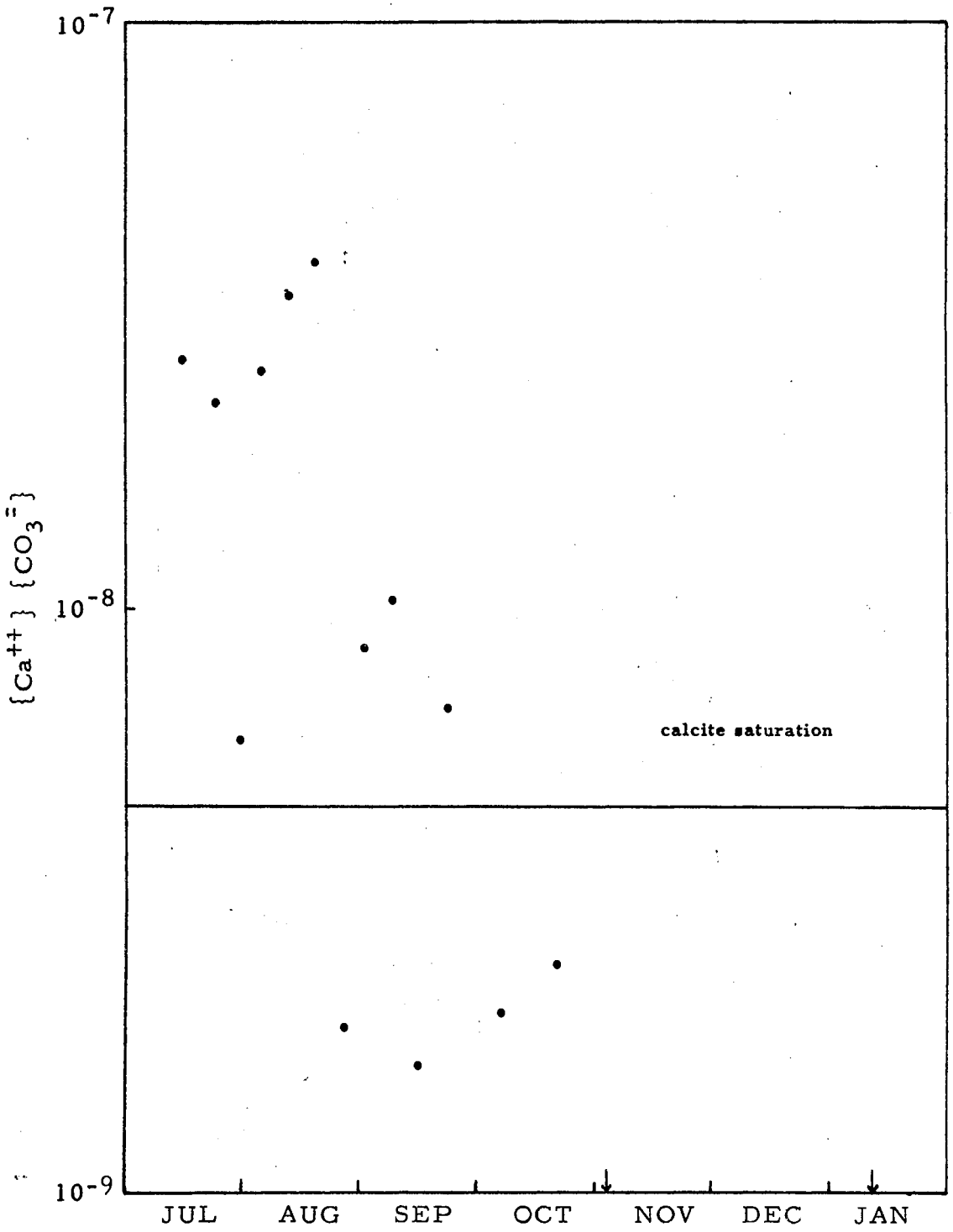

Figure 20. Calcite Saturation of Lake Carl Blackwell, Station Two Surface Water at 25°. Arrows designate points off scale.

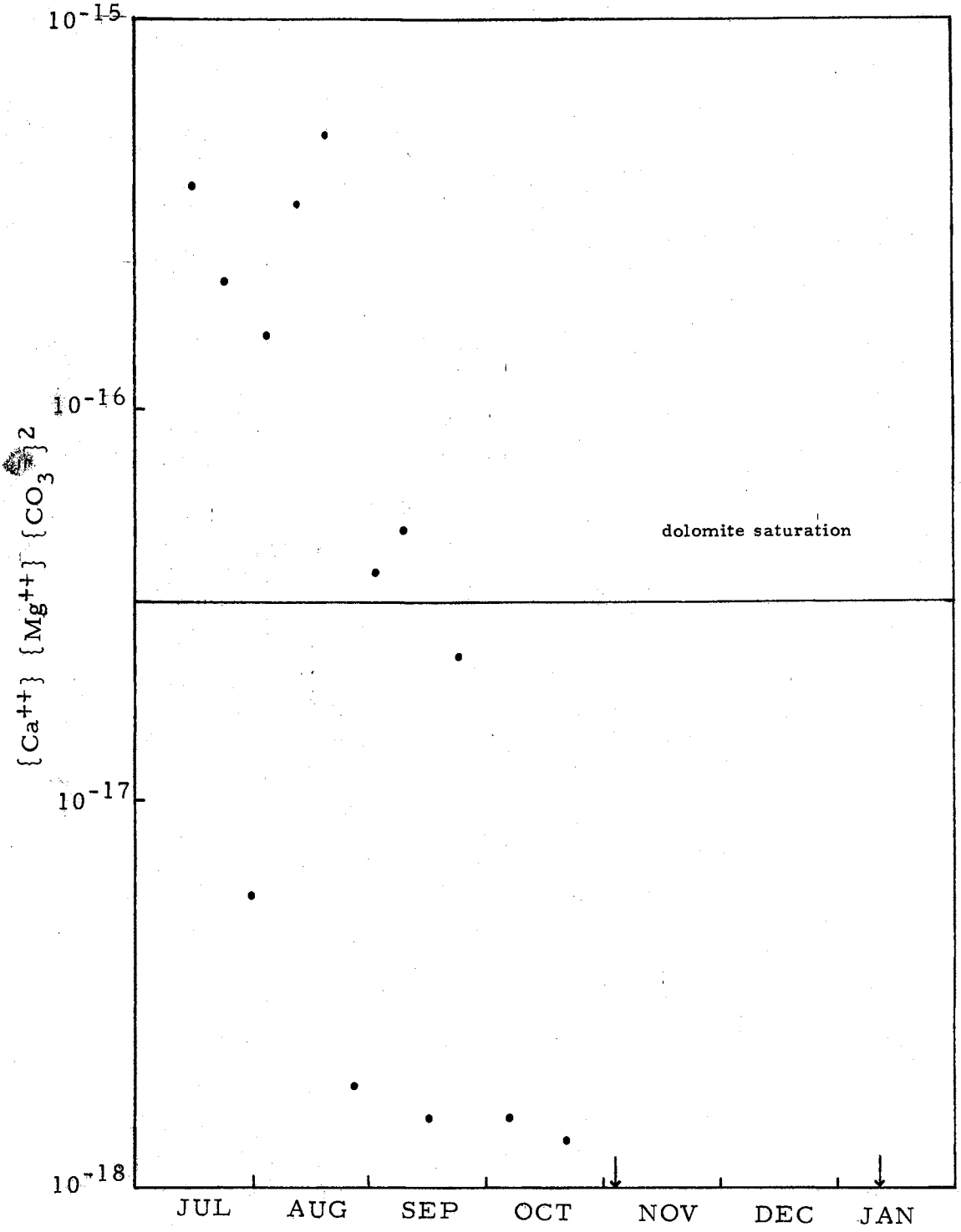

Figure 21. Dolomite Saturation of Lake Carl Blackwell, Station Two Surface Water at 25°. Arrows designate points off scale.

Phosphate Solubility

Kramer (87) has suggested that solubility of hydroxyapatite may control phosphate activity in the Great Lakes. Since Ca^{++} and H^{+} data is available from this study, it is possible to calculate the concentration of phosphate necessary to precipitate hydroxyapatite from solution. The pK_{SO} of $Ca_{10}(OH)_2(PO_4)_6$ is 113.9 at 25° (87).

$$[Ca^{++}]^{10}\,[OH]^{2}\,[PO_4^{3-}]^{6} = 10^{-113.9} \qquad (66)$$

The concentration of PO_4^{3-}, if phosphate in solution is in equilibrium with hydroxyapatite, can be calculated by rearranging Equation 66. At a pH of approximately 8.2, orthophosphate in Lake Carl Blackwell should exist in the form of $HPO_4^{=}$. The third acid dissociation constant for H_3PO_4 is $10^{-12.32}$ (88). Therefore,

$$[HPO_4^{=}] = [PO_4^{3-}]\,[H^{+}]/10^{-12.32} \qquad (67)$$

concentrations of $HPO_4^{=}$ necessary for equilibrium with hydroxyapatite are plotted for station two surface water in Figure 22. The particularly high values in November and January are due to low Ca^{++} activity on those dates.

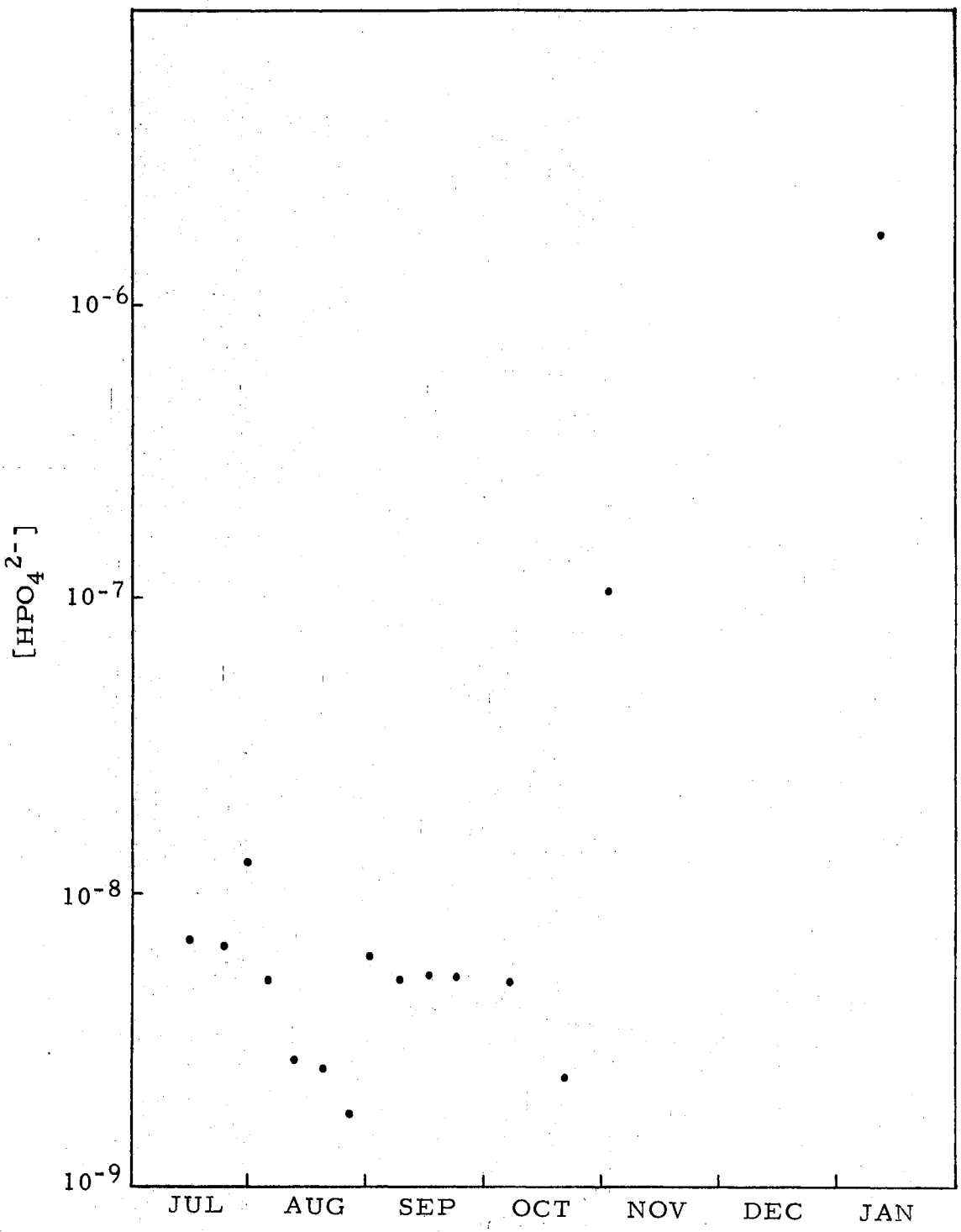

Figure 22. Concentration of Orthophosphate Required to Saturate Hydroxyapatite from Lake Carl Blackwell, Station Two Surface Water at 25°

CHAPTER VII

CONTINUOUS MONITORING OF A LABORATORY ALGAE CULTURE

The monitoring system described in Chapter III, which was designed for field data acquisition, is also useful for monitoring aquatic systems in the laboratory. A laboratory monitoring program was carried out as one of the final developmental stages leading to in situ monitoring of natural water systems.

Monitoring in the laboratory allowed the instrument hardware to operate under simulated field conditions. Minor design adjustments were made while in the laboratory that should eliminate some potential problems in the field. Operating and maintenance procedures were developed and practiced before adverse field conditions were encountered. A preliminary evaluation of sensor stability was made. Data acquired from laboratory algae cultures, while giving important information about the particular algae and support medium studied, provided a data set similar in content and volume to one that would be obtained from the field. This data set allowed development of computer programs for data reduction. Methods of data display and interpretation could be practiced. At the same time, continuous data was

obtained on diurnal variation of the carbonate system in an aquatic ecosystem which may prove useful for elucidating some of the interactions between the abiotic and biological aquatic systems.

Experimental Procedure

All algae cultures were contained in a rectangular glass aquarium containing 35 l of support solution. Rapid stirring of the solution was maintained by a stainless steel rotating paddle. The aquarium was housed inside a darkbox, so the only light available for photosynthesis was supplied by two 40-watt fluorescent grow-lamps[1] suspended 29 cm above the water surface. An electric timer turned the lights on at 0600 hrs and off at 1800 hrs each day. No attempt was made to control temperature of the culture, but the observed temperature remained constant at $26^{\circ} \pm 1^{\circ}$.

Electrodes sensitive to H^+, CO_2, Na^+, Ca^{++}, and Mg^{++} were calibrated as described in Chapter IV and placed in the aquarium. The data acquisition system described in Chapter III periodically recorded data from each electrode.

A culture medium with the composition given in Table VII was prepared from reagent grade chemicals in deionized water. Essential trace metals were assumed available from impurities in the added salts. Approximately 2×10^{-3} M NO_3^- and 1.7×10^{-4} M $HPO_4^=$

[1]Sylvania F40-GRO Gro-Lux

provided ample reserves of these nutrients. Carbon was initially available from approximately 2.5×10^{-4} M HCO_3^-.

TABLE VII

CULTURE MEDIUM FOR AQUARIUM MONITORING

Reagent	g/l	Concentration Approx. M
$MgSO_4 \cdot nH_2O$ assay 63.8% $MgSO_4$	0.16	8×10^{-4} Mg^{++}
$Ca(NO_3)_2 \cdot 4H_2O$	0.24	10^{-3} Ca^{++}
$NaCO_3$	0.026	2.5×10^{-4} CO_3^* } 10^{-3} Na^+
$Na_3PO_4 \cdot 12H_2O$	0.063	1.7×10^{-4} PO_4^{3-}
KCl	0.0007	10^{-5} K^+
1% $FeCl_3$ soln	0.1 ml/l	
adjust to pH = 8.2 with $HClO_4$		

The solution, after mixing and pH adjustment, was allowed to equilibrate with stirring in the aquarium for 24 hrs; then a small amount of Dactylococcopsis filtered from a natural culture was washed into the aquarium solution.

Since multiple depth capability was not required, the five electrodes were placed in the aquarium in direct contact with the surface of the solution. Electrode leads were passed through a hole in the side of the darkbox for connection to the multiplexer of the monitoring system. Data from each of the five electrodes was recorded every 12 minutes for 7 weeks. Data was taken in this manner continuously except for temporary shutdowns required for instrument service and electrode calibration.

Cell counts were taken daily by filtering a small aliquot of culture solution through a 0.45μ Millipore filter and averaging counts in ten microscope fields. No cell identifiable as other than Dactylococcopsis were ever observed during counting. Gravimetric determination of suspended matter gave a factor of 38.61 mg/l/10^6 cells/ml for converting cell counts to dry weight biomass.

As shown in Figure 23b an exponential growth curve started to form during the first week, but about the tenth day, growth became more or less linear with time at an approximate rate of 4.44 mg/l/day. Very little carbon was available in the original culture solution; therefore the main source of carbon for the observed biomass increase must have been atmospheric CO_2. An estimate of CO_2 necessary to produce a given biomass can be calculated from the very simplified photosynthesis reaction, Equation 68.

$$CO_2 + H_2O \xrightarrow{\text{photosynthesis}} CH_2O + O_2 \qquad (68)$$

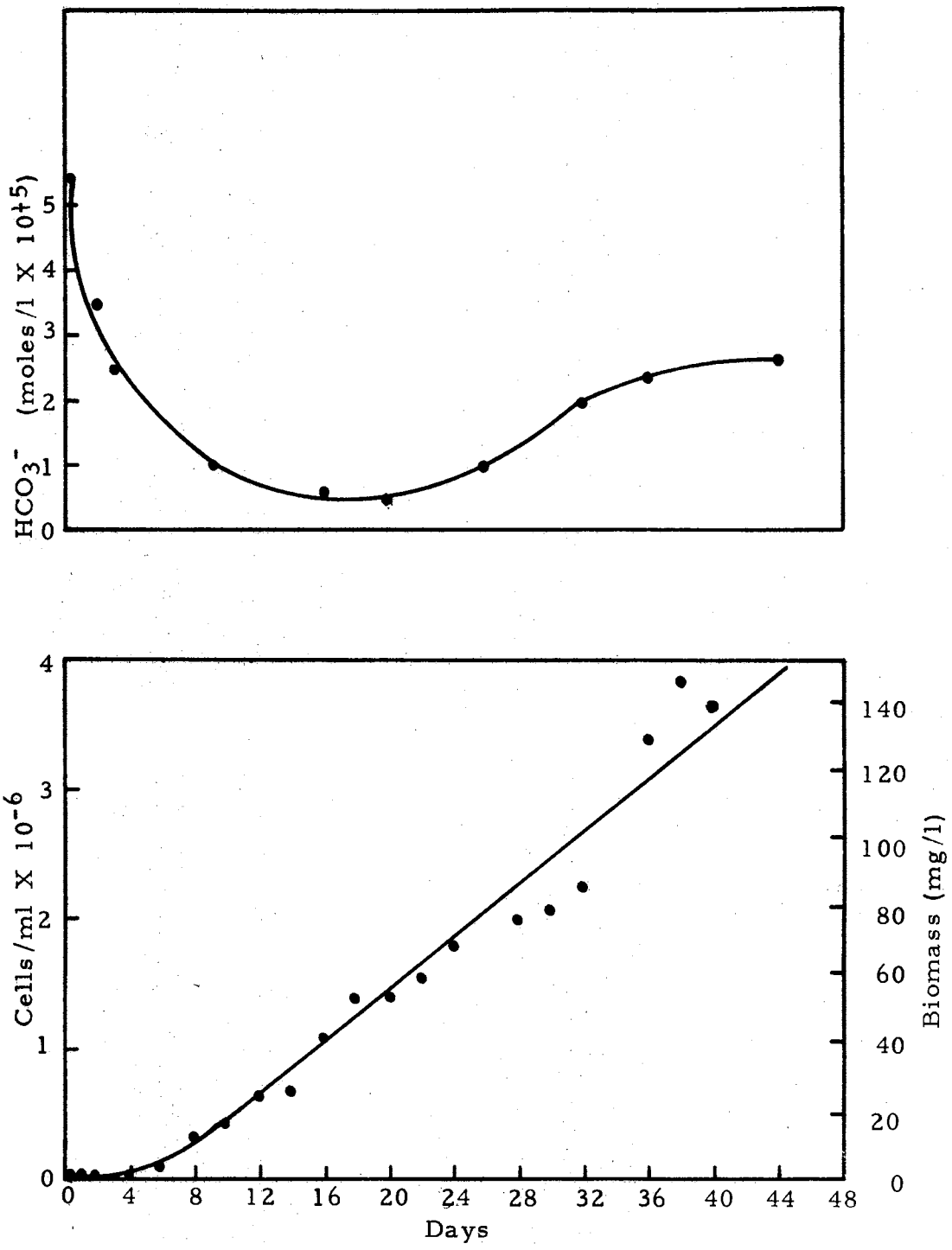

Figure 23. Dactylococcopsis Cell Counts and Daily Mean Bicarbonate Ion Activity During Continuous Monitoring

The observed biomass increase can be attributed to a daily influx of CO_2, $\Delta[CO_2]/\Delta t = +6.5$ mg/l/day, which corresponds to a surface diffusion rate of 0.16 mg/cm^2/day.

The instantaneous diffusion rate of CO_2, $d[CO_2]/dt$, depends upon the partial pressure of CO_2 in the water phase, a value which exhibits diurnal variation. The above rates may be considered as daily totals which are nearly constant for each 24 hr period.

The quantity of inorganic carbon available as HCO_3^- is depicted in Figure 23a where daily averages of $\{HCO_3^-\}$ are plotted on the same time scale as the growth curve in Figure 23b. By the eighth day $\{HCO_3^-\}$ had been decreased by fourfold, and biomass uptake decreased it even further during the following two weeks. The rise in $\{HCO_3^-\}$ about the twentieth day may have been due to decomposition of organic matter. Near the end of the experiment, $\{HCO_3^-\}$ apparently was asymptotically approaching a constant value well below that of the starting solution.

The paper tape data file was processed by computer. Calculations made were the same as those previously described for lake data. Chemical activity values were tabulated and plotted vs time for each day. Line printer plots for selected days are shown in Figures 24 through 28. Activity units are moles/l scaled according to the key below each graph and time of day is in hours and hundredths of hours. It is important to note that activity scales differ among the graphs.

Analysis of this data for the 50 day period monitored will require an interdisciplinary approach, and such analysis was not available at the time of this writing. A few selected graphs are presented here with general comment and should be regarded as examples of information available from continuous monitoring of aquatic ecosystems.

In Figure 24, during the second day of the experiment, biomass was small and only slight diurnal variation of the graphed parameters is evident. The metal ion activities, with the exception of some unexplained variation in $\{Mg^{++}\}$, were nearly constant for the day. Bicarbonate ion activity decreased slightly throughout the second day which is consistent with Figure 23a.

By the twelfth day, the rate of biomass increase became dependent on diffusion rate of CO_2. CO_2 and $CO_3^{=}$ in Figure 25 show the expected diurnal cycle while all the other chemical species were relatively constant. The rapid fall in CO_2 occurs at 0600 hrs when the light source turned on. CO_2 rise started shortly after 1800 hrs when the light was turned off. HCO_3^- and H^+ indicate a very small diurnal variation.

On the eighteenth day cell counts were 1.2×10^6 per ml and HCO_3^- activity was near the minimum in Figure 23. The computer plot for day number 18, Figure 26, shows a marked diurnal cycle for HCO_3^- in contrast with practically constant HCO_3^- in Figure 25. Even though the entire carbonate system was at very low activity, diurnal

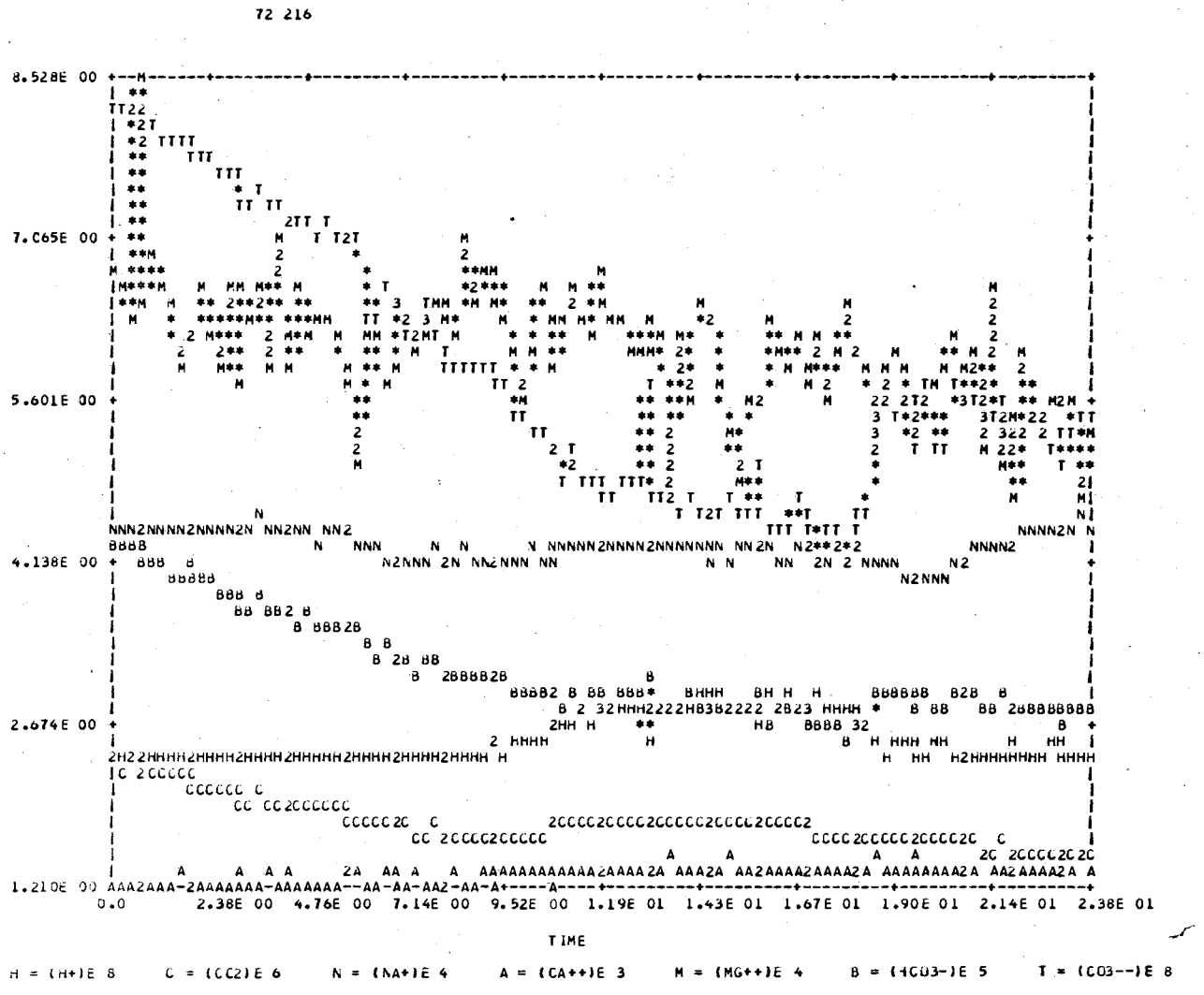

Figure 24. Monitor Data of Algae Culture During Experiment Day Two

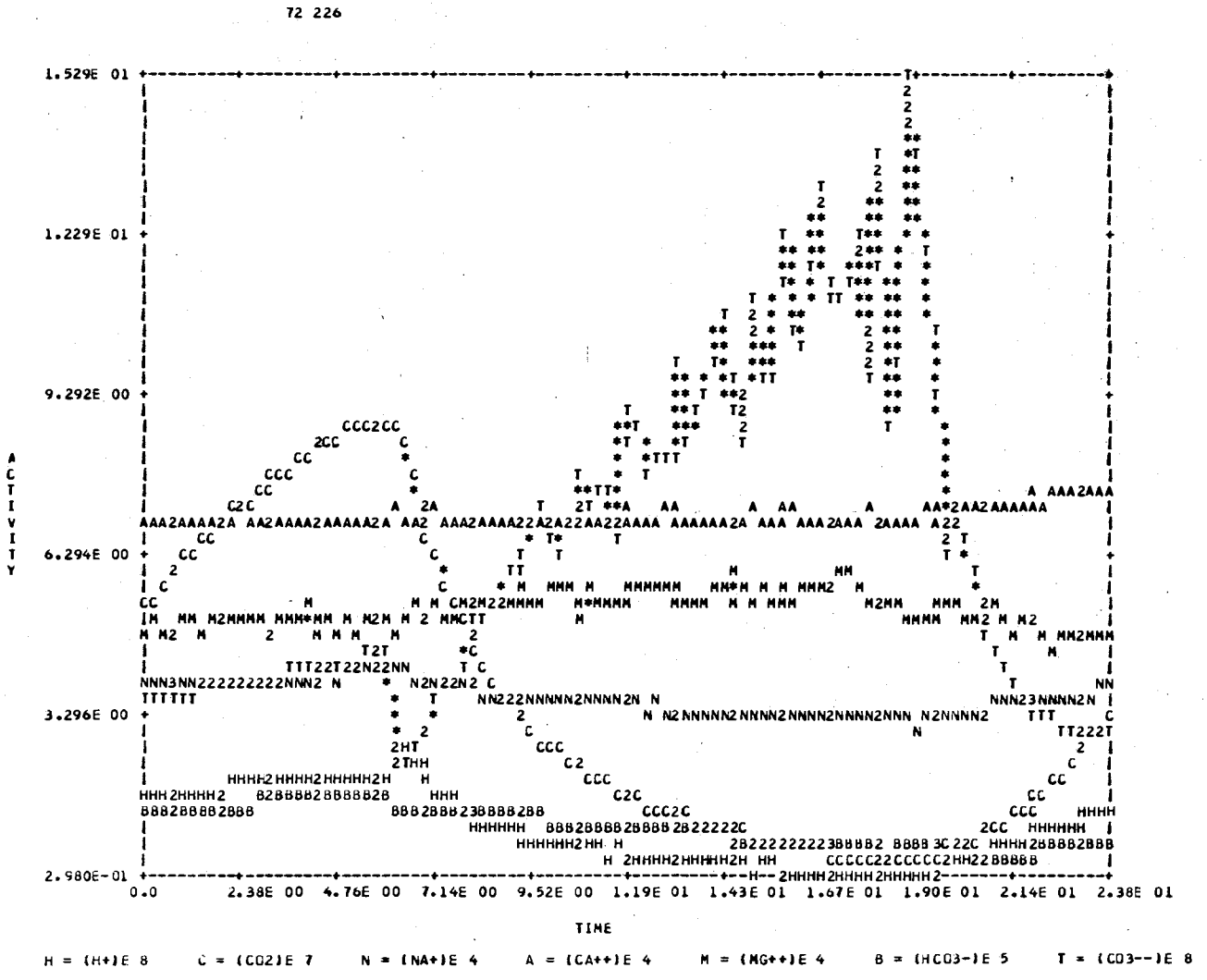

Figure 25. Monitor Data of Algae Culture During Experiment Day Twelve

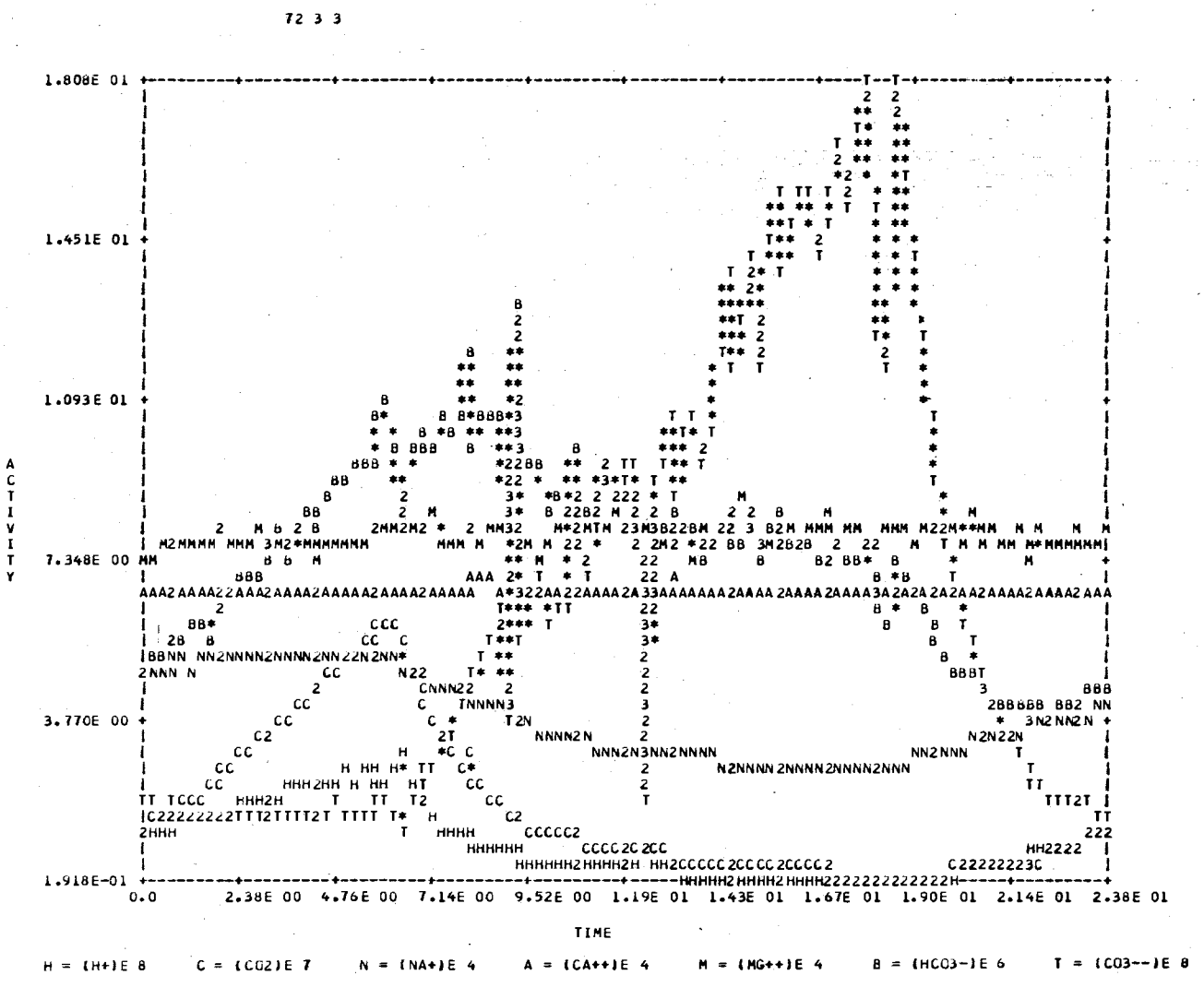

Figure 26. Monitor Data of Algae Culture During Experiment Day Eighteen

cycles are apparent in both CO_2 and $CO_3^=$. As would be expected, the metal ions were not affected by the changes in very low HCO_3^- and $CO_3^=$ activities. The nonlinearity of Na^+ which cannot be accounted for by formation of HCO_3^- or $CO_3^=$ complexes, was probably due to response of the Na^+ electrode to H^+. The Na^+ electrode manufacturer's selectivity condition for no H^+ interference of $[Na^+] > 10^4 [H^+]$ was just barely met by this solution.

On the twenty-nineth day of the experiment, total carbonate activity increased and the cell count doubled from that of the eighteenth day. The H^+ and CO_2 on the twenty-nineth day in Figure 27 are nearly parallel through the 24 hr period. A steep decrease in CO_2 activity at 0600 hrs occured as usual. The $CO_3^=$ peak increased earlier in the day than previously, but the trailing edge of the peak remained at 1800 hrs. Although magnitude of diurnal variation of HCO_3^- was larger than before, the daily average HCO_3^- activity was smaller on the twenty-nineth day than on the eighteenth.

Data for day number fourty-five in Figure 28 shows a stable system in which the CO_2 component exhibits typical diurnal characteristics. The HCO_3^- curve appears to be a damped function of CO_2. H^+ closely paralleling CO_2 indicates a system with low buffer capacity. The graph is dominated by the very large $CO_3^=$ peak which became wider throughout the experiment. On the fourty-fifth day the leading edge of the $CO_3^=$ peak was moved up to 0600 hrs, and the trailing edge

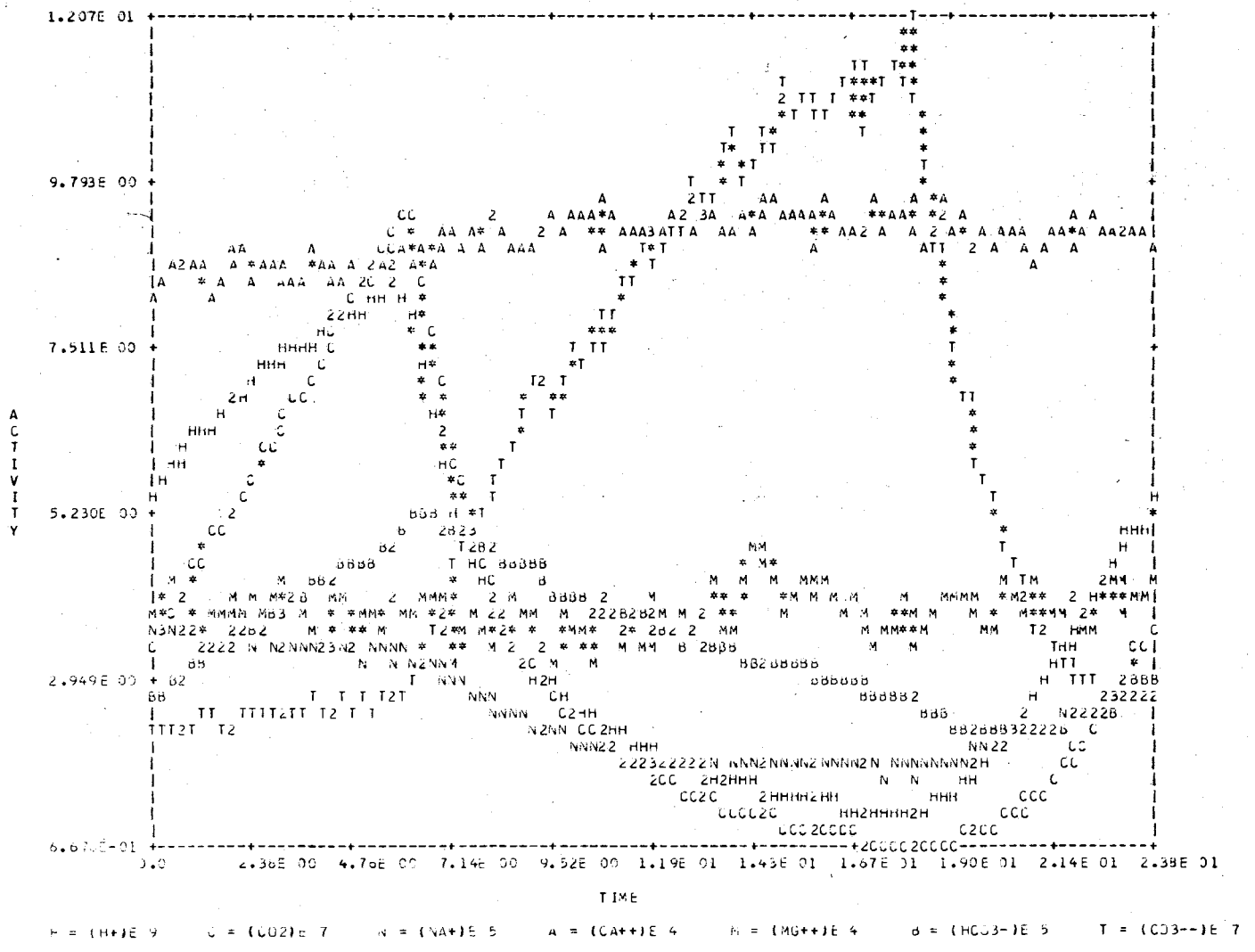

Figure 27. Monitor Data of Algae Culture During Experiment Day Twenty-nine

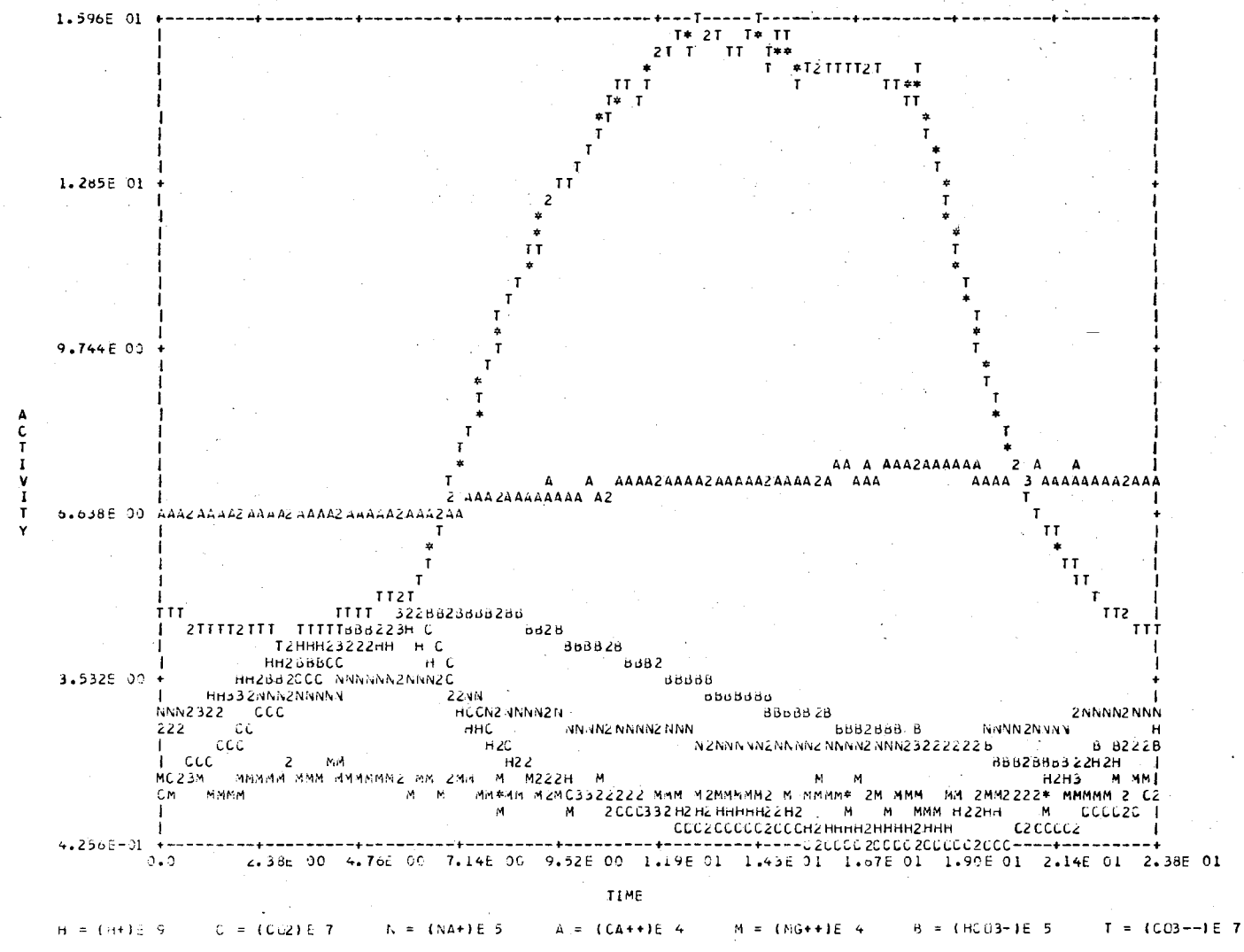

Figure 28. Monitor Data of Algae Culture During Experiment Day Fourty-five

remained at 1800 hrs. The divalent cations show no significant diurnal variation, and Na^+ changes may again be attributed to Na^+ electrode response to H^+.

The carbonate complex activities in Table II were also calculated and plotted for each day. Since the metal ion activities were nearly constant throughout each 24 hr period, the carbonate complex curves show the same structure as each respective anion curve. The line printer graph of the fourty-fifth day is presented in Figure 29 as an example.

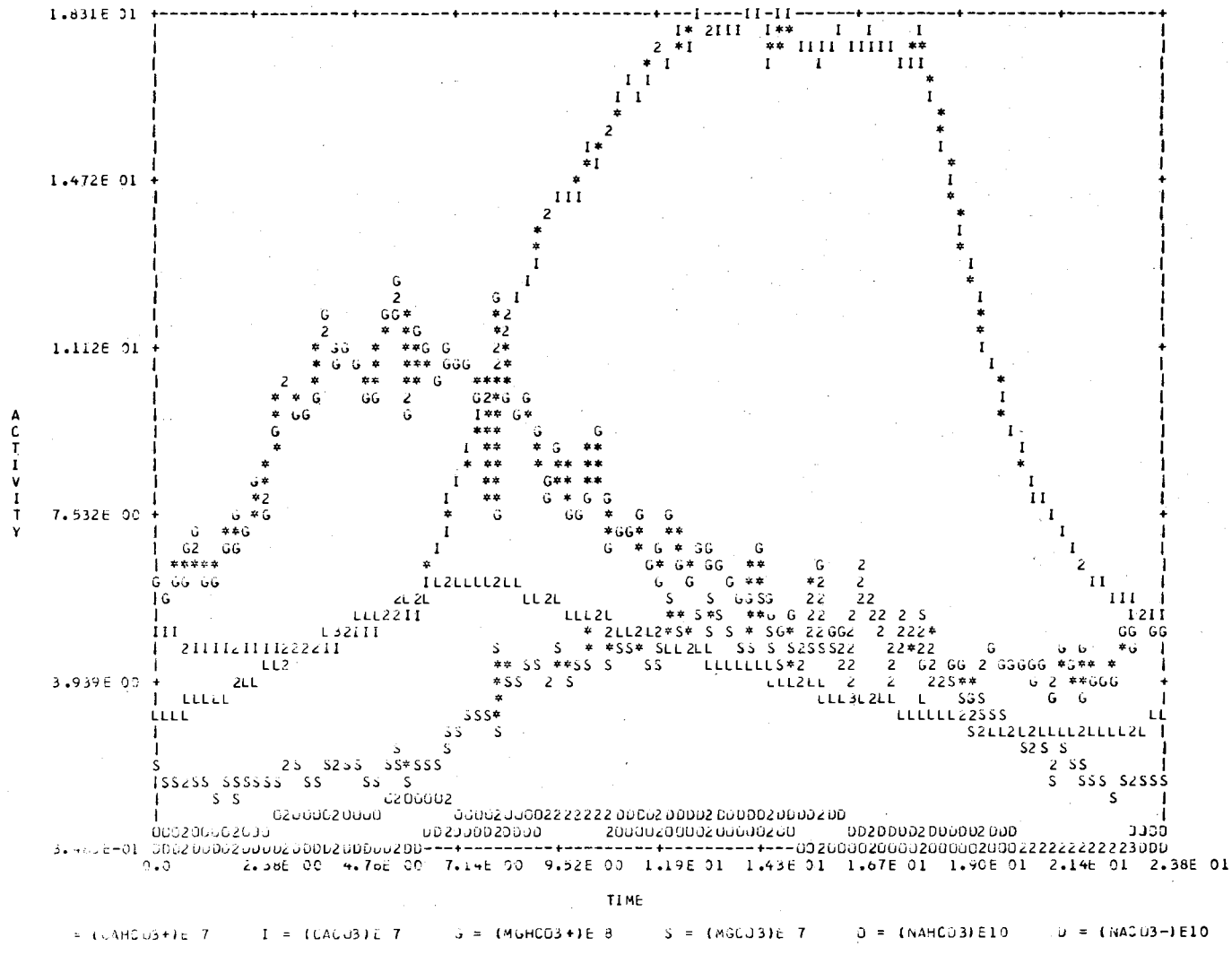

Figure 29. Carbonate Complexes of Algae Culture During Experiment Day Fourty-five

CHAPTER VIII

SUMMARY

The primary objective of this research was to develop a multiple-depth continuous monitoring system that would record ion-selective electrode data on a computer compatible medium. The monitoring system described in Chapter III has not undergone field evaluation, but has proved itself successful for monitoring in the laboratory.

This monitoring system will accept up to 25 sensor inputs, of which 19 can be high impedance electrodes. A facility for switching 18 reference electrodes was also provided. In its present form, the monitoring system will accept any analog signal between -1 and +1 volts. Digital mV data with sample and sensor identification codes is punched on computer readable paper tape. A provision is available for optional recording of time code. Water samples can be pumped from multiple depths through an electrode chamber. Samples and sensors can be scanned automatically and data for each can be punched under programmed control. The use of current saturated switching circuits in the digital logic modules will help insure error free operation under adverse environmental conditions.

All of the major inorganic carbonate species known to exist in

many natural waters can be determined by measurement of H^+, CO_2, Na^+, Ca^{++}, and Mg^{++}. The equilibria calculations require determination of ion activities which suggests the choice of ion-selective electrodes as chemical sensors. H^+, Na^+, and Ca^{++} were monitored directly by use of commercial electrodes and a suitable reference electrode. A CO_2 electrode of the Severinghaus type was developed to a degree where it could be used in natural water systems. Since there is no Mg^{++} electrode commercially available, a divalent cation electrode was used to measure Mg^{++} with only marginal success. All electrodes were found to exhibit drift of varying degrees which is a severe drawback for sensors to be used for continuous monitoring.

The function of the monitoring system has been demonstrated by monitoring a laboratory algae culture. The data that was obtained and analyzed from this experiment provided an example of diurnal data that could be expected from monitoring in a natural system. This laboratory monitoring experiment also pointed out that much valuable information about aquatic ecosystems may be obtained from laboratory studies where controlled conditions specify variables that may contain high degrees of uncertainty in the field.

The measuring techniques to be used for continuous monitoring were applied to analysis of grab samples from Lake Carl Blackwell. The chemical data along with biological studies has provided a means for formulating a general description of abiotic-biological interactions

in that particular water system. A background study is therefore available prior to more comprehensive efforts which should be implemented on a continuous basis. The data from Lake Carl Blackwell has also demonstrated the rate of change to be expected from environmental measurements and will be valuable for estimating frequency of future sampling.

Aquatic ecosystems are dynamic; therefore, in lieu of adequate theories for describing life processes, the determination of interconnections between abiotic and biological systems will require continuous monitoring. Both quanitative and qualitative data are required and information is needed for all interconnecting systems in a body of water. The carbonate chemical system certainly undergoes diurnal variations. In order to achieve continuous monitoring, measurements should be made on the chemical system described in Chapter VI at a rate of once per hour at 1 m depth intervals. The algae and bacteria populations in Figure 9 showed large weekly variations. Algae and bacteria counts may have to be made once per day or more often to enable derivation of continuous functions to adequately describe the population dynamics. Biological data should also be taken at multiple depths. Zooplankton were not considered in this study, but should be included in future efforts.

The monitoring techniques which have been developed during this study are applicable to obtaining continuous chemical data in

natural systems. Technology, unfortunately, has not progressed to the point where automated methods are available for determining the desired biological parameters. Highly automated particle counters are a step in the right direction, but they offer little information for discriminating different kinds of particles. Even though the biologist is presently fettered to his petri dish and microscope, the sampling part of biological investigations could be automated by integration with the chemical monitoring system. Computer data reduction of biological data is readily available when a mathematical analysis can be utilized.

Natural ecosystems consist of a large number of highly connected interrelated components. The various components can be described in terms of particular scientific disciplines, but nature is not delineated into specific disciplines. For this reason, a scientific study of aquatic ecosystems requires a simultaneous approach through several fields of study. Interdisciplinary cooperation and communication among scientists is required, for if a part of the whole system is neglected, or even minimized, a realistic explanation of any other part may be impossible.

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APPENDIX A

CARBON DIOXIDE ELECTRODE

CALIBRATION PROGRAM

```
      C   PROGRAM TO CALIBRATE H+ ELECTRODE AND THEN CALIBRATE CO2 ELECTRODE FROM
      C   PH DATA.  EQUATIONS ASSUME A PURE AQUEOUS CARBONATE SOLUTION.
0001        REAL RMV( 399,2),CO2CON( 399),K1,K2,KCO2,KW,Z( 399),LOGCO2( 199) ,
           &X(50 ),PH(10),HMV(10)
0002        INTEGER UNIT*2(8),SPILL*2(8),MV(8),PROB*2(8),SAMPL*2(8),PROBE*2( 9
           &99),SAMPLE*2( 999)
0003        DATA K/0/,J/0/,L/-1/,N/0/
      C     READ H+ ELECTRODE CALIBRATION DATA.  NPTS = NUMBER OF CALIBRATION POINTS.
0004        READ 11, NPTS,(PH(I),HMV(I),I=1,NPTS)
0005        PRINT 13
0006       13 FORMAT('    H+ ELECTRODE CALIBRATION DATA:')
0007        PRINT 11,NPTS,(PH(I),HMV(I),I=1,NPTS)
0008       11 FORMAT (I2/(2F10.1))
CC09        CALL LESQRE(NPTS,HMV,PH,AH,BH)
0010        PRINT 12, AH,BH
0011       12 FORMAT(' PH=',E13.6,'  MV + ',E13.6)
0012        6 J=J+1
      C     READ ALL PAPER TAPE DATA
0013        READ (5,1,END=9) (UNIT(M),SPILL(M),MV(M),PROB(M),SAMPL(M),M=1,8)
0014        1 FORMAT (8(2I1,I4,2I2))
0015        DO 2 M=1,8
0016        IF (UNIT(M) .EQ. 0) GO TO 9
0017        IF (PROB(M) .EQ. 1) K=K+1
0018        IF (UNIT(M) .NE.1) PRINT 3, UNIT(M),J
CC19        3 FORMAT (' UNIT NUMBER',I2,' ON CARD',I6)
0020        IF (SPILL(M) .EQ. 5) AMV   =(9999-MV(M))/10.0
0021        IF (SPILL(M) .EQ. 3) AMV   =-MV(M)/10.0
0022        IF (SPILL(M) .NE. 3 .AND. SPILL(M) .NE. 5) PRINT 5, SPILL(M),J
0023        5 FORMAT (' SPILL COUNTER CODE IS',I2,' ON CARD',I6)
0024        IF (PROB(M).NE.1  .AND. PROB(M).NE.2  ) PRINT 4,PROB(M),J
0025        4 FORMAT(' PROBE NO. IS',I3,' ON CARD',I6)
0026        2 RMV(K,PROB(M))=AMV
CC27        GO TO 6
      C   K VALUES ARE DISSOCIATION CONSTANTS
0028        9 K1=10.0**(-6.352)
0029        K2=10.0**(-10.332)
0030        KCO2=10.0**(-2.589)
0031        KW=1.0E-14
0032        DO 7 I=1,K
0033        X(I)=RMV(I,2)
      C   H = H+ CONC.
CC34        H=10.0**(-AH*RMV(I,1)-BH)
0035        CO2CON(I)=  ((H**4+K1*H**3+ (K1*K2-KW) *H**2-K1*KW*H-K1*K2*KW)/
           & (K1*(H**2+2*K2*H) * (1+K1/H+K1*K2/H**2)))/(1+KCO2)
0036        7 LOGCO2(I)=ALOG10(CO2CON(I))
0037        PRINT 10,(CO2CON(I),RMV(I,2),I=1,K)
CC38        CALL LESQRE(K,X  ,LOGCO2   ,A,B)
0039        PRINT 8,A,B
0040        8 FORMAT('0 LOG (CO2) = ',E13.6,' MV + ',E13.6)
CC41       10 FORMAT('-  CO2 CONC.      MV' /(1PE12.4,0PF8.1))
0042        CALL PLOT(X  ,0,CO2CON,5,Z,0,K,1,1,0,2,0,2)
CC43        STOP
CC44        END
```

```
0001            SUBROUTINE  LESQRE (N, X, Y, A, B)
                C     THIS IS A SUBPROGRAM FOR DETERMINING THE SLOPE (A) AND THE
                C     INTERCEPT (B) FOR A LINEAR PLOT BY THE LEAST SQUARES METHOD
                C     Y = AX + B
                C     N = NUMBER OF POINTS ON THE GRAPH
                C     SUM = SUM OF THE X VALUES
                C     SUN = SUM OF THE Y VALUES
0002            DIMENSION X(N), Y(N)
0003            SUM = 0.0
0004            SUN = 0.0
0005            DO 1 I = 1,N
0006            SUM = SUM + X(I)
0007          1 SUN = SUN + Y(I)
0008            R = N
0009            XAVE = SUM/R
0010            YAVE = SUN/R
0011            SUM1 = 0.0
0012            SUN1 = 0.0
0013            DO 2 I = 1,N
0014            SUM1 = SUM1 + ((X(I) - XAVE)*(Y(I) - YAVE))
0015          2 SUN1 = SUN1 + (X(I) - XAVE)**2
0016            A = SUM1/SUN1
0017            B = YAVE - A*XAVE
0018            RETURN
0019            END
```

H+ ELECTRODE CALIBRATION DATA:

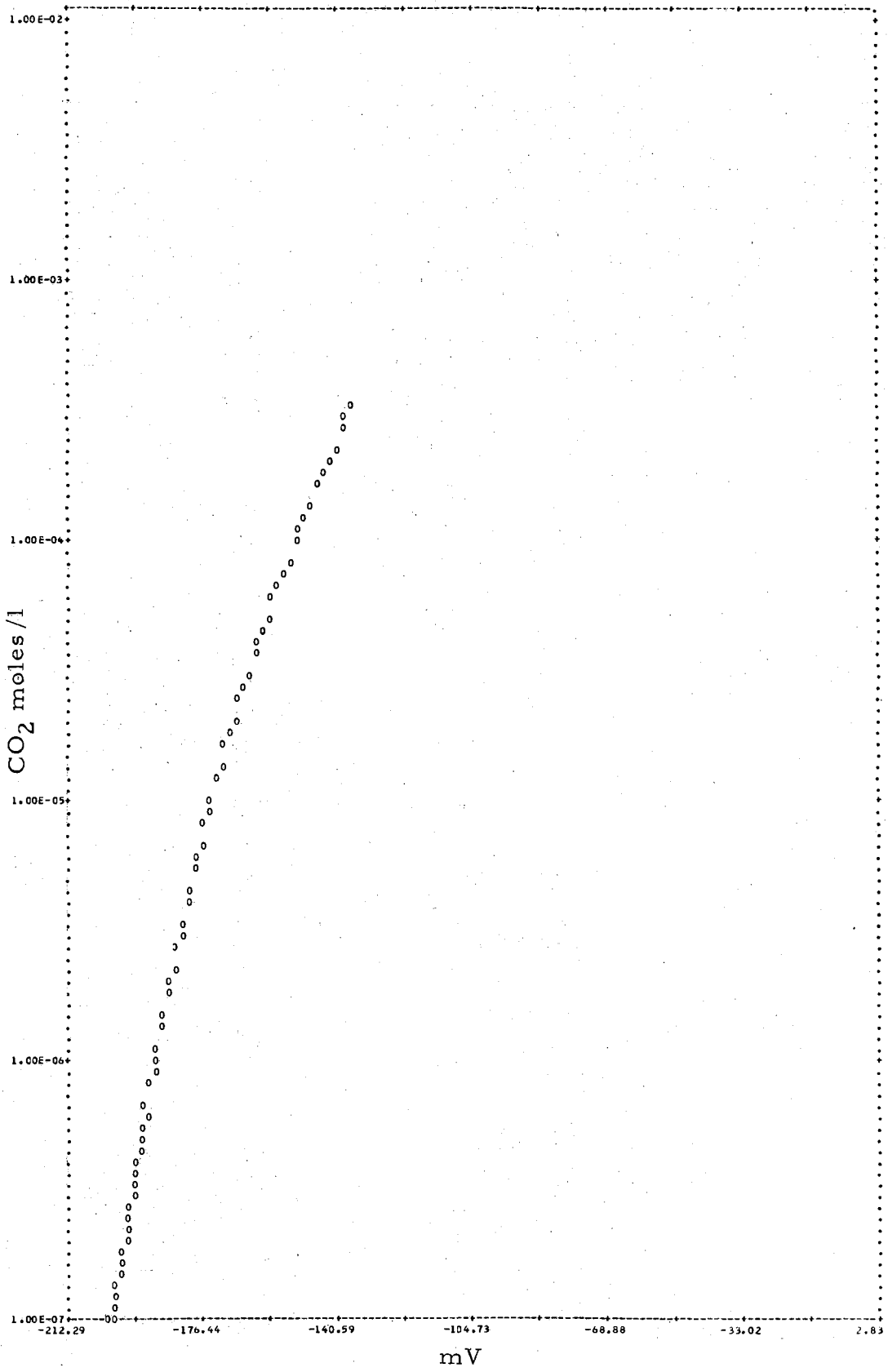
8

5.0	130.2
5.6	93.4
6.0	69.3
6.6	33.6
7.0	11.8
7.4	-19.4
8.0	-53.1
8.6	-82.1

PH=-0.16676BE-01 MV + 0.715793E 01

CC2 CONC.	MV
3.1989E-03	-136.9
2.7645E-03	-137.9
2.4262E-03	-139.6
2.1456E-03	-141.2
1.8975E-03	-142.7
1.6781E-03	-145.0
1.4955E-03	-145.8
1.3125E-03	-147.6
1.1607E-03	-148.8
1.0344E-03	-150.6
9.1479E-04	-151.9
7.9668E-04	-153.5
7.0999E-04	-154.8
6.2789E-04	-156.4
5.5104E-04	-157.7
4.8732E-04	-158.9
4.3097E-04	-160.3
3.7822E-04	-161.6
3.3448E-04	-162.9
2.9129E-04	-164.2
2.5761E-04	-165.3
2.2608E-04	-166.9
1.9840E-04	-167.9
1.7146E-04	-169.1
1.5163E-04	-170.2
1.3205E-04	-171.4
1.1589E-04	-172.4
1.0092E-04	-174.0
8.7889E-05	-174.6
7.6539E-05	-176.1
6.7168E-05	-176.7
5.8045E-05	-177.9
5.0548E-05	-178.7
4.4019E-05	-179.7
3.8333E-05	-180.5
3.3381E-05	-181.6
2.9292E-05	-182.3
2.5312E-05	-183.3
2.2211E-05	-183.9
1.9192E-05	-185.2
1.[illegible]971E-05	-185.9
1.[illegible]77E-05	-186.4
1.[illegible]866E-05	-187.4
1.1376E-05	-188.2
9.9805E-06	-188.6
8.7561E-06	-189.3
7.7411E-06	-190.1
6.8963E-06	-191.7
6.1434E-06	-191.0
5.4725E-06	-191.8
4.8746E-06	-192.5
4.3754E-06	-193.0
3.9270E-06	-193.5
3.5518E-06	-194.2
3.1874E-06	-194.6
2.8824E-06	-195.1
2.6470E-06	-195.4
2.4120E-06	-195.9
2.2148E-06	-196.5
2.0336E-06	-196.9
1.8525E-06	-197.3
1.7006E-06	-197.8
1.5733E-06	-198.1
1.4667E-06	-198.6
1.3566E-06	-199.1
1.2546E-06	-199.5
1.1694E-06	-199.9
1.0983E-06	-200.1
1.0315E-06	-200.5
9.7637E-07	-200.9
9.2410E-07	-201.2
8.7455E-07	-201.6
8.3415E-07	-201.9
7.9557E-07	-202.5
7.6476E-07	-202.5
7.3510E-07	-202.9
7.0098E-07	-203.2
6.8450E-07	-203.4
6.6312E-07	-203.8
6.3729E-07	-204.2
6.2226E-07	-204.3
6.0757E-07	-204.5
5.9322E-07	-204.8
5.7920E-07	-205.1
5.6550E-07	-205.3
5.5653E-07	-205.6
5.4771E-07	-205.7
5.3902E-07	-206.0
5.3046E-07	-206.2
5.2203E-07	-206.6
5.1786E-07	-206.7
5.0963E-07	-207.0
5.0152E-07	-207.1
5.0152E-07	-207.3
4.9353E-07	-207.5
4.9353E-07	-207.9
4.8958E-07	-207.9
4.6567E-07	-208.2
4.8178E-07	-208.4
4.7792E-07	-208.5
4.7792E-07	-208.7
4.7409E-07	-208.7
4.7409E-07	-208.9
4.7029E-07	-209.2
4.7029E-07	-209.3
4.6278E-07	-209.5

LOG (CO2) = 0.592895E-01 MV + 0.604245E 01


1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
CO_2 moles/l
-212.29
-176.44
-140.59
-104.73
-68.88
-33.02
2.83
mV

APPENDIX B

WATER ANALYSIS DATA REDUCTION PROGRAM

```
0001              REAL INTCPT(5,100),SLOPE(5,100),ION(13,100),XION(10),XDEPTH(10),
                 &MGHCO3,MGCO3,NAHCO3,NACO3
0002              INTEGER YR(50),MO(50),DY(50),       CYR(5,50),CMO(5,50),CDY(5,50),
                  &NCAL(5)/5*0/,N/1/,I/1/,JCAL/1/,J/1/,BLNK/'     '/,H/'H+  '/,CO2
                  &/'CO2 '/,NA/'NA+ '/,CA /'CA++'/,M /'M++ '/,
                  &MULT(13),                                STA(50),DEPTH(50),WORD(8)
                  &/6*'    ','DEPT','H   '/,         KHAR(13)/'H','C','N','A','M','B',
                  &'T','L','I','G','S','O','D'/
0003              HCO3=10**6.352
0004              CO3=10**10.332
0005              CAHCO3=10**1.26
0006              CACO3=10**3.20
0007              MGHCO3=10**1.16
0008              MGCO3=10**3.40
0009              NAHCO3=10**(-0.25)
0010              NACO3=10**1.27
                C   A BLANK CARD FOLLOWS THE CALIBRATION DATA
0011             18 READ 1,IX ,IYR,IMO,IDY,XSLOPE,XINT
0012              1 FORMAT (A4,5X,3I2,15X,E13.6,8X,E13.6)
0013                IF (IX .EQ. BLNK) GO TO 2
0014                I=0
                C   IF I REMAINS =0 THROUGH THE FOLLOWING STATEMENTS, AN ERROR WILL RESULT WHEN
                C   I IS USED AS AN ARRAY SUBSCRIPT INDICATING INVALID ID DATA
0015                IF (IX .EQ. H) I=1
0016                IF (IX .EQ. CO2) I=2
0017                IF (IX .EQ. NA) I=3
0018                IF (IX .EQ. CA) I=4
0019                IF (IX .EQ. M ) I=5
0020                NCAL(I)=NCAL(I)+1
0021                CYR(I,NCAL(I))=IYR
0022                CMO(I,NCAL(I))=IMO
0023                CDY(I,NCAL(I))=IDY
0024                SLOPE(I,NCAL(I))=XSLOPE
0025                INTCPT(I,NCAL(I))=XINT
0026                GO TO 18
0027              2 DO 6 K=N,50
                C   BLANK CARD MUST FOLLOW INPUT DATA
0028                READ (5,7,END=8) YR(K),MO(K),DY(K),STA(K),DEPTH(K),(ION(I,K),I=1,5
                   &)
0029              7 FORMAT (10X,3I2,4X,I1,1X,I2,6X,5F10.1)
0030                IF (.NOT.(YR(1) .EQ. YR(K) .AND. MO(1) .EQ. MO(K) .AND. DY(1) .EQ.
                   &DY(K))) GO TO 9
0031              6 CONTINUE
                C   PRINT COLUMN HEADINGS
0032              9 PRINT 20
0033             20 FORMAT ('1',1X,'DATE', 6X,'ID',10X,'H+',13X,'CO2',12X,'NA+',12X,
                   &'CA++',11X,'MG++',11X,'HCO3-',10X,'CO3--'/)
                C   K-1 = NUMBER OF DATA POINTS PER DAY
0034                KDO=K-1
0035                DO 10 J=1,KDO
0036                PRINT 11,YR(J),MO(J),DY(J),STA(J),DEPTH(J)
0037             11 FORMAT (' ',3I2, 5X,I1,'-',I2)
0038                DO 13 I=1,5
                C   CHECK FOR LAST CALIBRATION DATA SET
0039                IF (JCAL .GE. NCAL(I)) GO TO 13
                C   UPDATE CALIBRATION EQUATIONS
0040             19 IF (YR(J)-CYR(I,JCAL+1)) 13,14,15
0041             14 IF (MO(J)-CMO(I,JCAL+1)) 13,16,15
```

```
0042            16 IF (DY(J)-CDY(I,JCAL+1)) 13,13,15
0043            15 JCAL=JCAL+1
CC44               GO TO 19
0045            13 ION(I,JJ)=10.0**(INTCPT(I,JCAL)+SLOPE(I,JCAL)*ION(I,JJ))
0046               ION(5,J)=ION(5,J)-ION(4,J)
0047               ION(6,J)=ION(2,J)/ION(1,J)/HCO3
0048               ION(7,J)=ION(6,J)/ION(1,J)/CO3
0049            10 PRINT 17,(ION(I,J),I=1,7)
0050            17 FORMAT('+',15X,1P7E15.3)
              C   CALCULATE AND PRINT OTHER CARBONATE SPECIES FROM EQUILIBRIUM CONSTANTS
0051               PRINT 35
0052            35 FORMAT ('-', 1X,'DATE',6X,'ID', 9X,'CAHCO3+', 9X,'CACO3', 9X,'MGHC
                  &O3+', 9X,'MGCO3', 9X,'NAHCO3', 9X,'NACO3-'/)
0053               DO 33 J=1,KDO
0054               PRINT 11,YR(J),MO(J),DY(J),STA(J),DEPTH(J)
0055               ION(8,J)=ION(4,J)*ION(6,J)*CAHCO3
0056               ION(9,J)=ION(4,J)*ION(7,J)*CACO3
0057               ION(10,J)=ION(5,J)*ION(6,J)*MGHCO3
0058               ION(11,J)=ION(5,J)*ION(7,4)*MGCO3
0059               ION(12,J)=ION(3,J)*ION(6,J)*NAHCO3
0060               ION(13,J)=ION(3,J)*ION(7,J)*NACO3
0061            33 PRINT 36,(ION(JJ,J),JJ=8,13)
0062            36 FORMAT ('+',15X,1P6E15.3)
              C
              C
              C   PLOT DATA FOR EACH DAY BY STATION
0063               M=1
CC64               ISIG=0
0065            31 NTIMES=1
0066               IDO1=1
0067               IDO2=7
0068            32 KAR=BLNK
              C   MULTIPLIER FOR SCALING PLOTS IS CALCULATED FROM VALUE OF FIRST DATA FOR
              C   EACH STATION
0069               DO 21 I=1,13
0070            21 MULT(I)= INT(ABS(ALOG10(ION(I,M))))+1
0071               NSIG=0
0072               CALL NOGRID(1)
0073            28 DO 22 I=IDO1,IDO2
0074               N=0
0075               DO 23 J=M,KDO
0076               IF (STA(J) .NE. STA(M)) GO TO 24
0077               N=N+1
0078               XDEPTH(N)=DEPTH(J)
0079            23 XION(N)=ION(I,J)*10**MULT(I)
              C    ISIG=1 AT END OF DAY
0080               ISIG=1
0081            24 IF (NSIG .EQ. 1) KAR=KHAR(I)
0082            22 CALL PL23(KAR,XION,XDEPTH,-N)
0083               IF (NSIG .EQ. 1) GO TO 26
0084               NSIG=1
0085               GO TO 28
0086            26 PRINT 29,YR(1),MO(1),DY(1),STA(M)
0087            29 FORMAT ('1',T35,3I2,T50,'STATION NUMBER ',I2///)
0088               CALL PLOT4(32,WORD)
0089               PRINT 38
0090            38 FORMAT ('0',T60,'ACTIVITY IN MOLES/LITER')
0091               IF (NTIMES .EQ. 1) PRINT 30,(MULT(I),I=1,7)
```

```
0092          30 FORMAT ('0',                                    T10,'H = (H+)E',I2,
                & 5X,'C = (CO2)E',I2, 5X,'N = (NA+)E',I2, 5X,'A = (CA++)E',I2,
                & 5X,'M = (MG++)E',I2, 5X,'B = (HCO3-)E',I2, 5X,'T = (CO3--)E',I2)
0093            IF (NTIMES .EQ. 2) PRINT 37,(MULT(I),I=8,13)
C094          37 FORMAT ('0',T10,'L = (CAHCO3+)E',I2, 5X,'I = (CACO3)E',I2, 5X,
                &'G = (MGHCO3+)E',I2, 5X,'S = (MGCO3)E',I2, 5X,'O = (NAHCO3)E',I2,
                & 5X,'D = (NACO3-)E',I2)
C095            IF (NTIMES .EQ. 2) GO TO 34
0096            IDO1=8
0097            IDO2=13
C098            NTIMES=2
0099            GO TO 32
0100          34 IF (ISIG .EQ. 1) GO TO 25
0101            M=J
0102            GO TO 31
              C
              C
              C
0103          25 N=2
0104            YR(1)=YR(K)
0105            MO(1)=MO(K)
0106            DY(1)=DY(K)
0107            STA(1)=STA(K)
0108            DEPTH(1)=DEPTH(K)
C109            DO 12 I=1,13
0110          12 ION(I,1)=ION(I,K)
0111            GO TO 2
0112           8 STOP
0113            END
```

```
0001          SUBROUTINE PL (KHAR,X,Y,NPTS)                                    0010
              C                                                                0020
              C  SHORTCUT ROUTINE FOR PRINTER PLOTS.                           0030
              C  HAS OPTIONS TO SET XMAX ETC. AUTOMATICALLY TO FRAME THE SET OF 0040
              C  POINTS, AND TO CONNECT ADJACENT POINTS BY LINE SEGMENTS.      0050
              C  PL CALLS PLOT2, PLOT3, AND PLOT4.                             0060
              C                                                                0070
              C  TO DELETE INTERNAL GRID LINES, CALL WIPE(1).                  0080
              C                                                                0090
              C  TO PLOT FROM A SINGLE ARRAY, CALL PL.  SET NPTS NEGATIVE TO   0100
              C  CONNECT ADJACENT POINTS WITH LINE SEGMENTS.                   0110
              C  EXAMPLE....                                                   0120
              C     DIMENSION X(100),Y(100)                                    0130
              C     CALL PL(1HY,X(1),Y(1),-100)                                0140
              C                                                                0150
              C  TO PLOT FROM MULTIPLE ARRAYS, CALL PL23 FOR EACH ARRAY WITH KHAR=1H 0160
              C  TO FRAME ALL OF THE POINTS, CALL PL23 FOR EACH ARRAY WITH KHAR SET 0170
              C  EQUAL TO THE DESIRED SYMBOL (AND NPTS NEGATIVE IF THE POINTS IN 0180
              C  THAT ARRAY ARE TO BE CONNECTED BY LINE SEGMENTS), AND CALL PL4. 0190
              C  THE SIGN OF NPTS IN THE FIRST SET OF CALLS TO PL23 IS IMMATERIAL. 0200
              C  EXAMPLE....                                                   0210
              C     DIMENSION X(100),Y(100),Z(100)                             0220
              C     CALL PL23(1H ,X(1),Y(1),100)                               0230
              C     CALL PL23(1H ,X(1),Z(1),100)                               0240
              C     CALL PL23(1HY,X(1),Y(1),-100)                              0250
              C     CALL PL23(1HZ,X(1),Z(1),-100)                              0260
              C     CALL PL4                                                   0270
              C                                                                0280
              C  THE LAST OF THE FIRST SET OF CALLS TO PL23 CAN BE COMBINED WITH THE 0290
              C  FIRST CALL OF THE SECOND SET.                                 0300
0002          CONTINUE
              C  EXAMPLE....                                                   0310
              C     DIMENSION X(100),Y(100),Z(100)                             0320
              C     CALL PL23(1H ,X(1),Y(1),100)                               0330
              C     CALL PL23(1HZ,X(1),Z(1),-100)                              0340
              C     CALL PL23(1HY,X(1),Y(1),-100)                              0350
              C     CALL PL4                                                   0360
              C                                                                0370
              C  TO SET THE PLOT LIMITS TO ARBITRARY VALUES,                   0380
              C  CALL PL2(XMAX,XMIN,YMAX,YMIN), CALL PL23 FOR EACH ARRAY, AND  0390
              C  CALL PL4.                                                     0400
              C  EXAMPLE....                                                   0410
              C     DIMENSION X(100),Y(100)                                    0420
              C     CALL PL2(20.,10.,50.,0.)                                   0430
              C     CALL PL23(1HY,X(1),Y(1),-100)                              0440
              C     CALL PL4                                                   0450
              C                                                                0460
              C  PL AND PL4 BOTH SKIP TO A NEW PAGE BEFORE PLOTTING.  THE USER CAN 0470
              C  CALL PLOT4 HIMSELF AFTER CALLING PL23, IF A LABEL IS DESIRED  0480
              C  AT THE TOP AND/OR LEFT SIDES OF THE PLOT.                     0490
              C  EXAMPLE....                                                   0500
              C     DIMENSION X(100),Y(100)                                    0510
              C     CALL PL23(1H ,X(1),Y(1),100)                               0520
              C     CALL PL23(1HY,X(1),Y(1),-100)                              0530
              C     PRINT 10                                                   0540
              C 10 FORMAT(1H1,20X48HIMPEDANCE VS. FREQUENCY FOR A SERIES RLC CIRCUIT 0550
              C    X   //10X13HR = 1000 OHMS,5X11HL = 100 MH.,5X16HC = 200 MICRO F. ) 0560
              C     CALL PLOT4(40,40H                          IMPEDANCE IN OHMS   ) 0570
```

```
                C     PRINT 20                                                          0580
                C  20 FORMAT(//40X22HFREQUENCY IN KILOHERTZ    )                        0590
                C                                                                       0600
0003                  DIMENSION X(1),Y(1),KH(1)
0004                  COMMON /BLOK1/JWHICH
                C                                 XX AND YY MUST BOTH BE DIMENSIONED AS 0630
                C                                     LARGE AS MAX(ROWS,COLUMS).        0640
0005                  DIMENSION XX(100),YY(100)                                         0650
                C                                 GRAPH IS NEEDED WITH UMPLOT, BUT NOT WITH 0660
                C                                     JPLOT.                            0670
                C     DIMENSION GRAPH(867)                                              0680
                C                                                                       0690
0006                  EQUIVALENCE (XMAX,KX),(YMIN,KY)                                   0700
                C                                                                       0710
0007                  DATA ROWS/50./,COLUMS/100./                                       0720
0008                  DATA KLEAN/0/
0009                  DATA KBL/1H /,KDL/1H$/,KAS/1H*/                                   0740
                C                                                                       0750
                C                                 JUMP=0 IF PL WAS CALLED, =1 IF PL23 WAS 0760
                C                                     CALLED, =-1 IF PL2 WAS CALLED.    0770
0010                  JUMP=0                                                            0780
0011                  GO TO 10                                                          0790
                C                                                                       0800
                C  ENTRY PL23....  FRAME THE POINTS.                                    0810
                C                                                                       0820
                C     ENTRY PL23                                                        0830
0012                  ENTRY PL23 (KHAR,X,Y,NPTS)                                        0840
0013                  JUMP=1                                                            0850
0014                  IF(JWHICH)20,10,20                                                0860
0015               10 XMAX=X(1)                                                         0870
0016                  XMIN=X(1)                                                         0880
0017                  YMAX=Y(1)                                                         0890
0018                  YMIN=Y(1)                                                         0900
0019                  JWHICH=1                                                          0910
0020               20 NSIGN=NPTS                                                        0920
0021                  NP=IABS(NSIGN)                                                    0930
0022                  IF(JWHICH)150,30,30                                               0940
0023               30 DO 40 N=1,NP                                                      0950
0024                  IF(X(N)-XMAX)31,31,32                                             0960
0025               32 XMAX=X(N)                                                         0970
0026                  GO TO 33                                                          0980
0027               31 IF(X(N)-XMIN)34,33,33                                             0990
0028               34 XMIN=X(N)                                                         1000
0029               33 IF(Y(N)-YMAX)35,35,36                                             1010
0030               36 YMAX=Y(N)                                                         1020
0031                  GO TO 40                                                          1030
0032               35 IF(Y(N)-YMIN)37,40,40                                             1040
0033               37 YMIN=Y(N)                                                         1050
0034               40 CONTINUE                                                          1060
0035                  IF(JUMP)60,60,50                                                  1070
0036               50 IF(KHAR-KBL)60,260,60                                             1080
                C                                                                       1090
                C  ENTRY PL2....  SET UP THE GRID.                                      1100
                C                                                                       1110
                C     ENTRY PL2                                                         1120
0037                  ENTRY PL2 (XMX,XMN,YMX,YMN)                                       1130
0038                  JUMP=-1                                                           1140
                C                                 MOVE THE ARGUMENTS.                   1150
```

```
0039              XMAX=XMX                                                    1160
0040              XMIN=XMN                                                    1170
0041              YMAX=YMX                                                    1180
0042              YMIN=YMN                                                    1190
                C                              DE-COMMENT FOR CDC FORTRAN ....  1200
                C     KX=KHAR                                                1210
                C     XMIN=X(1)                                              1220
                C     YMAX=Y(1)                                              1230
                C     KY=NPTS                                                1240
0043             60 CALL PLOT2(GRAPH,XMAX,XMIN,YMAX,YMIN)                    1250
0044                IF(KLEAN)70,140,70                                       1260
                C                              WIPE OUT THE INTERNAL GRID LINES. 1270
0045             70 XD=(XMAX-XMIN)/COLUMS                                    1280
0046                YD=(YMAX-YMIN)/ROWS                                      1290
0047                NCM=COLUMS-.5                                            1300
0048                NRM=ROWS-.5                                              1310
0049                NCMM=NCM-9                                               1320
0050                NRMM=NRM-9                                               1330
0051                DO 80 J=1,NCM                                            1340
0052             80 XX(J)=XMIN+FLOAT(J)*XD                                   1350
0053                DO 100 J=10,NRMM,10                                      1360
0054                YT=YMIN+FLOAT(J)*YD                                      1370
0055                DO 90 K=1,NCM                                            1380
0056             90 YY(K)=YT                                                 1390
0057            100 CALL PLOT3(KBL,XX,YY,NCM)                                1400
0058                DO 110 J=1,NRM                                           1410
0059            110 YY(J)=YMIN+FLOAT(J)*YD                                   1420
0060                DO 130 J=10,NCMM,10                                      1430
0061                XT=XMIN+FLOAT(J)*XD                                      1440
0062                DO 120 K=1,NRM                                           1450
0063            120 XX(K)=XT                                                 1460
0064            130 CALL PLOT3(KBL,XX,YY,NRM)                                1470
                C                                                            1480
0065            140 JWHICH=-1                                                1490
0066                IF(JUMP)260,150,150                                      1500
                C                              PUT THE NP POINTS INTO THE GRID. 1510
0067            150 CALL PLOT3 (KHAR,X,Y,NP)                                 1520
0068                IF(NSIGN)160,230,230                                     1530
                C                              LINEAR INTERPOLATION WAS REQUESTED. 1540
0069            160 NGMAX=.5+AMAX1(ROWS,COLUMS)                              1550
0070                XD=(XMAX-XMIN)/COLUMS                                    1560
0071                YD=(YMAX-YMIN)/ROWS                                      1570
0072                XBOT=XMIN-0.5*XD                                         1580
0073                YUP=YMAX+1.5*YD                                          1590
0074                NRB=(YUP-Y(1))/YD                                        1600
0075                NCB=(X(1)-XBOT)/XD                                       1610
0076                IF(NP.LT.2) GO TO 230                                    1620
                C                              LOOP OVER PAIRS OF ADJACENT POINTS. 1630
0077                DO 220 J=2,NP                                            1640
0078                NROW=(YUP-Y(J))/YD                                       1650
0079                NCOL=(X(J)-XBOT)/XD                                      1660
                C                              COMPUTE NG, THE NUMBER OF INTERPOLATING 1670
                C                                   CHARACTERS.              1680
                C                                                           1690
0080                NG=MAXO(IABS(NROW-NRB),IABS(NCOL-NCB))-1                 1700
0081                IF(NG)210,210,170                                        1710
0082            170 IF(NG-NGMAX)180,180,210                                  1720
                C                              PUT IN THE NG UNIFORMLY SPACED 1730
```

```
                C                                   INTERPOLATING CHARACTERS.                    1740
0083              180 ANGP=NG+1                                                                  1750
0084                  DX=X(J)-X(J-1)                                                             1760
0085                  DY=Y(J)-Y(J-1)                                                             1770
0086                  DO 190 K=1,NG                                                              1780
0087                  FRAC=FLOAT(K)/ANGP                                                         1790
0088                  XX(K)=X(J-1)+FRAC*DX                                                       1800
0089              190 YY(K)=Y(J-1)+FRAC*DY                                                       1810
                C                                INTERPOLATE WITH ASTERISKS UNLESS THE          1820
                C                                    PLOTTING CHARACTER IS AN ASTERISK.         1830
                C                                    IN THAT CASE, USE A DOLLAR SIGN.           1840
0090                  IF(KHAR.EQ.KAS) GO TO 200                                                  1850
0091                  CALL PLOT3(KAS,XX,YY,NG)                                                   1860
0092                  GO TO 210                                                                  1870
0093              200 CALL PLOT3(KDL,XX,YY,NG)                                                   1880
0094              210 NRB=NROW                                                                   1890
0095              220 NCB=NCOL                                                                   1900
0096              230 IF(JUMP)260,240,260                                                        1910
                C                                                                              1920
                C  ENTRY PL4....  CALL PLOT4 TO PRINT THE GRAPH.                               1930
                C                                                                              1940
0097                  ENTRY PL4                                                                1950
0098              240 PRINT 250                                                                1960
0099              250 FORMAT(1H1)                                                              1970
0100                  CALL PLOT4 (0,KH)                                                        1980
0101                  JWHICH=0                                                                 1990
                C                                                                              2000
0102              260 RETURN                                                                   2010
                C                                                                              2020
                C  ENTRY WIPE....  SET KLEAN FOR GRID LINES (=0) OR NO GRID LINES (=1).        2030
                C                                                                              2040
                C  SETTING KLEAN TO 1 SLOWS DOWN EXECUTION VERY GREATLY.  IF PL IS             2050
                C  BEING USED WITH JPLOT (AS OPPOSED TO UMPLOT, IUPLOT, ETC.),                 2060
                C  CALL NOGRID(1) TO ACCOMPLISH THE SAME THING AS CALLING WIPE(1).             2070
                C                                                                              2080
                C     ENTRY WIPE                                                               2090
0103                  ENTRY WIPE (KHAR)                                                        2100
0104                  KLEAN=KHAR                                                               2110
0105                  GO TO 260                                                                2120
0106                  END                                                                      2130
```

```
CC01            BLOCK DATA
0002            COMMON /BLOK1/JWHICH
0003            DATA JWHICH/0/
CC04            END
```

```
0001              SUBROUTINE PLOT2 (DUMMY,XMX,XMN,YMX,YMN)                                2140
0002              LOGICAL*1 LA,LB                                                         2150
0003              COMMON /BLOK1/JWHICH
0004              DIMENSION JRAPH(26,51),LABEL(52),ABSC(11)                               2160
0005              DIMENSION JA(5),JAA(5),JB(5),JBB(5),JC(5),LA(4),LB(4),INTEGR(9)         2170
0006              EQUIVALENCE (LA(1),IA,XA),(LB(1),MM)                                    2180
0007              DATA NOK/0/,MULT/1/,KHPWD/4/,MM/4H    /,KBITCH/8/                       2190
0008              DATA JAA/4H+---,4H----,4H--+-,4H----,4H----/                            2200
0009              DATA  JA/4H+---,4H----,4H--+-,4H----,4H----/                            2210
0010              DATA  JB/4H|   ,4H    ,4H  | ,4H    ,4H    /
0011              DATA JBB/4H|   ,4H    ,4H  | ,4H    ,4H    /
0012              DATA INTEGR/1H1,1H2,1H3,1H4,1H5,1H6,1H7,1H8,1H9/                        2240
0013              DATA KPL/4H+   /,KI/4H|   /,KBL/4H    /,KMI/4H-   /
0014              XMAX=XMX                                                                2260
0015              XMIN=XMN                                                                2270
0016              YMAX=YMX                                                                2280
0017              YMIN=YMN                                                                2290
0018              IF(XMAX.NE.XMIN  .AND.  YMAX.NE.YMIN)  GO TO 20                         2300
0019              NOK=0                                                                   2310
0020              PRINT 10,XMAX,XMIN,YMAX,YMIN                                            2320
0021           10 FORMAT(/45H BAD PLOT2 ARGUMENTS.  XMAX,XMIN,YMAX,YMIN = 4E21.8)         2330
0022              GO TO 200                                                               2340
0023           20 NOK=1                                                                   2350
0024              XD=0.01*(XMAX-XMIN)                                                     2360
0025              XBOT=XMIN-0.5*XD                                                        2370
0026              YD=0.02*(YMAX-YMIN)                                                     2380
0027              YUP=YMAX+1.5*YD                                                         2390
0028              DO 21 K=1,5                                                             2400
0029           21 JC(K)=JAA(K)                                                            2410
0030              DO 22 J=1,51,10                                                         2420
0031              KP=-5                                                                   2430
0032              DO 23 K=1,5                                                             2440
0033              KP=KP+5                                                                 2450
0034              DO 23 L=1,5                                                             2460
0035           23 JRAPH(KP+L,J)=JC(L)                                                     2470
0036              JRAPH(26,J)=KPL                                                         2480
0037              IF(JA(1).EQ.KBL)  JRAPH(1,J)=KPL                                        2490
0038              IF(J.EQ.1  .OR.  J.EQ.51)  JRAPH(1,J)=JAA(1)                            2500
0039              IF(J-41)28,25,200                                                       2510
0040           28 IF(J.NE.1)  GO TO 26                                                    2520
0041              DO 24 K=1,5                                                             2530
0042           24 JC(K)=JA(K)                                                             2540
0043              GO TO 26                                                                2550
0044           25 DO 27 K=1,5                                                             2560
0045           27 JC(K)=JAA(K)                                                            2570
0046           26 DO 22 L=1,9                                                             2580
0047              JPL=J+L                                                                 2590
0048              KP=-5                                                                   2600
0049              DO 29 K=1,5                                                             2610
0050              KP=KP+5                                                                 2620
0051              DO 29 M=1,5                                                             2630
0052           29 JRAPH(KP+M,JPL)=JB(M)                                                   2640
0053              JRAPH(1,JPL)=KI                                                         2650
0054           22 JRAPH(26,JPL)=KI                                                        2660
0055              GO TO 200                                                               2670
0056              ENTRY PLOT3 (MSY,X,Y,NPTS)                                              2680
0057              DIMENSION X(1),Y(1)
0058              IF(NOK.NE.1) GO TO 200                                                  2700
```

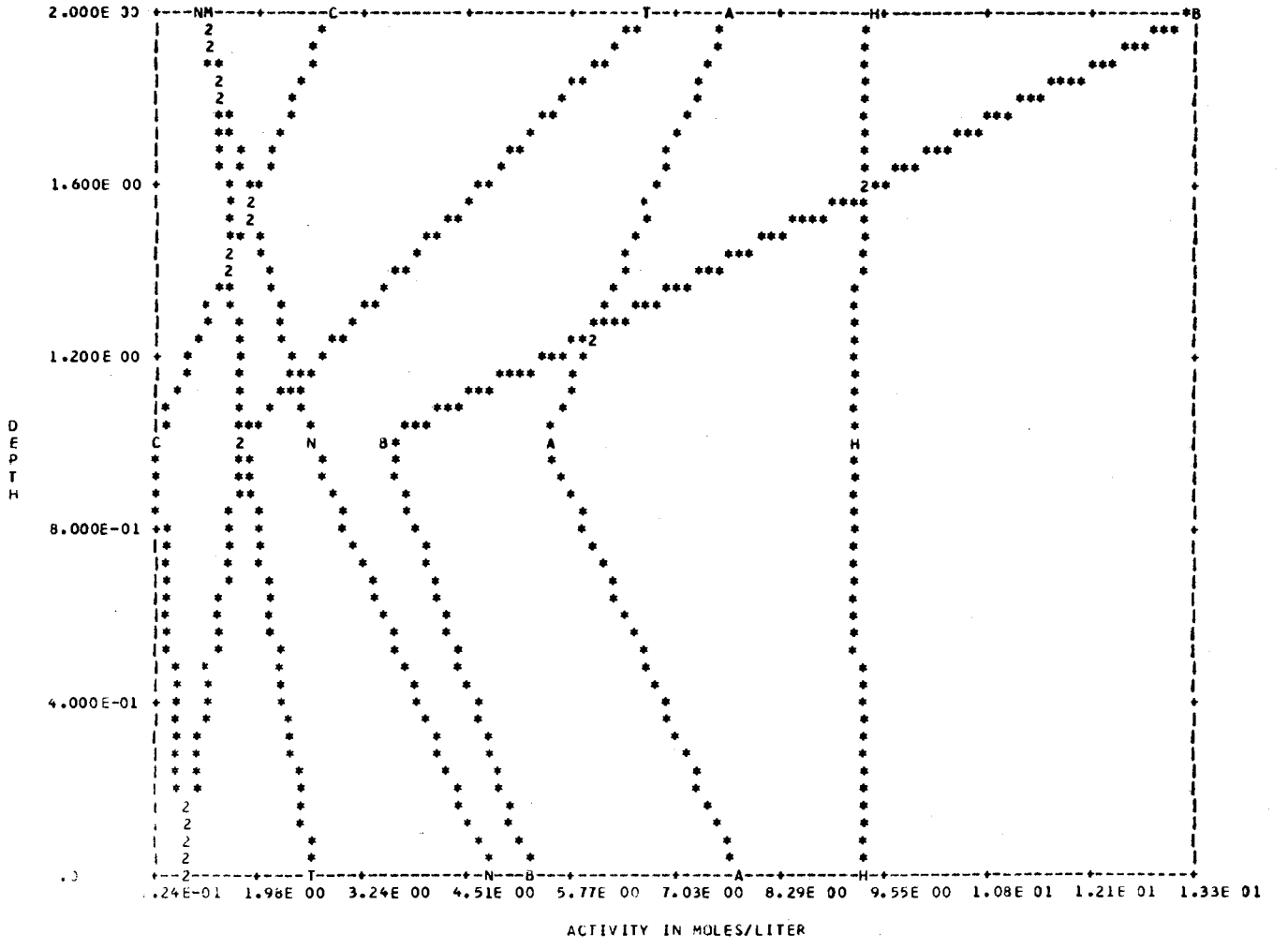
```
0059            MSYM=MSY                                                        2710
0060            NP=NPTS                                                         2720
0061            DO 100 N=1,NP                                                   2730
0062            NROW=(YUP-Y(N))/YD                                              2740
0063            NCOL=(X(N)-XBOT)/XD                                             2750
0064            IF(IABS(NROW-26).GT.25 .OR. IABS(NCOL-50).GT.50) GO TO 100      2760
0065            NTRUNC=NCOL/KHPWD                                               2770
0066            NWD=NTRUNC+1                                                    2780
0067            IA=JRAPH(NWD,NROW)                                              2790
0068            NBYTE=NCOL-KHPWD*NTRUNC+1                                       2800
0069            LB(1)=LA(NBYTE)                                                 2810
0070            IF(MULT.EQ.0  .OR.  MSYM.EQ.KBL)  GO TO 80                      2820
0071            IF(MM.EQ.KBL.OR.MM.EQ.KI.OR.MM.EQ.KMI.OR.MM.EQ.KPL)  GO TO 80   2830
0072            IF(MM-INTEGR(2))52,51,50                                        2840
0073         51 MM=INTEGR(3)                                                    2850
0074            GO TO 90                                                        2860
0075         52 IF(MM-INTEGR(9))50,100,53                                       2870
0076         50 MM=INTEGR(2)                                                    2880
0077            GO TO 90                                                        2890
0078         53 IF(MM-INTEGR(5))56,55,54                                        2900
0079         55 MM=INTEGR(6)                                                    2910
0080            GO TO 90                                                        2920
0081         54 IF(MM-INTEGR(3))58,58,57                                        2930
0082         57 MM=INTEGR(3)                                                    2940
0083            GO TO 90                                                        2950
0084         58 MM=INTEGR(4)                                                    2960
0085            GO TO 90                                                        2970
0086         56 IF(MM-INTEGR(7))61,60,59                                        2980
0087         59 MM=INTEGR(7)                                                    2990
0088            GO TO 90                                                        3000
0089         60 MM=INTEGR(8)                                                    3010
0090            GO TO 90                                                        3020
0091         61 MM=INTEGR(9)                                                    3030
0092            GO TO 90                                                        3040
0093         80 MM=MSYM                                                         3050
0094         90 LA(NBYTE)=LB(1)                                                 3060
0095            JRAPH(NWD,NROW)=IA                                              3070
0096        100 CONTINUE                                                        3080
0097            GO TO 200                                                       3090
0098            ENTRY PLOT4 (NCH,KH)                                            3100
0099            DIMENSION KH(1)
0100            IF(NOK.NE.1) GO TO 200                                          3120
0101            JTOP=(NCH+3)/4                                                  3130
0102            IF(JTOP.LE.0)  GO TO 111                                        3140
0103            DO 110 J=1,JTOP                                                 3150
0104            IA=KH(J)                                                        3160
0105            KADD=4*J-4                                                      3170
0106            DO 110 K=1,4                                                    3180
0107            LB(1)=LA(K)                                                     3190
0108        110 LABEL(KADD+K)=MM                                                3200
0109        111 NL=MAXO(1,MINO(52,NCH+1))                                       3210
0110            IF(NL.GT.51) GO TO 130                                          3220
0111            DO 120 N=NL,51                                                  3230
0112        120 LABEL(N)=KBL                                                    3240
0113        130 DO 150 I=1,6                                                    3250
0114            ORD=YMAX-(FLOAT(I-1)/5.)*(YMAX-YMIN)                            3260
0115            IF(I.EQ.6) ORD=YMIN                                             3270
0116            NR=10*I-9                                                       3280
```

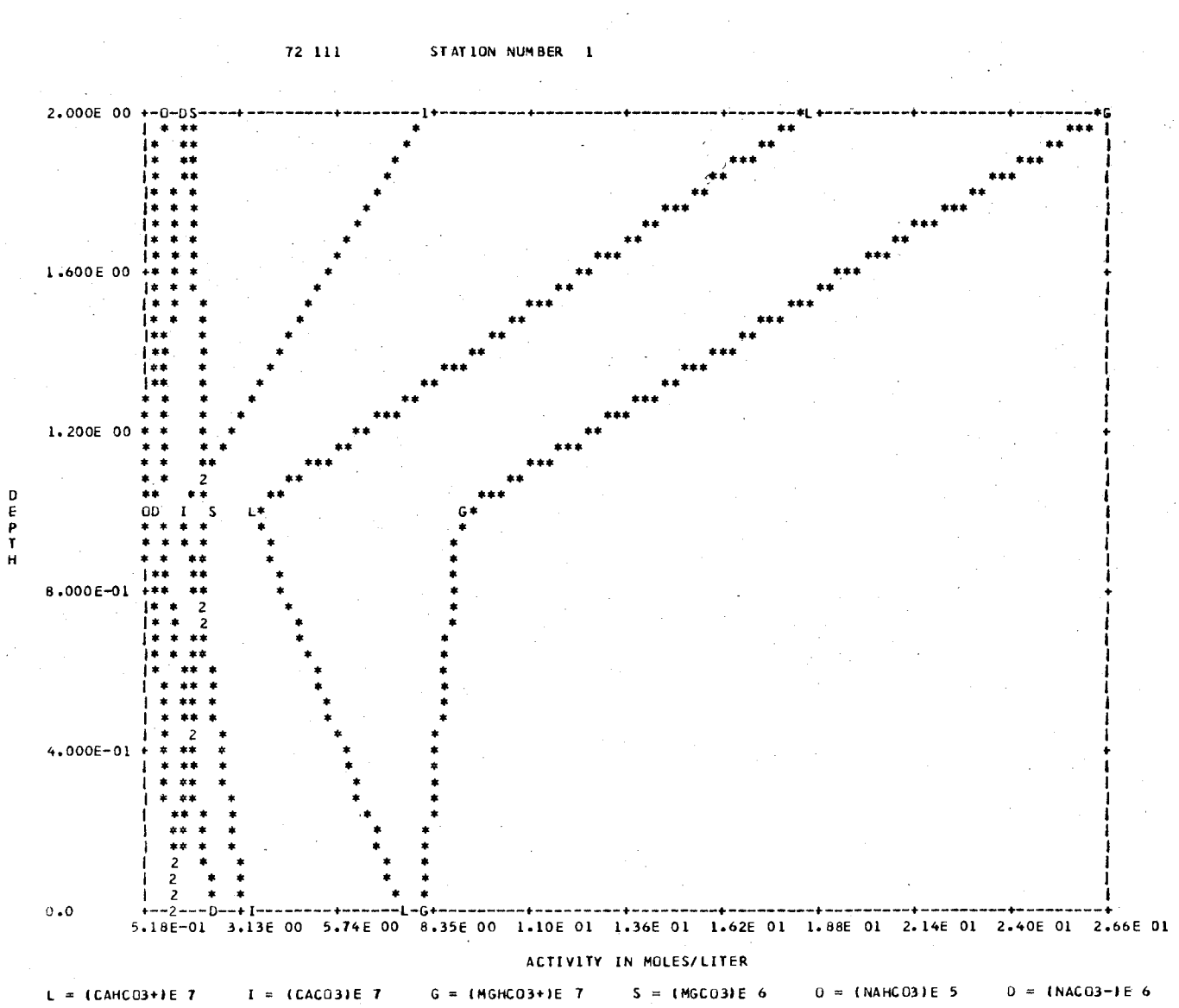
```
0117            PRINT 140,LABEL(NR),ORD,(JRAPH(J,NR),J=1,26)                    3290
0118        140 FORMAT(5XA1,2X,1PE10.3,1X26A4)
0119            IF(I.GE.6) GO TO 170                                            3310
0120            NRP=NR+1                                                        3320
0121            NCP=NR+9                                                        3330
0122            DO 150 NA=NRP,NCP                                               3340
0123        150 PRINT 160, LABEL(NA),(JRAPH(J,NA),J=1,26)                       3350
0124        160 FORMAT(5XA1,13X26A4)                                            3360
0125        170 DO 180 I=1,10                                                   3370
0126        180 ABSC(I)=XMIN+(FLOAT (I-1)/10.0)*(XMAX-XMIN)                     3380
0127            ABSC(11)=XMAX                                                   3390
0128            PRINT 190,ABSC                                                  3400
0129        190 FORMAT(16X1P11E10.2)
0130            JWHICH=0
0131            ENTRY PLOT1                                                     3420
0132        200 RETURN                                                          3430
0133            ENTRY MULTIP (NSW)                                              3440
0134            MULT=NSW                                                        3450
0135            GO TO 200                                                       3460
0136            ENTRY NOGRID (NSW)                                              3470
0137            IF(NSW)210,220,210                                              3480
0138        210 DO 211 J=1,5                                                    3490
0139            JA(J)=KBL                                                       3500
0140        211 JB(J)=KBL                                                       3510
0141            GO TO 200                                                       3520
0142        220 DO 221 J=1,5                                                    3530
0143            JA(J)=JAA(J)                                                    3540
0144        221 JB(J)=JBB(J)                                                    3550
0145            GO TO 200                                                       3560
0146            END                                                             3570
```

DATE	ID	H+	CO2	NA+	CA++	MG++	HCO3-	CO3--
72 111	1- 0	9.316E-09	1.106E-05	4.782E-02	7.810E-05	1.045E-04	5.277E-04	2.637E-06
72 111	1- 1	9.148E-09	7.242E-06	2.620E-02	5.454E-05	1.785E-04	3.520E-04	1.791E-06
72 111	1- 2	9.359E-09	2.805E-05	1.248E-02	7.656E-05	1.383E-04	1.333E-03	6.630E-06
72 111	2- 0	9.530E-09	2.176E-05	1.330E-02	6.792E-05	1.469E-04	1.015E-03	4.960E-06
72 111	2- 1	9.574E-09	1.641E-05	8.755E-03	6.148E-05	1.490E-04	7.622E-04	3.707E-06
72 111	2- 2	9.705E-09	1.366E-05	8.720E-03	6.026E-05	1.728E-04	6.259E-04	3.003E-06
72 111	2- 4	9.838E-09	1.736E-05	8.052E-03	6.929E-05	1.686E-04	7.848E-04	3.714E-06
72 111	2- 6	9.617E-09	1.890E-05	7.230E-03	6.026E-05	1.635E-04	8.737E-04	4.230E-06
72 111	2- 8	9.793E-09	1.596E-05	7.768E-03	5.907E-05	1.693E-04	7.244E-04	3.444E-06
72 111	2-10	1.006E-08	9.739E-06	6.519E-03	5.564E-05	1.681E-04	4.303E-04	1.991E-06
72 111	3- 0	9.574E-09	1.090E-05	7.465E-03	5.676E-05	1.763E-04	5.063E-04	2.462E-06
72 111	3- 1	9.705E-09	1.310E-05	7.145E-03	5.241E-05	1.760E-04	6.000E-04	2.879E-06
72 111	3- 2	9.838E-09	8.339E-06	7.259E-03	6.658E-05	1.665E-04	3.769E-04	1.784E-06
72 111	4- 0	9.444E-09	2.550E-06	5.153E-03	8.291E-05	1.234E-04	1.201E-04	5.919E-07
72 111	4- 1	9.274E-09	2.623E-06	5.112E-03	6.792E-05	1.384E-04	1.258E-04	6.313E-07
72 111	5- 0	9.148E-09	1.978E-06	6.838E-03	6.929E-05	1.248E-04	9.614E-05	4.893E-07
72 111	5- 1	9.530E-09	2.660E-06	5.995E-03	6.398E-05	1.341E-04	1.241E-04	6.064E-07
72 111	6- 0	9.530E-09	2.343E-06	5.715E-03	6.026E-05	1.299E-04	1.093E-04	5.341E-07
72 111	6- 1	9.530E-09	2.410E-06	4.464E-03	6.527E-05	1.369E-04	1.124E-04	5.493E-07
72 111	6- 2	9.359E-09	2.479E-06	4.025E-03	6.398E-05	1.341E-04	1.178E-04	5.860E-07

DATE	ID	CAHCO3+	CACO3	MGHCO3+	MGCO3	NAHCO3	NACO3-
72 111	1- 0	7.500E-07	3.264E-07	7.970E-07	1.302E-06	1.419E-05	2.348E-06
72 111	1- 1	3.493E-07	1.549E-07	9.082E-07	2.224E-06	5.185E-06	8.738E-07
72 111	1- 2	1.857E-06	8.045E-07	2.664E-06	1.723E-06	9.355E-06	1.541E-06
72 111	2- 0	1.255E-06	5.340E-07	2.156E-06	1.831E-06	7.596E-06	1.229E-06
72 111	2- 1	8.527E-07	3.612E-07	1.642E-06	1.857E-06	3.753E-06	6.043E-07
72 111	2- 2	6.864E-07	2.868E-07	1.563E-06	2.153E-06	3.069E-06	4.876E-07
72 111	2- 4	9.895E-07	4.079E-07	1.912E-06	2.100E-06	3.554E-06	5.569E-07
72 111	2- 6	9.581E-07	4.040E-07	2.065E-06	2.037E-06	3.553E-06	5.695E-07
72 111	2- 8	7.787E-07	3.224E-07	1.773E-06	2.109E-06	3.164E-06	4.982E-07
72 111	2-10	4.357E-07	1.755E-07	1.046E-06	2.095E-06	1.577E-06	2.416E-07
72 111	3- 0	5.230E-07	2.215E-07	1.290E-06	2.196E-06	2.125E-06	3.423E-07
72 111	3- 1	5.722E-07	2.391E-07	1.526E-06	2.192E-06	2.411E-06	3.830E-07
72 111	3- 2	4.566E-07	1.882E-07	9.069E-07	2.074E-06	1.539E-06	2.411E-07
72 111	4- 0	1.811E-07	7.778E-08	2.141E-07	1.537E-06	3.479E-07	5.679E-08
72 111	4- 1	1.554E-07	6.796E-08	2.515E-07	1.724E-06	3.615E-07	6.010E-08
72 111	5- 0	1.212E-07	5.374E-08	1.734E-07	1.555E-06	3.697E-07	6.230E-08
72 111	5- 1	1.445E-07	6.148E-08	2.405E-07	1.671E-06	4.184E-07	6.769E-08
72 111	6- 0	1.199E-07	5.101E-08	2.053E-07	1.619E-06	3.513E-07	5.684E-08
72 111	6- 1	1.335E-07	5.682E-08	2.224E-07	1.705E-06	2.823E-07	4.566E-08
72 111	6- 2	1.371E-07	5.941E-08	2.283E-07	1.671E-06	2.666E-07	4.391E-08

72 111 STATION NUMBER 1

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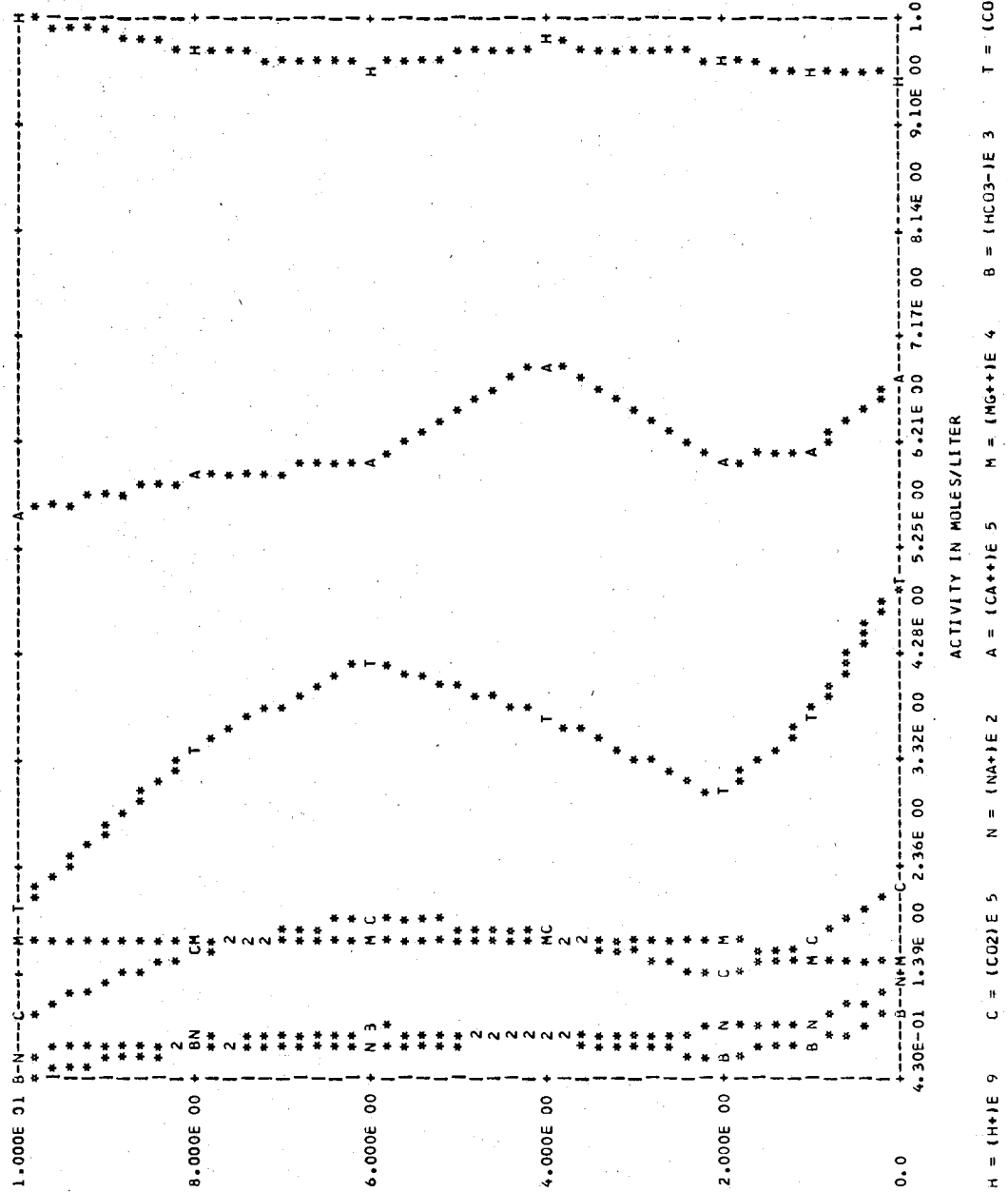
ACTIVITY IN MOLES/LITER
L = (CAHCO3+)E 7 I = (CACO3)E 7 G = (MGHCO3+)E 7 S = (MGCO3)E 6 O = (NAHCO3)E 5 D = (NACO3-)E 6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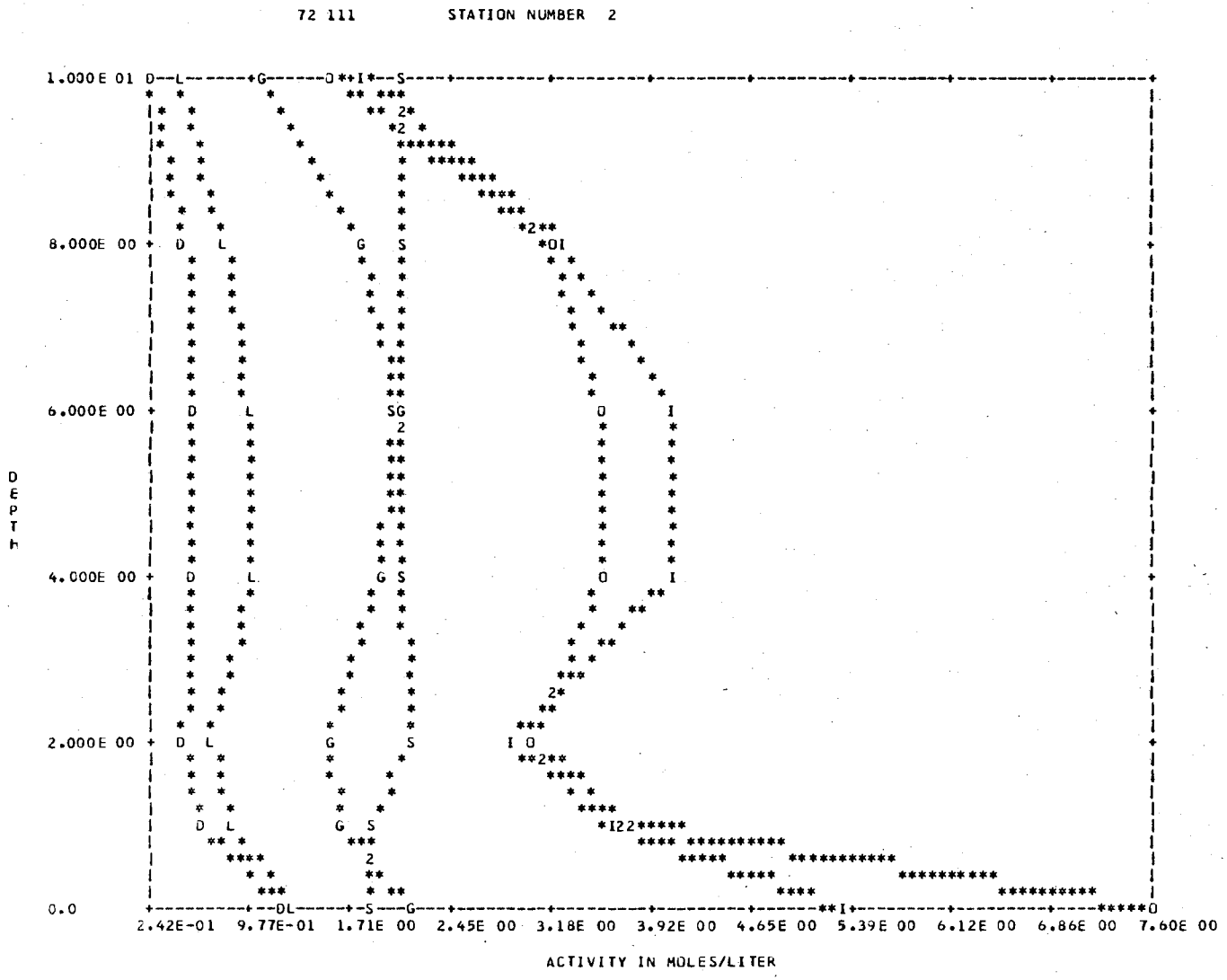
ACTIVITY IN MOLES/LITER
H = (H+)E 9 C = (CO2)E 5 N = (NA+)E 2 A = (CA++)E 5 M = (MG++)E 4 B = (HCO3-)E 3 T = (CO3--)E 6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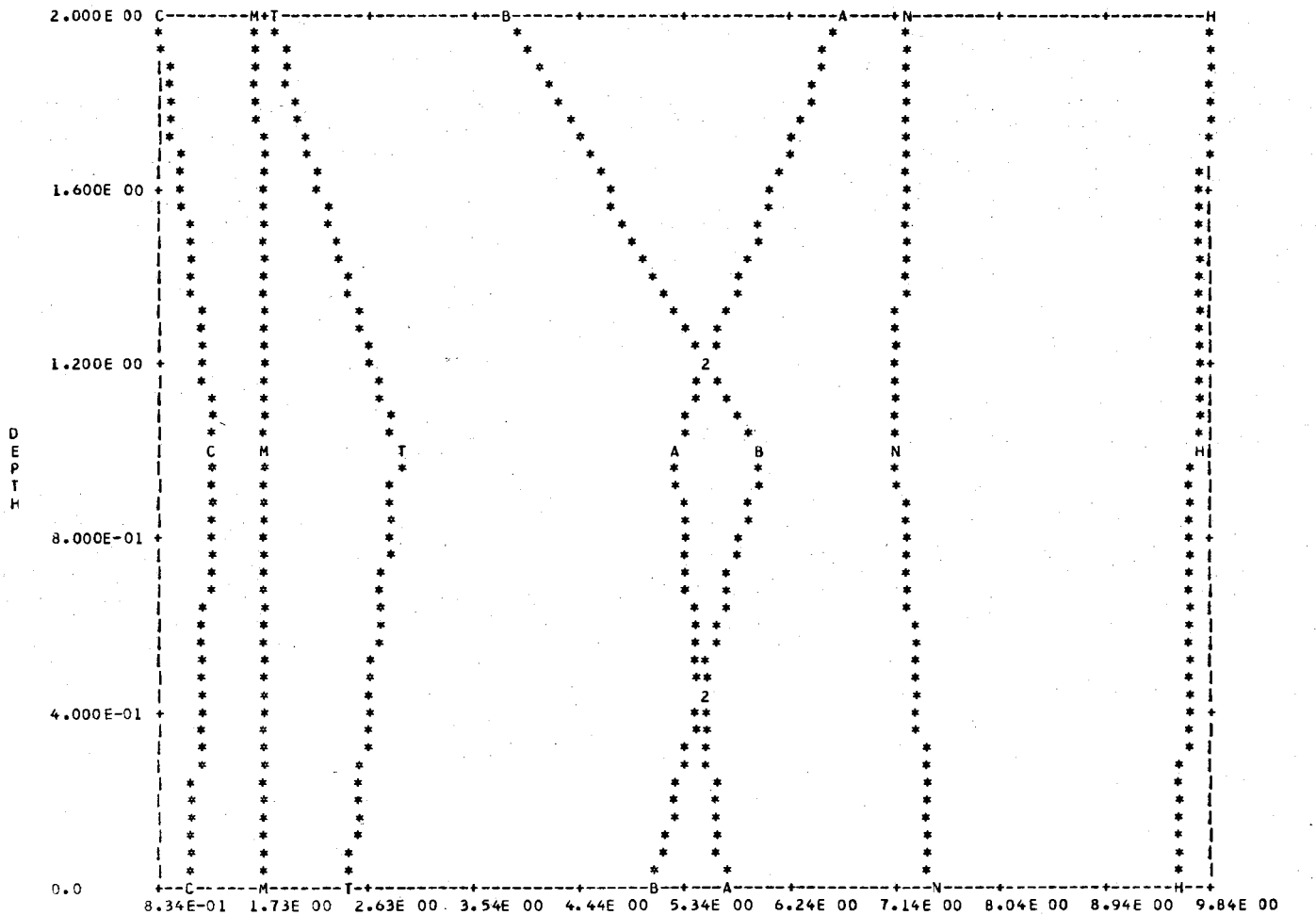
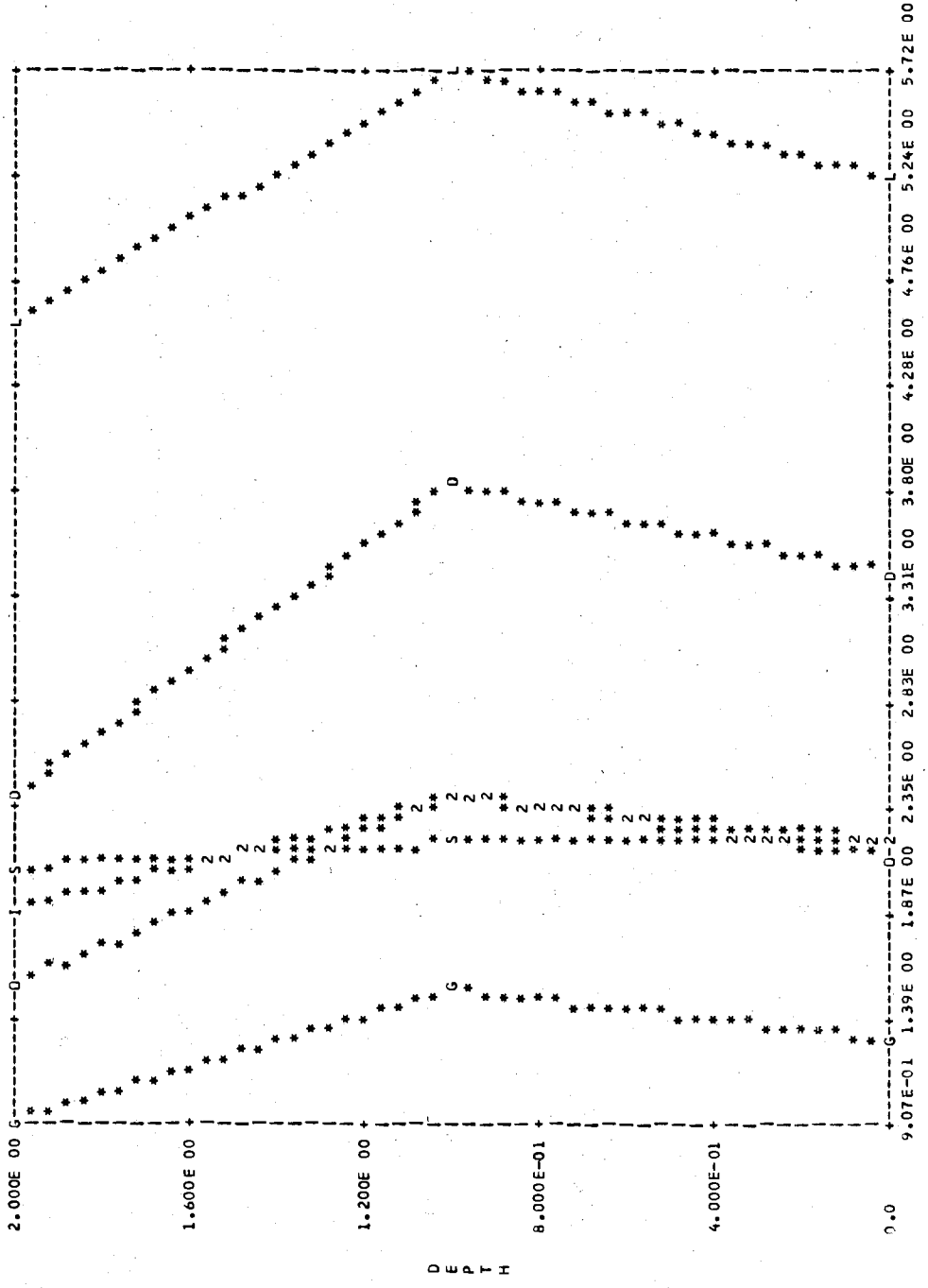
2.45E 00
3.18E 00
3.92E 00
4.65E 00
5.39E 00
6.12E 00
6.86E 00
7.60E 00
ACTIVITY IN MOLES/LITER
L = (CAHCO3+)E 6
I = (CACO3)E 7
G = (MGHCO3+)E 6
S = (MGCO3)E 6
O = (NAHCO3)E 6
D = (NACO3-)E 6

72 111 STATION NUMBER 3



H = (H+)E 9 C = (CO2)E 5 N = (NA+)E 3 A = (CA++)E 5 M = (MG++)E 4 B = (HCO3-)E 4 T = (CO3--)E 6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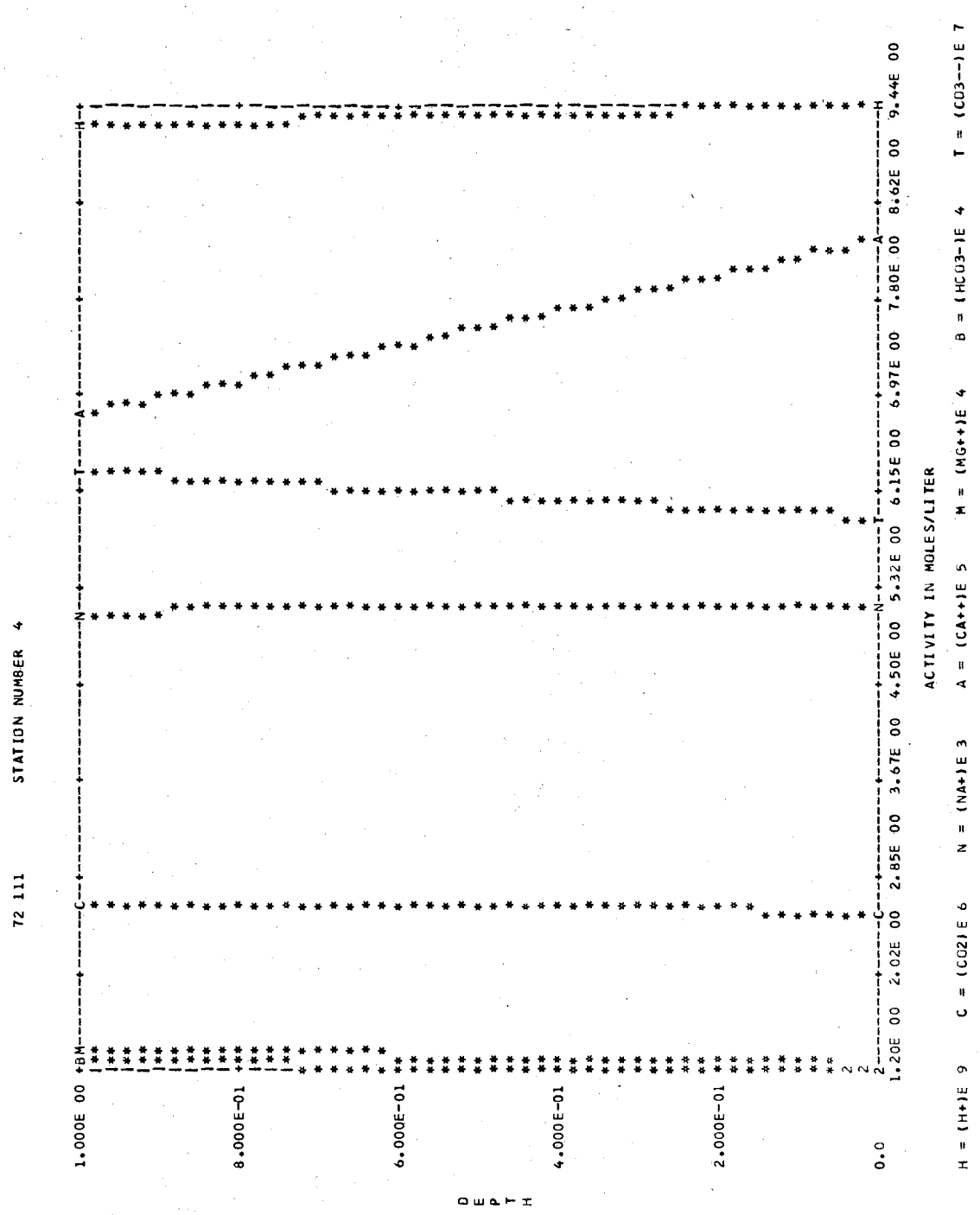
ACTIVITY IN MOLES/LITER
L = (CAHCO3+)E 7 I = (CACO3)E 7 G = (MGHCO3+)E 6 S = (MGCO3)E 6 D = (NAHCO3)E 6 D = (NACO3-)E 7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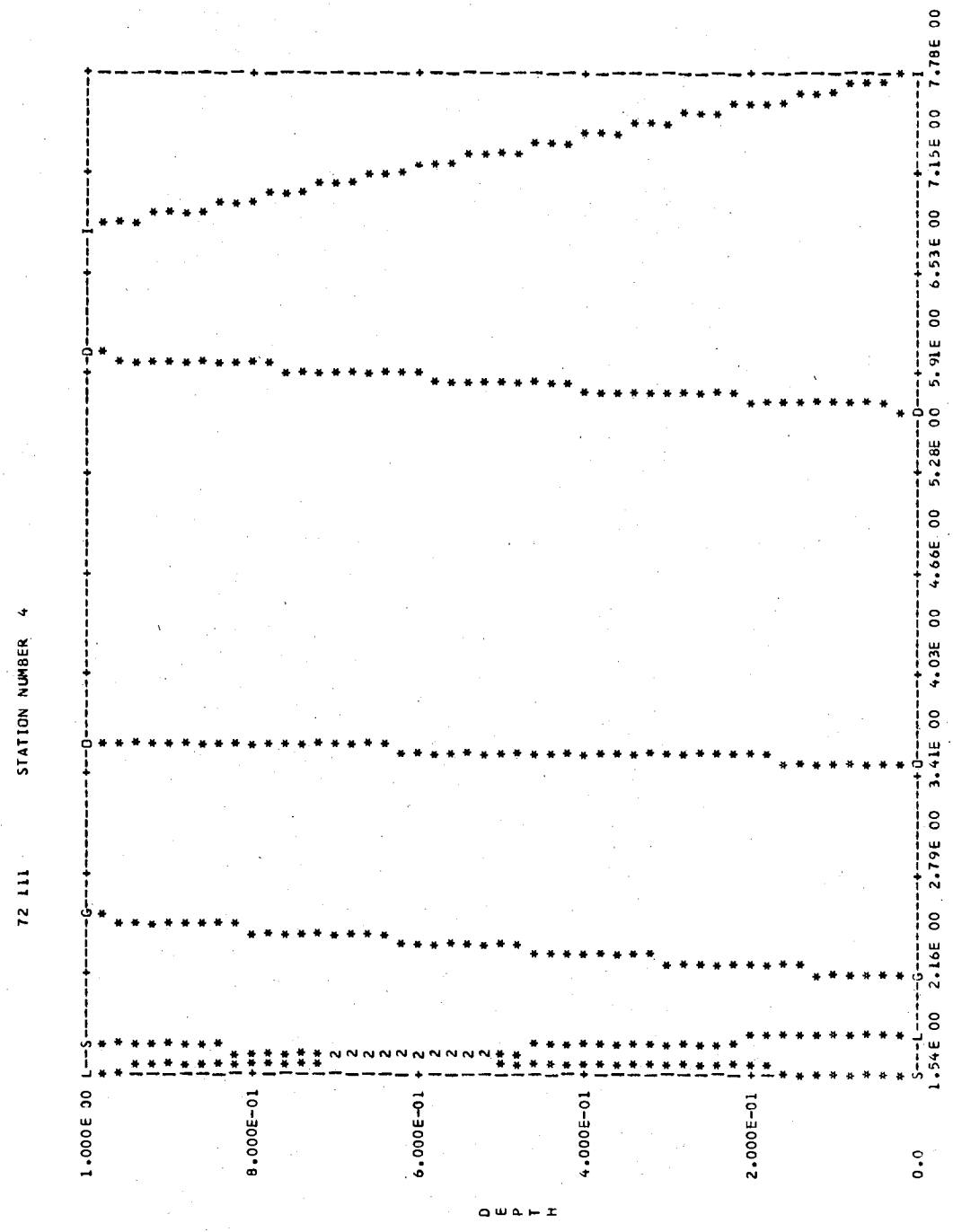
ACTIVITY IN MOLES/LITER
H = (H+)E 9 C = (CO2)E 6 N = (NA+)E 3 A = (CA++)E 5 M = (MG++)E 4 B = (HCO3-)E 4 T = (CO3--)E 7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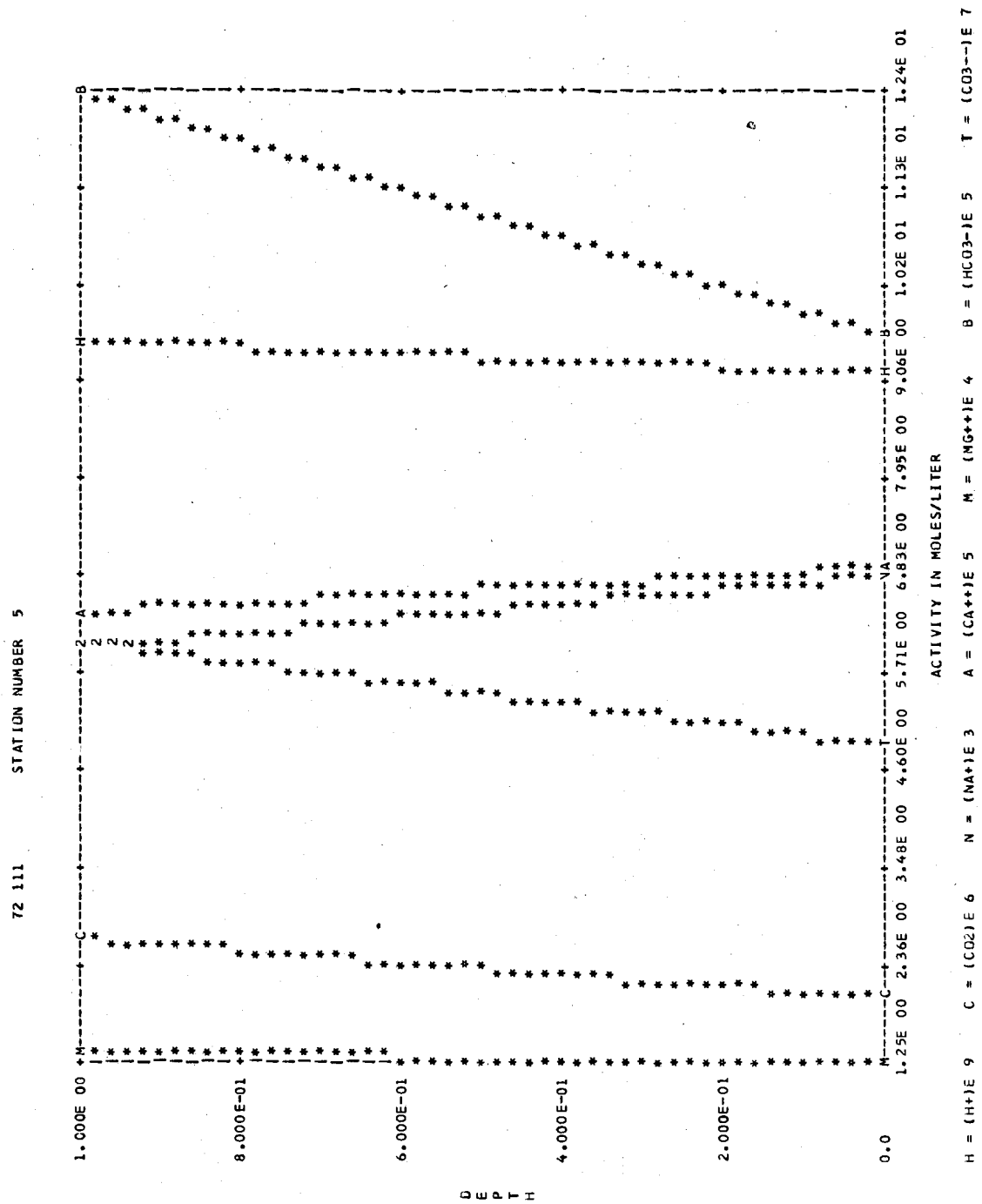
ACTIVITY IN MOLES/LITER
L = (CAHCO3+)E 7 I = (CACO3)E 8 G = (MGHCO3+)E 7 S = (MGCO3)E 6 O = (NAHCO3)E 7 D = (NACO3-)E 8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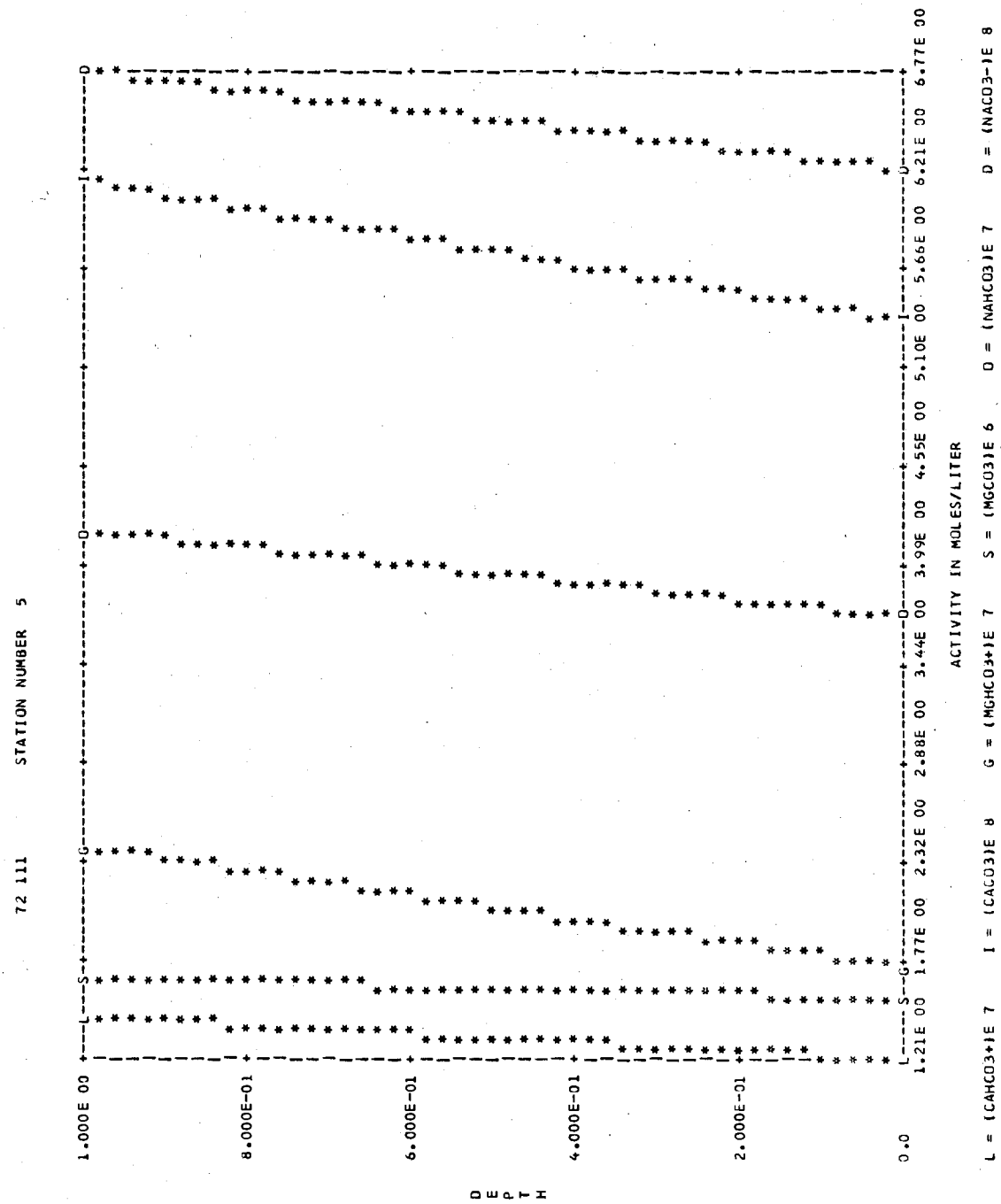
ACTIVITY IN MOLES/LITER
H = (H+)E 9 C = (CO2)E 6 N = (NA+)E 3 A = (CA++)E 5 M = (MG++)E 4 B = (HCO3-)E 5 T = (CO3--)E 7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DEPTH
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ACTIVITY IN MOLES/LITER
L = (CAHCO3+)E 7 I = (CACO3)E 8 G = (MGHCO3+)E 7 S = (MGCO3)E 6 D = (NAHCO3)E 7 D = (NACO3-)E 8

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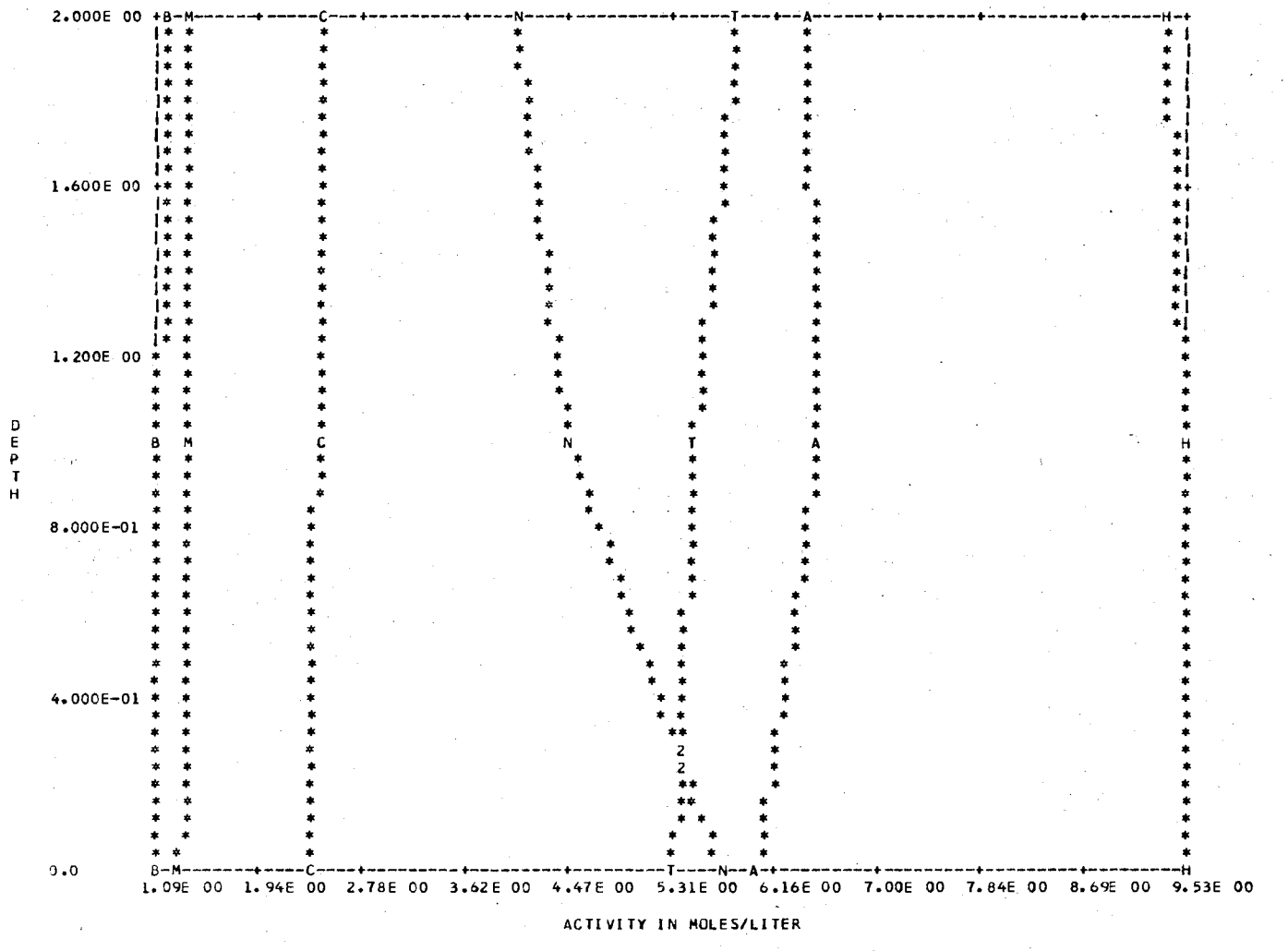

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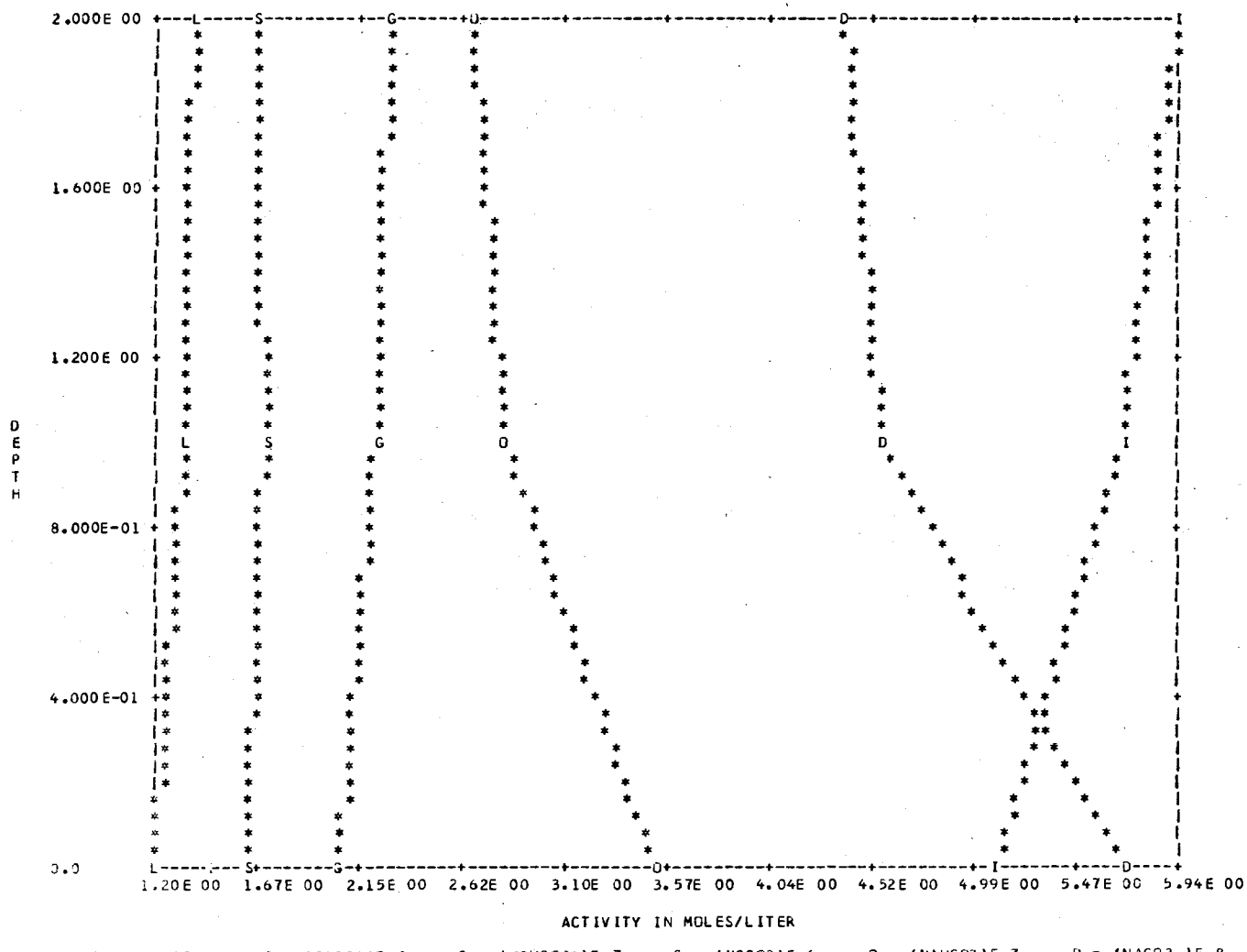

APPENDIX C

DETERMINATION OF CHEMICAL ACTIVITY BY THE KNOWN-INCREMENT METHOD

The principle of known-increment, also called standard addition, can be applied to any analytical technique in which measured response is a nonlinear function of the variable of interest. The Nernst equation for electrode potential is logarithmic in terms of activity and therefore fits the above requirement. The known-increment principle has been described and is in common usage for determining ion concentrations by ion-selective electrode measurements (25, 89, 90, 91, 92). The technique consists of two or more measurements taken before and after a known concentration of the ion being measured is added. A variation known as known-decrement, or standard subtraction, which involves complexation or precipitation of the ion being measured, is also used (90, 93). Instruments with direct reading scales for both known-increment and known-decrement are available (90, 91).

It would be possible to employ the same principle to determine ion activities if the activities could be changed by a known amount. No method for incrementing activities has been described; for that reason, the following derivation is presented as a theoretical treatment only. The equations derived here apply to cation sensitive electrodes and the known-increment principle. Other electrode systems and the known-decrement method can be derived by a similar treatment.

The usual response of a cation electrode in a solution containing activity, $\underline{a}$, of an ion to which the electrode responds is given by Equation 69.

$$E = E_o + \frac{RT}{nF} \ln a \tag{69}$$

If a known increment, Δa of the ion is added such that a different activity, $a' = a + \Delta a$, is obtained; a potential response, E', will result.

$$E' = E_o + \frac{RT}{nF} \ln a' \tag{70}$$

By subtracting Equation 69 from Equation 70, Equation 71 is obtained.

$$\Delta E = E' - E = \frac{RT}{nF} \ln \frac{a'}{a} \tag{71}$$

Equation 71 can be rearranged to give the resulting activity expression, Equation 72.

$$a = \frac{\Delta a}{\exp(\frac{nF\Delta E}{RT})-1} \tag{72}$$

In Equation 72, activity of the original solution is expressed in terms of the known increment, the difference in potential due to the increment, and known constants. The E_o terms which are implicitly assumed unchanged by addition of the increment, have been eliminated. Any changes in E_o due to drift or temperature variations are unimportant as long as the E_o terms in Equations 69 and 70 are equal. A theoretical Nernstian slope is implied in this development, but if a

better value for the electrode slope is known from calibration, that term can be substituted into Equation 72.

Furthermore, the slope term can be eliminated by adding a second known-increment, Δa_2.

$$E'' = E_o + \frac{RT}{nF} \ln a'' \tag{73}$$

Where $a'' = a' + \Delta a_2$ and $E'' = E' + \Delta E_2$. Equation 73 when combined with Equation 70 where the first increment and first ΔE are labeled with subscript (1)'s gives Equation 74.

$$\frac{\Delta E_2}{\Delta E_1} = \frac{\ln \left(1 + \frac{\Delta a_2}{a + \Delta a_1}\right)}{\ln \left(1 + \frac{\Delta a_1}{a}\right)} \tag{74}$$

Equation 74 can be solved for the variable a by successive approximations, or if the second increment can be added so that $\Delta E_2 = \Delta E_1$, Equation 75 results.

$$a = \frac{(\Delta a_1)^2}{\Delta a_2 - \Delta a_1} \tag{75}$$

Equations 74 and 75 both express a as functions independent of any electrode parameters which were subject to considerable drift in Table V. Unfortunately, double known addition has the disadvantage that small errors in potential determinations cause large errors in

the value of a (92).

The known-increment method can also be used when an electrode such as the divalent cation electrode responds to more than one ion in solution. Equation 76 is assumed to describe the electrode selectivity response.

$$E = E_o + \frac{RT}{nF} \ln (a_1 + Ka_2) \tag{76}$$

After addition of a known increment of a_2, which may or may not change a_1, the change in response is given by Equation 77.

$$\Delta E = E' - E = \frac{RT}{nF} \ln \left(\frac{a_1' + K\Delta a_2 + Ka_2}{a + Ka_2}\right) \tag{77}$$

Equation 77 can be solved for a_2.

$$a_2 = \frac{\dfrac{a_1 \exp \left(\frac{nF\Delta E}{RT}\right) - a_1'}{K} - \Delta a_2}{1 - \exp \left(\frac{nF\Delta E}{RT}\right)} \tag{78}$$

The determination of a_2 in the presence of a_1 by the known-increment method requires that values be known for a_1, a_1' if different from a_1, and the selectivity coefficient, in addition to Δa_2 and ΔE.

VITA

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Doctor of Philosophy

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Professional Organizations: American Chemical Society, Phi Lambda Upsilon and Sigma Xi.