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KINETICS OF 12-MOLYBDOPHOSPHORIC ACID
AND 12-MOLYBDOSILIC ACID FORMATION
AND THE OPTIMIZATION OF THEIR RATE
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KINETICS OF 12-MOLYBDOPHOSPHORIC ACID AND 12-MOLYBDOSILIC ACID FORMATION AND THE OPTIMIZATION OF THEIR RATE METHODS OF ANALYSIS

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ABSTRACT

KINETICS OF 12-MOLYBDOPHOSPHORIC ACID AND 12-MOLYBDOSILIC ACID FORMATION AND THE OPTIMIZATION OF THEIR RATE METHODS OF ANALYSIS

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The construction and characterization of a computerized precision source ratioing system for stopped-flow data acquisition is described. The hardware interface developed to interact with a PDP 8/e computer is presented in detail. In addition, the software developed to operate this interface as well as analyze the data acquired by this system is described.

A study of the dependence of the rates of formation of 12-molybdophosphate and 12-molybdosilicate on both nitric acid and molybdate concentration at constant ionic strength is presented. The conditions are chosen so that only one modification of the heteropolymolybdate is formed. The experimental rate laws for the formation reactions of these two compounds are given.

The feasibility of using a rate method to simultaneously determine the concentrations of these species is investigated. The Simplex method is used to optimize the experimental conditions for the individual or simultaneous determination of these compounds based upon the experimental rate equations for the formation reactions of phosphate and silicate heteropolymolybdates. The results of the Simplex Optimization along with the experimental results obtained under the optimal experimental conditions are presented.

To My Family

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CHAPTER I

INTRODUCTION

Optimization is a keyword in the scientific community. Those who have not attained this condition seek it and those who formerly thought they had an optimized system seek further improvements. An optimized system is one in which all of the components are used in the most effective manner. The central theme of this dissertation revolves around the optimization of the phosphate and silicate determinations.

Scientists have been interested in studying these compounds for many reasons. Silica is present in natural waters in both soluble and colloidal forms. Silica cycles, where silica is used for skeletal structure by living organisms and returned to the water system by re-solution of the dead organisms, have been studied in several lakes. Phosphate pollution through detergent products has been linked with early eutrophication of many lakes and streams. Phosphates also cause troublesome algae growth in water reservoirs. The biological importance of phosphate determination stems not only from the fact that it constitutes one of the main buffer systems in the human body, but also as an indication of other ailments. Hyperphosphatemia (where there is an increase in serum phosphorous levels) is found in hypoparathyroidism, hypervitaminosis D and renal failure, whereas hypophosphatemia (low levels of phosphorous in serum) is found in hyperparathyroidism, rickets and the Fanconi syndrome.

The standard method for phosphate and silicate determinations involves the formation of the heteropoly acid containing P or Si and conversion into the heteropoly blues. The intensity of the color developed after ten minutes is measured between 700 and 800 nm. Other compounds such as germanium and arsenic, which also form heteropoly blues will interfere with the determination. Separation techniques as well as complexometric techniques have been employed to eliminate these interferences. Since these compounds form at different rates, it is possible to determine the concentration of these compounds using a rate method without prior separation.

Chapter II gives an overview of reaction-rate methods of analysis. This chapter also presents the fundamentals of the initial rate method of analysis which will be used throughout this work. The second chapter also discusses the chemistry of molybdenum and of the heteropolymolybdates of phosphorous and silicon as it pertains to this work.

The remainder of the thesis can be divided into two categories: instrumental improvements and chemical system optimization. The third chapter presents a computerized precision source rationing system suitable for the rapid data acquisition necessary in fast reaction-rate analysis. It is unique in that it uses real time division by a minicomputer to ratio the sample and reference beams. The interfacing and characterization of this system are also presented in this chapter. Chapter IV presents the software developed to operate this system.

One way to optimize a system is to monitor the system while perturbing some of the experimental conditions. In the past this is how the determination of phosphate by the 12-molybdophosphoric acid method was optimized. The choice of experimental conditions was haphazard since there was no sound theoretical basis to indicate what the best conditions were. Chapter V presents an experimental rate law determined for the 12-molybdophosphate reaction and Chapter VI presents the rate law for the 12-molybdosilicate reaction.

In the final chapter the information from the rate equations for the formation of phosphate and silicate heteropolymolybdates is used to optimize experimental conditions for the individual or simultaneous determination of these species. The results have implications for both routine equilibrium methods and rate methods of analysis.

CHAPTER II

BACKGROUND

Reaction-rate methods of analysis have become increasingly useful in recent years. They are being applied in such diverse areas as clinical chemistry, environmental science and pharamcology. In this chapter the basic approaches to reaction-rate methods are first described. Then a brief summary of the chemistry of Mo(VI) as it pertains to the work in this thesis is presented to put the present work in perspective. Additional background materials for more minor subjects are presented in later chapters along with the actual work accomplished.

A. Reaction-Rate Methods of Analysis

The detection system employed in an analytical determination can be based either on an equilibrium or reaction-rate method. Equilibrium methods involve monitoring a signal proportional to the analyte after the system has attained equilibrium. In reaction-rate methods, however, the signal is monitored after initiation of the reaction, but before equilibrium is attained. Several recent reviews (1-27) have focused on the classification, theory and instrumentation involved in applying rate methods to analytical chemistry.

A first-order or pseudo-first-order irreversible reaction can be represented by the general stoichiometric equation

$$aA + bB \xrightarrow{k} mM + nN$$

where k is the first-order or pseudo-first-order rate constant. The rate of formation of M or the rate of disappearance of A can be represented as

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A] = \frac{1}{m}\frac{d[M]}{dt} \qquad (1)$$

Integration of this equation from time t equal to 0, at the initiation of the reaction, to time t, (time of measurement) gives the relationship between the value of A at any time t and the initial concentration A_o. For reactant A at time t; where A_o is the initial concentration of A

$$A_t = A_o \exp(-akt) \qquad (2)$$

or for product M at time t where M_o is the initial concentration of M

$$M_t = M_o + \frac{m}{a} A_o (1-\exp(-akt)) \qquad (3)$$

Substitution of Equation (2) into (1) and (3) into (1) yields,respectively

$$-\left(\frac{d[A]}{dt}\right)_t = k\ [A_o]\ \exp(-akt) \qquad (4)$$

$$-\left(\frac{d[M]}{dt}\right)_t = mk\ [A_o]\ \exp(-akt) \qquad (5)$$

Equations (4) and (5) form the basis for the derivative approach to rate analysis (6). They also form the basis for simultaneous multicomponent analysis (1). These equations can be further simplified if the measurement of $\Delta A/\Delta t$ or $\Delta M/\Delta t$ is made during the initial portion of the reaction where concentration changes are insignificant. Under these conditions the exponential terms in Equations (4) and (5) are approximately unity. The experimental conditions for which this is true have been reported in the literature (6,8,28).

The obvious advantage to kinetics-based methods is that the time required for analysis, after initiation of the reaction, can be much less than that required for equilibrium based methods. Since the reaction is monitored before reaching equilibrium, the change in signal used to monitor the analyte will be of a lesser magnitude than if the system was monitored after equilibrium was established. Thus, the precision of rate methods of analysis will be inherently less than for equilibrium based methods.

There are numerous other advantages to rate methods of analysis. The measurement is usually made during the initial stages of a reaction, which minimizes effects of unfavorable side reactions. Kinetics can also lead to a more specific analysis if the compounds undergoing the reaction react at significantly different rates. This leads to simultaneous multicomponent analysis without prior separation. Finally, since the reaction rate analysis involves a relative measurement, constant interferences will not give rise to errors in the analysis as they would in an equilibrium-based method.

The inherently lower signal-to-noise ratio is not the only disadvantage of rate methods. Since the rate of the reaction is the measured quantity, all factors affecting the rate must be controlled. Factors such as pH, ionic strength, temperature and pressure must be controlled or at least monitored during the reaction to obtain reproducible rates. Equilibrium-based methods do not depend on the rate at which equilibrium is reached. The only measured quantity is the signal value after attaining equilibrium.

The derivative method, recently reclassified as a regression method (25), has been used in this work to find the rate of formation of 12-molybdophosphate and 12-molybdosilicate. These two compounds form at sufficiently different rates that they can be determined simultaneously. The last chapter deals with this problem.

B. Molybdenum Chemistry

The 12-molybdophosphate (12-MPA) and 12-molybdosilicate (12-MSA) anions are formed by the reaction of the heteroatom with a molybdenyl species in an acidic medium. The characterization of this reaction has been hampered by the lack of knowledge of the exact form of the reactive molybdenyl species present in the acidic medium. The complex chemistry of molybdenum has been the subject of reviews by several authors (29-34). However, several recent papers (35,36) have been published casting doubts on the validity of former work done in this field. A brief summary of this work as it pertains to the formation of 12-MPA and 12-MSA follows.

1. Molybdenum (VI)

In aqueous solutions at pH values greater than 7, molybdenum (VI) exists as the tetrahedral molybdate ion $[MoO_4]^{2-}$ (37). However, as the acid concentration of this solution is increased, several Mo(VI) species are produced. Mononuclear products $HMoO_4^-$ and H_2MoO_4 form initially; however, coordination with water produces $[MoO(OH)_5]^-$ and $Mo(OH)_6$ respectively (38-44). Recent ^{95}Mo and ^{97}Mo NMR data indicate the possibility that these two octahedral forms are not the correct species but rather the less symmetric cis-dioxo $MoO_2(H_2O)(OH)_3^-$ form

(45). Hydroxyl groups in the trans position should be labile, and an oxo bridge can form to produce the dimeric species (38)

$$[(HO)_4OMo\text{-}O\text{-}MoO(OH)_4]^{2-}$$

As the solution reaches a pH of approximately 6, further polymerization is detected. Lindqvist (38) proposed the formation of the heptamolybdate ion, $Mo_7O_{24}{}^{-6}$.

$$7MoO_4^{2-} + 8H^+ \rightarrow Mo_7O_{24}^{6-} + 4H_2O$$

Other workers have shown this to happen when the bound acid-to-molybdate ratio (z or n) reaches 1.14 (40,46-48). Further acidification to a z value equal to 1.5 leads to the formation of the octamer $Mo_8O_{26}^{4-}$ (38,40,48,49), which is assumed to be produced by the addition of a MoO_6 octahedral unit to the heptamer (40). Other researchers, however, have found no evidence for the octamer in solution (46,47,50,51).

Increasing the acidity of the solution causes the precipitation of molybdenum trioxide (MoO_3) at the isoelectric point, pH 0.9 (52). Further acidification dissolves the MoO_3 precipitate and forms both monomeric (53,54) and dimeric species (47,55-59). Krummenacker and co-workers (60-66) interpreted their experimental results by assuming that four molybdenyl species coexist in perchloric acid. The forms suggested were A, AH, A_2 and A_2H_9 where A represents a singly charged monomeric molybdenyl species. The formation constants of these species were determined as a function of acidity. The latest work available (54,65,67) indicates that the monomeric species are $[HMoO_3]^+$ and $[H_2MoO_3]^{2+}$, and the dimeric species are $[H_2Mo_2O_6]^{2+}$ and $[H_3Mo_2O_6]^{3+}$. The equilibrium constants for the protonation and dimerization of these molybdenyl species determined in the latest study (54) agree with those presented by Krummanacker (65).

2. 12-Molybdophosphate

The overall stoichiometry for the formation of 12-MPA in nitric acid solutions, first proposed by Souchay (55,56),

$$H_3PO_4 + 6HMo_2O_6^+ = 12\text{-MPA} + 9H^+$$

has been supported by further investigations (57). The protonated 12-MPA has been obtained in a solid form, and the crystal structure corresponds to a molecular formula of $H_3Mo_{12}PO_{40}$ with 29-31 water molecules. The Mo atoms form a dodecahedron surrounding the central phosphate tetrahedron. Each Mo atom is surrounded by an octahedron of oxygen atoms (68,69). It should be noted that other compounds less condensed than 12-MPA can form, but these are not of interest in this work.

The anion, 12-MPA, can exist in two isomeric forms α and β, (70-72) similar to those proposed for 12-MSA (73-75). The β form of 12-MPA is assumed to be stable (70,71,73-75) and does not spontaneously transform into the α form. Work done in this laboratory (30) indicates that this is not true for solutions with acid concentrations less than 0.25 M.

The rate for the formation of 12-MPA has been reported (29,59) as

$$\frac{d[12\text{-MPA}]}{dt} = \frac{K_1[\text{Mo(VI)}_t][H_3PO_4]}{K_2\frac{[H^+]^8}{[\text{Mo(VI)}_t]^5} + K_3\frac{[H^+]^4}{[\text{Mo(VI)}_t]^4} + K_4[H^+]^2 + 1}$$

where Mo(VI)_t represents the total molybdenum concentration in solution.

A follow up investigation (30) into the complex acid dependence of the formation reaction of 12-MPA reached a different conclusion. The acid dependence of the rate equation was reported as

$$\text{Rate} = \frac{1}{K_1[H^+]^9 + K_2[H^+]}$$

Unfortunately, the Mo(VI) dependence of the rate was not investigated. In all previous studies, the reaction was found to be first-order in phosphate over the range of concentrations (5.0×10^{-5} to 1.5×10^{-4}M) considered here.

A reaction mechanism has been proposed for this system which involves the initial reaction of the phosphate with a protonated molybdenyl dimer. The final product is obtained through three more condensation steps (59).

3. 12-Molybdosilicate

The stoichiometry for the formation of $[Mo_{12}SiO_{40}]^{4-}$ (12-MSA) has been reported for the α form (76) as

$$Si(OH)_4 + 6Mo(VI)_2 = \alpha 12\text{-MSA} + 6H^+$$

The following mechanism has been proposed for the formation of β-12-MSA (77)

$$Si(OH)_4 + HMo_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SiO_4 - Mo_2^{-4} + 5H^+$$

$$SiO_4\text{-}Mo_2^{-4} + 5HMo_2^+ \xrightarrow{k_2} \beta\ 12\text{-MSA} + 5H^+$$

Strickland was the first to point out the existence of the α and β forms (72-74) and proposed the z value to describe the system. Other researchers have since reported only z values. Unfortunately, without reference to a specific acid or molybdate concentration, z values alone do not completely describe the acid-molybdate system. A system which unambiguously defines which modification will form in solution (35,36), should be dependent on both the solution pH and the molybdate concentration. The α-12-MSA anion is formed at a pH between 3.8 and 4.8. The β-12-MSA is formed at a pH between 1.0 and 1.8 and a mixture of α and β is formed at a pH between 1.8 and 3.8, for molybdenum concentrations between 0.015 and 0.1 M (35).

Several procedures were developed for the analysis of silicate assuming that the α and β form had the same molar absorptivity at a certain wavelength (70,71). When the conditions of formation are controlled in terms of pH and total Mo concentration rather than by the z value, one finds that in the spectral region from 300 to 400 nm the two absorption curves do not cross. The two curves possess the same general shape and wavelength maxima (36). However, the molar absorptivity of the β isomer is approximately twice that of the α isomer. The β-to-α isomer transformation has been studied for pH and molybdate concentration dependence (78,79).

The rate for the formation of the β isomer was determined to be (76,77)

$$\frac{d[\beta\text{-12-MSA}]}{dt} = \frac{k_1 k_2 [Si(OH)_4][HMo_2^+]^6}{k_{-1}[H^+]^5 + k_2[HMo_2^+]^5}$$

where the constants refer back to the mechanism for β-12-MSA. The rate of formation of α-12-MSA has not yet been determined.

CHAPTER III

A COMPUTERIZED PRECISION SOURCE RATIOING SYSTEM FOR STOPPED-FLOW DATA ACQUISITION

Kinetics information can be obtained through many different methods. This chapter presents an overview of the techniques developed to monitor fast reactions. The major emphasis, however, lies in the area of source ratioing in spectrophotometric monitoring. A history of the methods used to obtain source ratioing is presented. A source ratioing system built in our laboratory for a stopped-flow spectrophotometer is presented along with the hardware interface and the software developed to operate the system. Experimental results obtained from this system are also presented.

A. Methods Used for the Study of Kinetics

Almost any conventional analytical technique can be applied to a slow reaction to derive information about its reaction kinetics. However, the same cannot be said for fast reactions. In the case of fast reactions, the monitoring system has to be fast enough to track a signal proportional to the reaction accurately. There are, however, two general classes of techniques which have been applied to the study of fast reactions.

1. Relaxation Methods

The first class of techniques can be termed relaxation methods, since they involve the sudden perturbation of a system at equilibrium and the subsequent monitoring of the return of that system to equilibrium. The most common mode of perturbation involves a temperature jump, pressure jump or ultrasonic absorption (80). These methods can be used to follow reactions with half lives on the order of microseconds. Unfortunately, these methods do not allow for the mixing of reagents to initiate a reaction. Rather, they start with an equilibrium system. These limitations decrease the usefulness of these techniques for deriving analytical information.

2. Mixing Methods

The second class of techniques involves fast mixing methods. All of these methods use the mixing of solutions containing the reacting species to initiate the reaction. After mixing, the solution then flows into an observation cell where the detector monitors the progress of the reaction. These methods, although limited by the time required for the physical mixing of the reactant solution, are capable of monitoring reactions with half lives on the order of milliseconds. Fast mixing methods can be further subdivided into three categories:

continuous flow, accelerated flow and stopped flow methods.

a. The Continuous Flow Method - The continuous flow method, which was developed in 1923 by Hartridge and Roughton (81,82), was the first technique designed specifically to monitor fast reactions in solution. The reacting solutions are allowed to flow from reagent reservoirs into a mixer and then into a long observation tube. Since the flow rate is held constant, movement of the detector along the observation tube produces a concentration versus time profile for the reaction. The main advantage of this method is that detectors with a slow response time can be used to monitor the reaction. The disadvantages include the consumption of large solution volumes, which range from several milliliters to several liters, and the time loss due to repositioning the detector along the observation tube.

b. The Accelerated Flow Method - The accelerated flow method of Chance (83-85) consists of flowing reactant solutions through a mixer and into an observation tube at rapidly increasing rates. The detector is fixed in a stationary position while the reaction mixture is accelerated past it. The simultaneous measurement of flow rate is used with the detector response to obtain a concentration versus time profile. This technique requires a detector with a fast response time, and an additional simultaneous measurement of solution flow rate. However, in comparison to the continuous flow method, it represents a substantial savings in the quantity of solutions consumed, since only 0.1 milliliter is required.

c. The Stopped Flow Method - The stopped flow method also used by Chance (83-85) involves flowing the reactant solutions through a mixer and into an observation cell and rapidly stopping the flow. The concentration versus time profile of the reaction is obtained by monitoring the system after the flow is stopped. The complete time profile is obtained in one run. The obvious advantage to this system is that the solution is not moving when the observations are made; but, rather, it is at rest. Thus, the solution inhomogeneities which plague the continuous flow method are virtually absent in stopped flow. The solution volumes required are on the same order as required for the accelerated flow method, about 0.5 ml. This method also requires detectors with fast response times to monitor the progress of the reaction. The advantages of the stopped-flow mixing method prompted the use of the stopped-flow system developed by Beckwith and Crouch (29) for the rate analyses of the heteropolymolybdate system presented in this work.

3. Modifications to the Stopped Flow Mixing System

Since lower precision is inherent whenever rate methods are used instead of equilibrium methods, the researcher should make an effort to obtain the best precision possible from the reaction monitoring device. The stopped-flow unit in our lab has undergone several modifications in an attempt to achieve this end.

The basic design and modifications of this system have already been presented in previous theses (29,30,86) and will merely be cataloged here. The pneumatic solenoid valves which control the solution flow in the system are actuated by TTL signals. Thus, the flexibility of computer control of the stopped-flow system was introduced (30). An additional shut off valve was included in the flow stream between the mixer and the observation cell to prevent diffusion of the unmixed reagents into the observation cell during long periods of data acquisition. The mixer has also undergone several modifications in an attempt to improve mixing efficiency.

The observation cell was modified to allow conductance and temperature information to be taken in addition to the absorbance data (86). The modification included using a fiber optic bundle to transmit light from the exit slit of the monochromator to the solution in the observation cell. The fiber optic bundle actually forms one window of the observation cell. The flexible fiber optic bundle reduces noise due to vibration caused by the sequencing of the valves and light loss due to reflections at air-glass interfaces. The other window of the observation cell is formed from one end of a rigid quartz light pipe coated for internal reflection. A photomultiplier tube (PMT) is rigidly fixed to the stopped-flow unit itself and is butted against the opposite end of the quartz light pipe. This also increases the light throughput of the system.

More intense light sources were utilized to increase the light throughput of the system. A 40 W quartz iodine car lamp was used as the source, but the source flicker limited the precision. It is obvious that light throughput can be increased by utilizing more intense light sources. However, an efficient and accurate means for source fluctuation correction must be used to gain any real benefit from the more intense light sources.

B. Source Ratioing

Source ratioing is important in many types of spectrometric measurements, where source intensity fluctuations reduce precision. As a result there have been many different approaches to the problem. The source stabilization technique (87), which involves an optical feedback loop to the power supply to stabilize source output, has met with some success. But, recent attempts at source noise reduction have concentrated on the detection system.

Dual wavelength spectrophotometers have been designed (88,89) to expose the sample alternately to two different wavelengths of light; one wavelength which the sample absorbs and another wavelength near the first that the sample does not absorb. This necessitates the use of two monochromators. A beam splitter separates the beam so that 90 percent of the light falls upon the measuring PMT while 10 percent falls upon a compensating PMT. The anodes of these two photomultiplier tubes are connected to the inputs of a differential amplifier which, in turn, is connected to a regular double beam detector circuit (90). This subtraction method only gives an approximation to true source ratioing (7,91,92).

A double beam, single detector, wavelength-modulated spectrometer was developed for derivative spectroscopy (93). This system was based on a servomotor-helipot method. Wavelength modulation was achieved by a vibrating mirror. Gating electronics derived the signal and background information which was then put through a differential lock-in amplifier. This system was slow and only useful for equilibrium measurements.

The potentiometric recorder slide wire method (94) involved two detectors. The sample detector was connected to the recorder inputs and the reference detector was amplified, integrated and used as the supply voltage for the slide wire recorder instead of a constant voltage source. This system only compensated for low frequency noise fluctuations. The slide wire system was tried for Raman spectroscopy, but it was too slow and could not compensate for the quicker fluctuations encountered. This method was improved (95) by introducing an analog division before integration. However, it did not have a sufficient frequency response for measurements in the millisecond range.

A system which can be used for fast kinetic measurements was developed by Hironi and coworkers (96). In this method the PMT high voltage servo mechanism was controlled by a reference PMT. This system can only be used by detectors with a linear dependence of gain on voltage, and it is usually limited to a small control range because of this nonlinear dependence.

Analog dividers have been used to assist in source flicker correction for position sensitive detectors (97). Analog multipliers connected as dividers for source ratioing have also been presented in the literature (98,99). A source ratioing system suitable for fast reaction analysis has been developed based on an analog divider (91,92). This system consists of a beam splitter to direct the beam to both a sample and reference photodiode, high impedance FET operational amplifiers for signal conditioning and a Burr Brown Corp. No. 4290 high precision divider module. The DC performance of this system gave an accuracy of ±0.15 percent for a range equivalent to a 10:1 variation in source intensity which indicates its usefulness for long term drift corrections. The rejection of source noise from DC to 10 kHz is approximately 100 fold with a 10 μsec time constant. This results in a 0.2 percent output deviation for a 20 percent source fluctuation. The suitability for use in fast kinetic measurements is demonstrated by its rise time of 11 μsec.

A system which used a digital computer to store and ratio the sample and reference signals has been presented by Malmstadt and coworkers (100,101). The system was tested with the output of a small nitrogen laser. It gave a relative standard deviation of 0.65% for a repetition rate of 1 Hz, 0.26% for a repetition rate of 10 Hz and 1.37% for a repetition rate of 100 Hz. These measurements were based on the average of ten pulses each.

This type of system was chosen for several reasons. The accuracy and precision of digital raticing with a minicomputer is better than with ordinary analog dividers. The cost is less for computer owners since no analog divider must be purchased. Finally, it requires no more computer time than the initial single channel configuration. Rather, it makes better use of the computer's calculating ability.

C. The Source-Corrected Spectrophotometric Detection System

The source-corrected detection system used in the present study is illustrated in Figure 1. The light source is a 40 watt quartz iodine car lamp. The beam splitter module consists of a National Photocolor Corporation 1 inch, uncoated pellicle. This pellicle transmits 92% at an angle of incidence of 45 degrees for the spectral range 400 to 2400 nm. The reflected light is directed toward a reference PMT (RCA 1P28) within the beam splitter module. The only effect the beam splitter has on the transmitted light is the power loss associated with the 2 inch light path required to pass through the module.

A 2 mm diameter flexible quartz fiber optic bundle transmits the light from the exit slit of the monochromator to the solution in the observation cell. The other window in the observation cell is a 3 mm diameter internally reflecting quartz rod which has a PMT (RCA 1P28) butted against its other end.

Both photomultiplier tubes are powered by the same Heath model EU-42A high voltage power supply. The output of each PMT is connected to a Keithly Model 427 current amplifier which in turn is connected to an Analog Devices SHA-5 sample-and-hold module. The sample-and-hold modules, as well as the rest of the detection circuitry

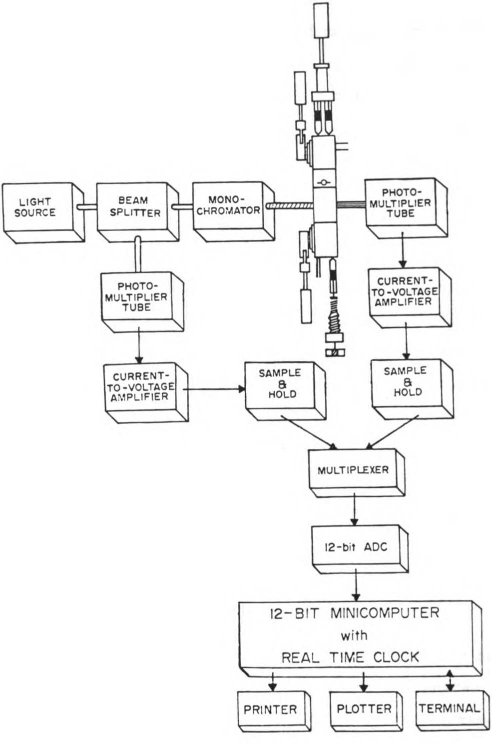

Figure 1. Stopped flow detection system.

are under direct computer control and are discussed in detail later. Both sample-and-hold modules are multiplexed to the analog-to-digital converter (ADC) through an Intersil IH5042 C-MOS SPDT analog switch. Since both photomultiplier tubes are connected to the same high voltage power supply to reduce the effect of source voltage fluctuation, they cannot be balanced by adjusting the high voltage power supply. The amplification adjustments on the current amplifiers are not continuously variable, but change by factors of ten. However, continuously varying offset currents are available on the amplifier. The system is balanced by first adjusting the response of the sample PMT for a range of 0 to 10 volts by varying the high voltage supply, the amplification, and current offset of the amplifier. The light directed at the reference PMT is then attenuated by occluding the light path with a metal cylinder until the reference signal matches the sample signal.

1. PDP 8/e Interfacing Capabilities

The PDP 8/e computer can be interfaced directly on the internal bus or the external bus. Data transfer can be done in three possible ways: 1) program interrupt transfers; 2) data break transfers (direct memory access); or 3) programmed input/output transfers (IOT). The method used for this interface was programmed IOT with the external bus. It is instructive to examine what is involved in this method to understand the interfacing circuitry better.

Input/output transfer instructions initiate a programmed transfer of status information of up to twelve bits of data either to or from a peripheral. These instructions are twelve bits long and can be broken down into three parts. Bits 0-2 identify the instructions as an IOT if they have an octal value of 6. Bits 3-8 contain the device selection code (DS) which determines which device the IOT addresses. Bits 9-11 contain the operation specification code which determines the specific operation to be performed by the designated device.

Signals between the various boards comprising the computer system, such as the central processing unit and memory boards, are routed through edge connectors or along the OMNIBUS. Some of the signals in the OMNIBUS are routed to an external bus through the use of either a data break interface (KD8-E board) or a Positive I/O Bus interface (KA8-E). Only the Positive I/O Bus interface board was utilized for the interface described here (102).

The signals from this board are daisy-chained to a Sykes dual floppy disk system and to a Heath Interface Buffer Box. The buffered I/O lines appear at the top of two Heath EU-801-21 I/O Patch cards for patch wiring of interfaces. The Positive I/O Bus interface board supplies: 1) twelve buffered accumulator lines representing the content of the PDP 8/e accumulator register, 2) twelve accumulator lines for the transfer of signals from a peripheral register to the PDP 8/e accumulator register, 3) twelve buffered memory data lines which carry the device selection code, 4) three buffered IOP timing lines for timing pulses IOP 1, 2, and 4, which are generated by the Positive I/O Bus interface card in response to the operation specification code of the IOT instruction, 5) an initialize pulse generated at power turn on and by the clear key on the computer front panel; and 6) a skip line, which, when asserted, causes the next instruction in a program to be skipped. Several other I/O lines are also available, but were not used in this interface.

2. Data Acquisition Interface

The initializing pulse (INIT) is used to clear the flip-flop shown in Figure 2. Circuit A is used for control of the sample-and-hold module and circuit B controls the multiplexer. The outputs of both of these circuits appear in Figure 3. The circuit depicted in Figure 2C generates a flag to indicate when the ADC is finished. The instructions that operate this interface as well as the logic waveforms they generate are illustrated in Figure 4.

The 6531 instruction sets the S/H flip-flop (Figure 2A)

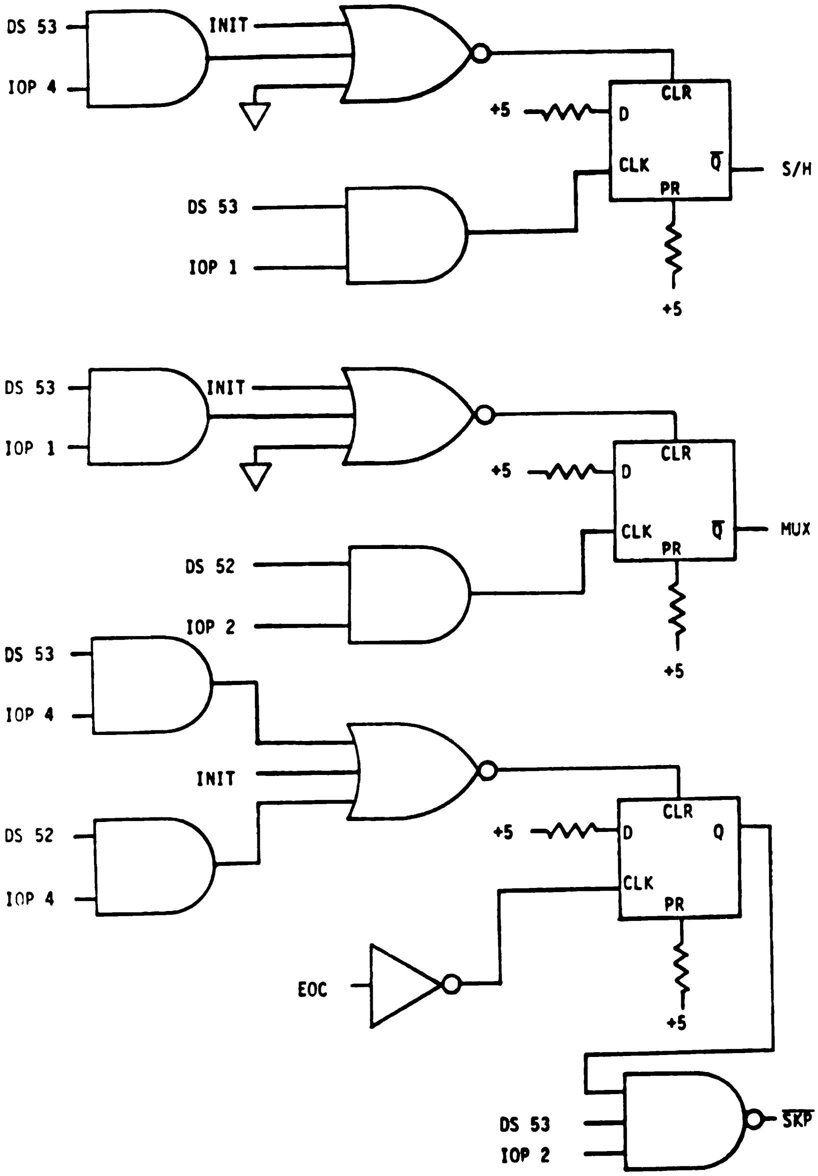

Figure 2. Data acquisition interface.

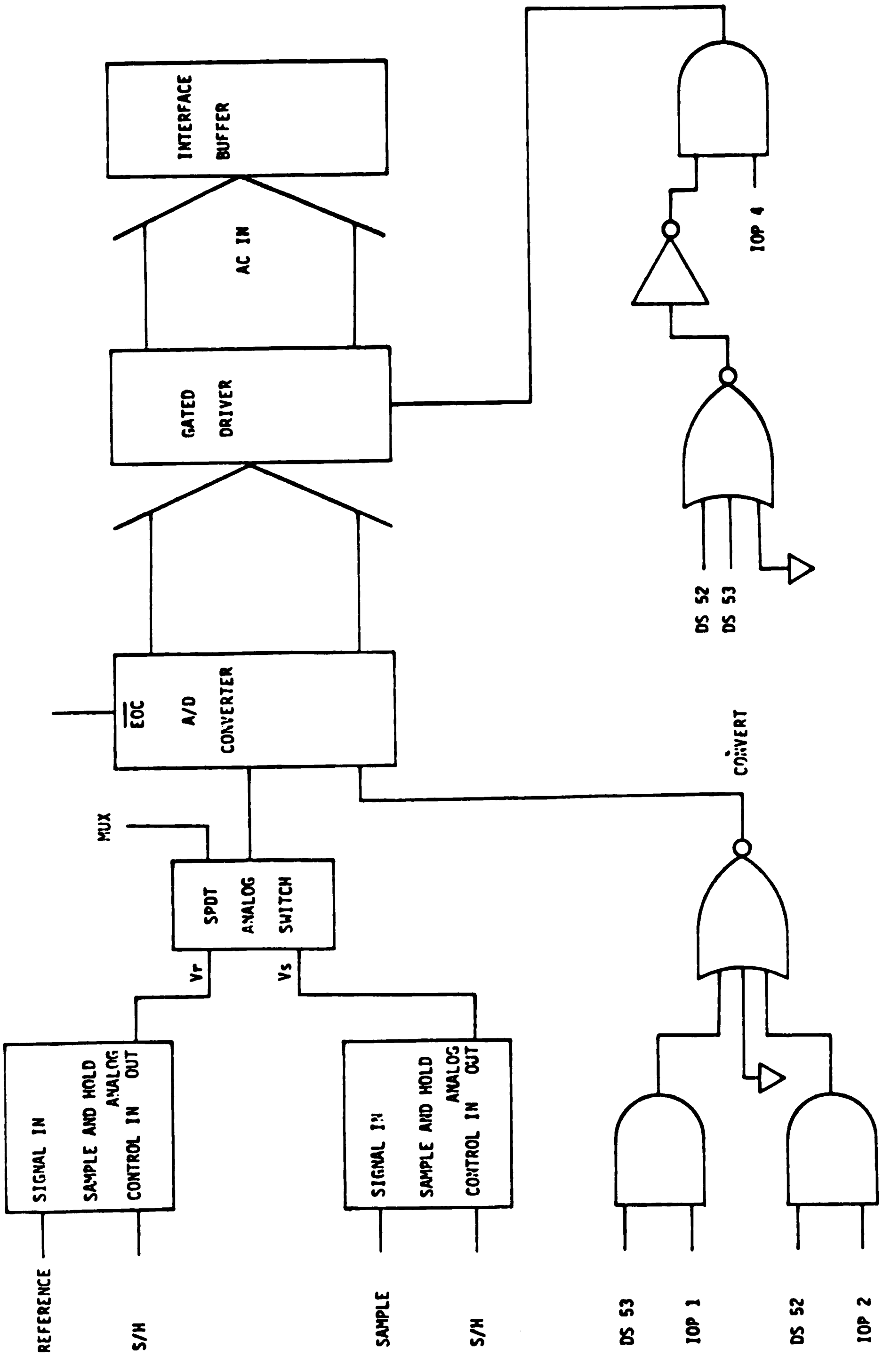

Figure 3. Data acquisition system.

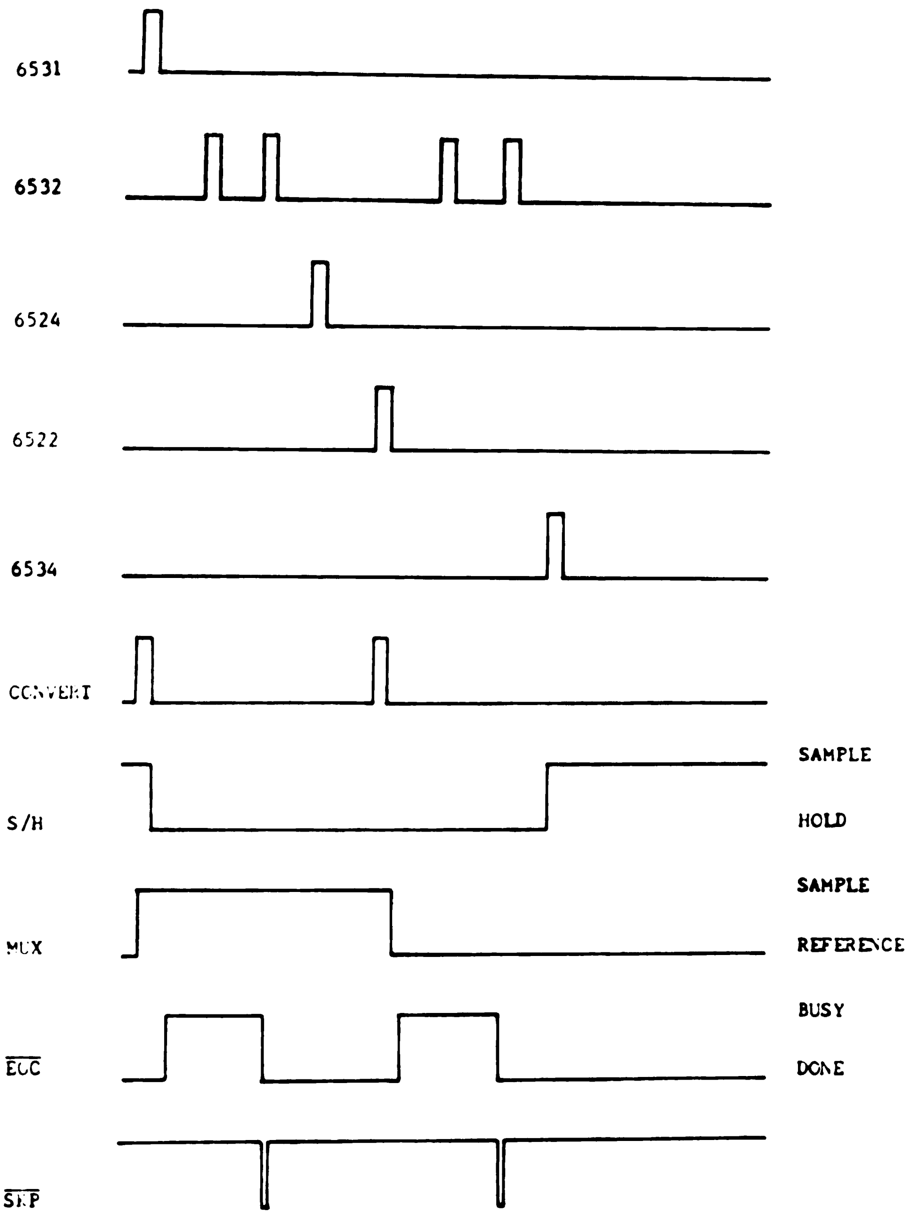

Figure 4. Logic waveforms.

and causes both S/H modules to simultaneously hold the current voltage level. This instruction also clears the multiplexer flip-flop (Figure 2B), which causes the analog switch to connect the S/H module holding the sample signal to the ADC (Figure 3). Finally, the ADC is triggered by the convert pulse to start conversion. This causes the end of conversion ($\overline{\text{EOC}}$) output of the ADC to go high until the conversion is completed. At that time $\overline{\text{EOC}}$ will go low and trigger the flip-flop in Figure 2C. During this time, the 6532 instruction is used to check the status of this flip-flop. If it has been enabled, the 6532 instruction asserts the skip line ($\overline{\text{SKP}}$ goes low), which causes the program counter to be incremented by one. The 6524 instruction causes the 12-bit digital number available from the ADC to be driven onto the external bus (Figure 3). It also clears the flip-flop triggered by the $\overline{\text{EOC}}$ pulse. The 6522 instruction causes the reference channel to be connected to the ADC. It also triggers the ADC to begin conversion. It differs from the 6531 instruction in that it does not influence the state of the S/H modules. The $\overline{\text{EOC}}$ triggers the done flag in Figure 2C at the end of the conversion and the 6532 instruction checks the status of this flag. The last instruction, 6534, drives the data into the accumulator, clears the EOC flag and returns the S/H modules to the sample mode. These instructions and their functions are summarized in Table 1.

The interface is operated by the programs discussed in Chapter IV. These programs are written in FORTRAN II and SABR, the assembly language for FORTRAN II. An example of a SABR routine utilizing the interface instructions for programmed IOT's follows:

```
S     6531     /hold sample signal, end convert
SX,   6532     /skip on EOC flag
S     JMP X    /check flag again
S     6524     /drive data, clear EOC flag
S     DCA   I  /store data
S     6522     /start conversion of reference
SY,   6532     /skip on EOC flag
S     JMP Y    /check flag again
S     6534     /drive data, clear EOC flag, sample
S     DCA   J  /store data
```

This program instructs the interface to simultaneously hold the sample and reference voltage levels, and then converts the sample voltage to a digital number which is stored in a FORTRAN II variable I. The reference voltage is converted to a digital number and stored in a FORTRAN II variable J. These numbers can then be treated as any other FORTRAN II integer variable.

Table 1. Command Set for Data Acquisition Interface.

Instruction	Function
6531	Enable the S/H to hold Connect the sample channel to the A/D Start conversion
6532	Check for the end of conversion Skip if done
6534	Drive data into the accumulator Enable the S/H to sample Clear EOC flag
6522	Connect the reference channel to the A/D Start conversion
6524	Drive data into the accumulator Clear EOC flag

D. Evaluation of the Precision Source Ratioing System

This section studies the response of the precision source ratioing system to several types of common mode source variations. The following six figures all follow the same format: curve R represents the reference signal, curve S represents the sample signal and curve D represents their ratio scaled up by a factor of 1000. The reference and sample curves are offset to allow them to be plotted on the same graph as their ratio.

The first experiment utilized a Heath Light Source Model EU-701-50 in the constant voltage mode. The reference and sample signals, along with their ratio, were recorded for a series of single analog-to-digital conversions, first with no obstruction in the light path, next with the light path interrupted by several neutral density filters and finally, with the path blocked by an opaque object. The filters used were Corion Instrument Corporation 1 inch filters with optical densities of 0.15, 0.3, 0.5, 1.0 and 2.0, respectively. The results are illustrated in Figure 5. The reference signal varied from 3894 to 407 with an average of 1833 and a relative standard deviation (RSD) of 67%. The sample signal ranged from 3860 to 411 with an average 1724 and an RSD of 69%. The ratio of the two signals ranged from 0.97 to 1.2 with an average of 1.00 and a RSD of 6.2%. The ratioed signal remains stable over a tenfold change in the signal

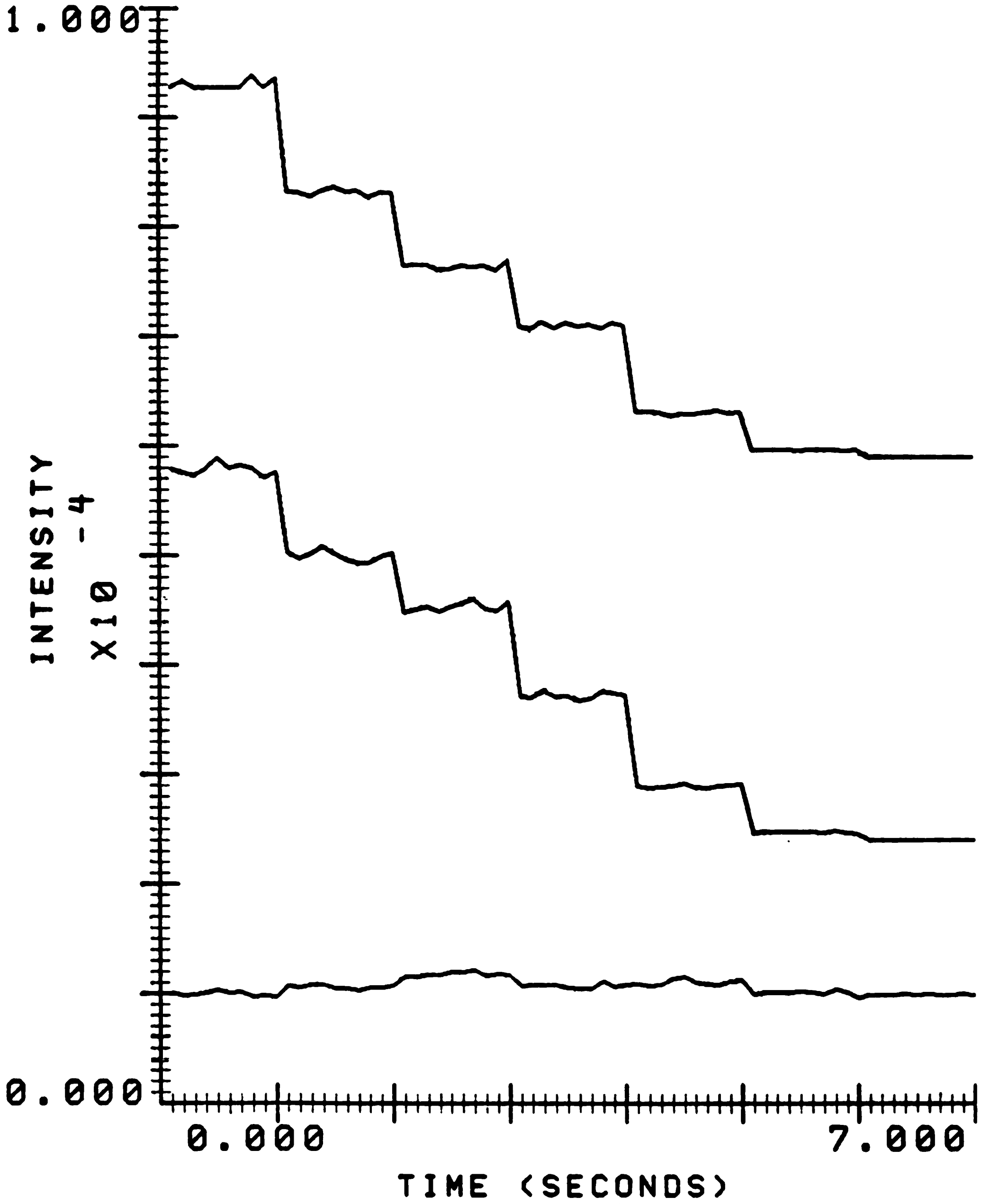

Figure 5. Response to source variation: (R) reference signal; (S) sample signal; (D) S/R x 1000.

intensity.

Figure 6 illustrates the warm up time necessary for the system. Data were taken immediately after the circuitry was turned on. It appears that both PM tubes have the same warm up characteristics since the ratioed output has a 1.3% RSD. These data were the result of one data acquisition of sample and reference signals every 15 minutes. This system decreases the warm up time required before system operation.

Figure 7 is a study of long term drift, a problem which usually limits the maximum time of a kinetic run. The data points plotted in this graph are the result of an average of 10 individual data acquisitions. The reference signal has a 2.8% RSD, the sample signal a 3.1% RSD and the ratio has a 0.8% RSD over the 40 hour time period. The value of the ratio at the beginning of the experiment was 0.9995, at the end the value was 1.0001. This represents a total change of only 0.06%. The low drift of this system can greatly extend the monitoring period for a given reaction.

The frequency response of the system was investigated initially by partially chopping the light signal with a gear attached to a Mabuchi model 25 motor, specified to run at 10.100 rpm. The gear, which was relatively heavy and not flat, taxed the capabilities of the small motor. As a result, this system was not capable of

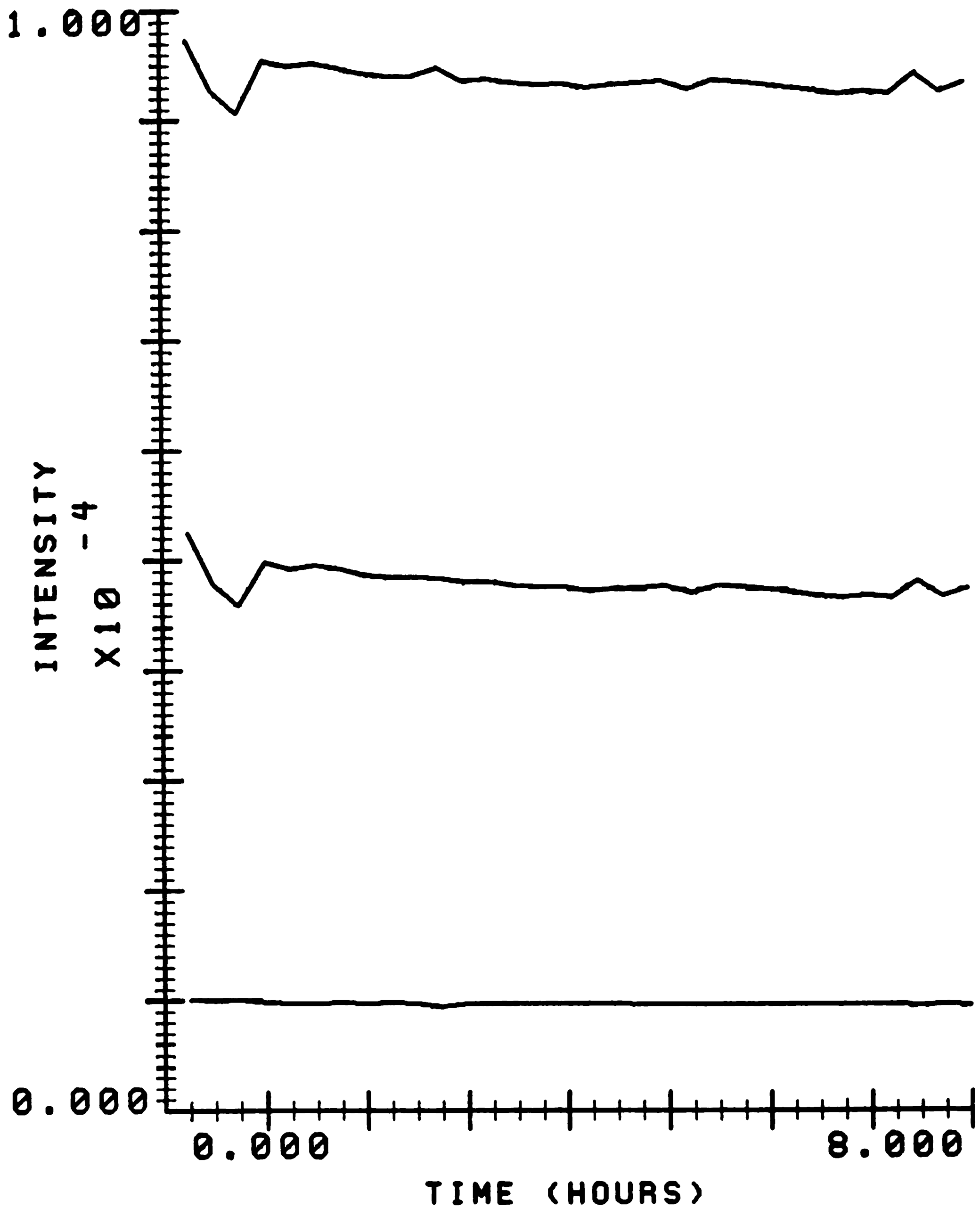

Figure 6. Warm up characteristics: (R) reference signal; (S) sample signal; (D) S/R x 1000.

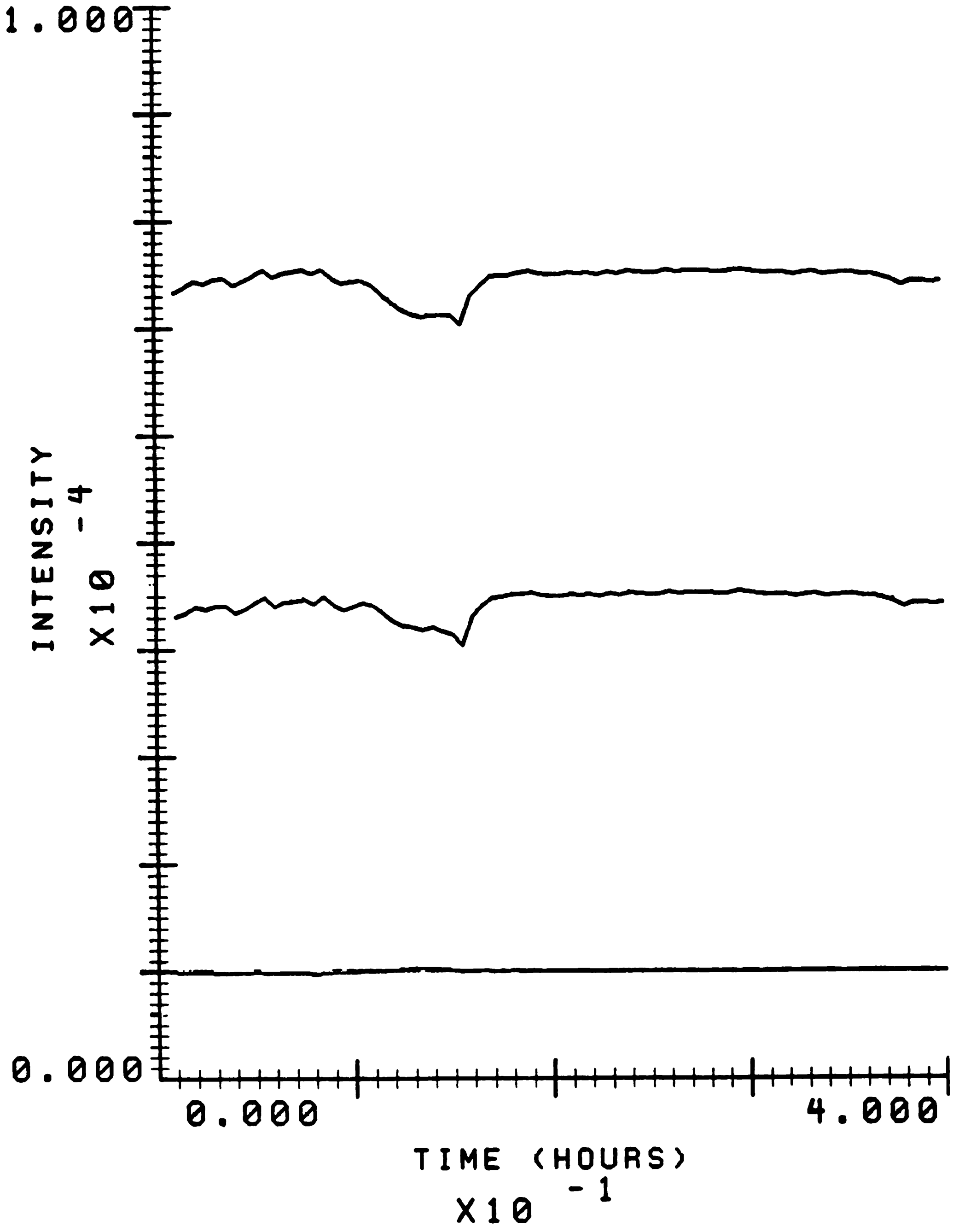

Figure 7. Long term drift: (R) reference signal; (S) sample signal; (D) S/R x 1000.

chopping frequencies over 1 kHz, and a new system was developed. The new system consisted of a light emitting diode (LED) mounted in the entrance of the beam splitter module. Due to the low light level available from the LED, the output of the beam splitter bypassed the monochromator and passed directly into the observation cell of the stopped-flow system. The LED was pulsed on by the TTL output of a Wavetek model 184 5 MHz sweep generator. The current amplifiers were adjusted to produce an output voltage of 2 volts when the diode was off and 8 volts when the diode was pulsed on. The rise time of the system, which is limited by the current amplifiers and the sample-and-hold modules, is estimated to be on the order of 10 μsec.

Figure 8 illustrates the response of the source corrected ratioing system to a source fluctuation of 500 Hz. The ratioed output has an average of 1.00 and a 2.2% RSD. Figure 9 represents the response of the system to a source fluctuation of 1 kHz. The sample to reference ratio has an average of 1.00 and a 3.1% RSD. The ratioed response given in Figure 10 is due to a source fluctuation of 5 kHz and has an average of 0.99 and a 6.8% RSD. The RSD rose to 15% for a 20 kHz source fluctuation. However, this was still a factor of 50 better than the sample or reference channel. All of the data in these figures were individual data acquisitions. The precision

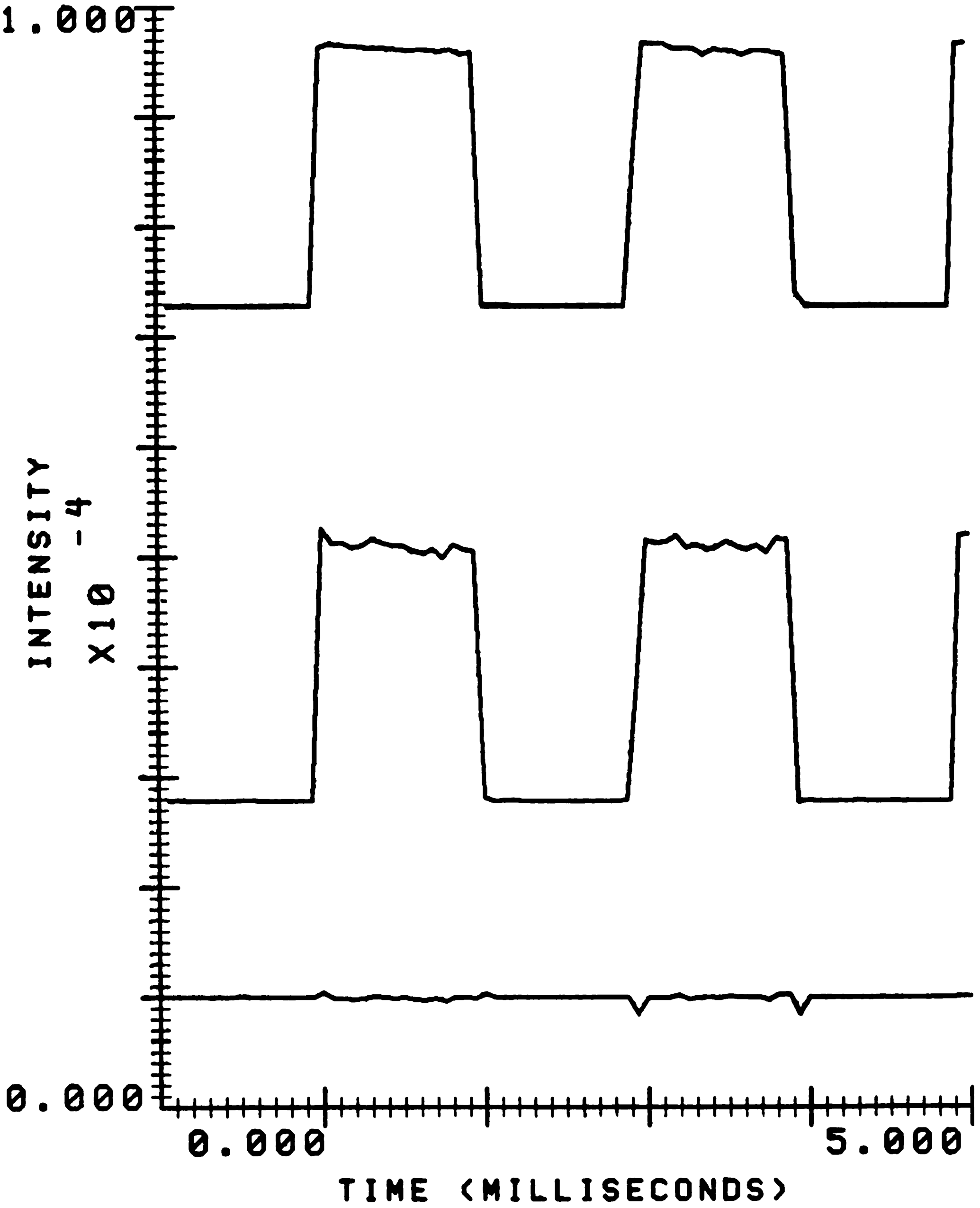

Figure 8. Response at 500 Hz: (R) reference signal; (S) sample signal; (D) S/R x 1000.

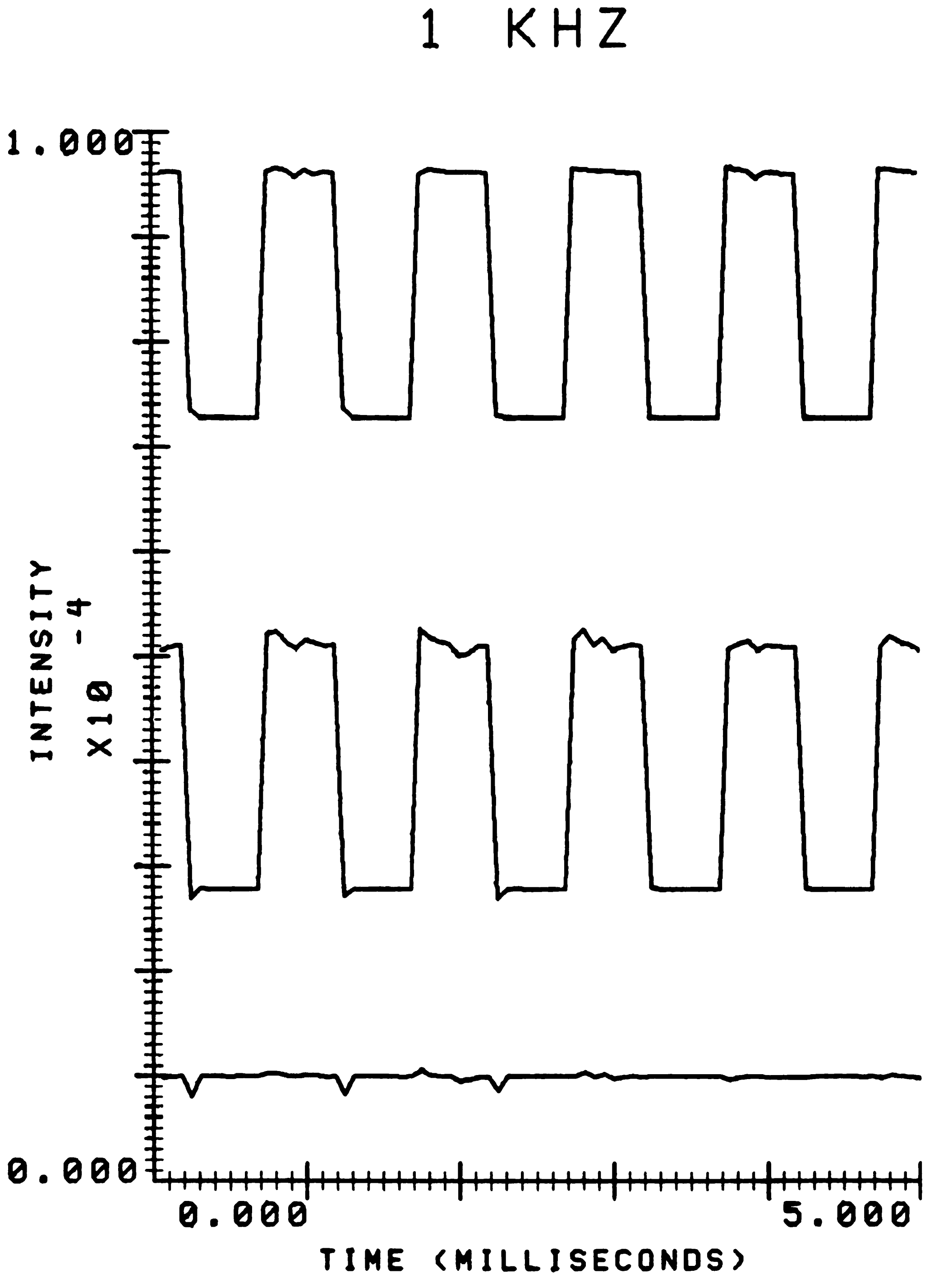

Figure 9. Response at 1 kHz: (R) reference signal; (S) sample signal; (D) S/R x 1000.

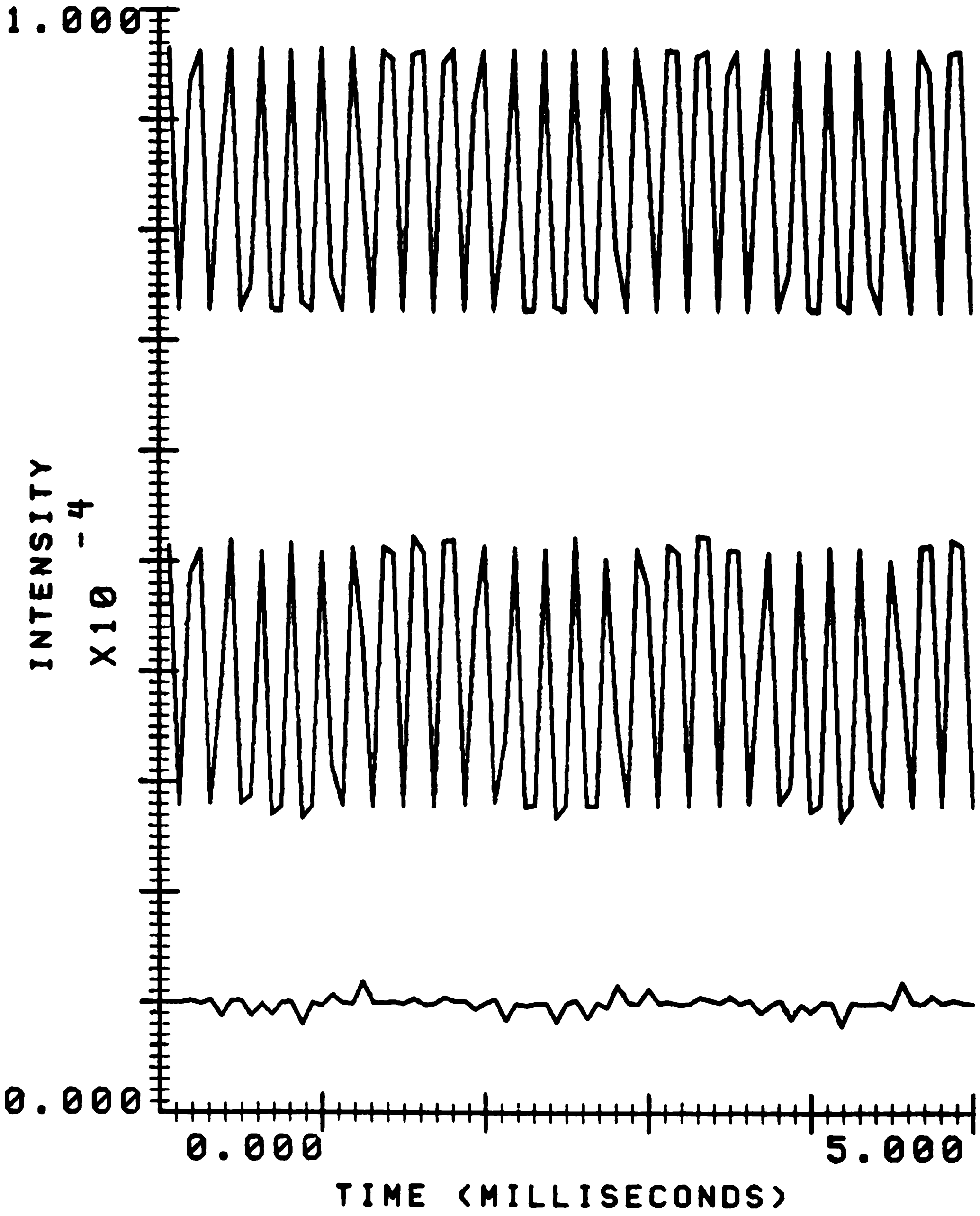

Figure 10. Response at 5 kHz: (R) reference signal; (S) sample signal; (D) S/R x 1000.

of the results can be increased by averaging several individual data acquisitions. Since the light illuminating the reference and sample PM tubes does not come from the same area of the LED, this could induce a variation in the observed signal. In the normal mode of data acquisition, the light from the filament would be more homogeneous, and several data points would be averaged into one point. Both of these factors would lead to better precision than indicated by these results.

This raticing system should be useful in slow scanning spectrometers as well as in compensating for long term drift. The frequency response of the system shows that it can also be useful for the correction of high frequency source fluctuations.

CHAPTER IV

SOFTWARE

The software developed for use with the stopped-flow system can be divided into two separate sections. The first section is a data acquisition package and the second section is a data analysis package. However, before the details of these two packages are presented, a brief description of the computer and its operating system will be given along with the basic reasons for using the language utilized for the software routines.

A. Description of the Computer System

The computer utilized in this study was a PDP 8/e minicomputer equipped with a programmable real-time clock, extended arithmetic element, 16K words of random access memory (RAM), RK05 cartridge disk, Sykes dual floppy disks, Decwriter II, and both a Tektronix 4006 graphics terminal and an ADDS consul 980 graphics terminal.

The 16K of RAM is divided into 4 fields each containing 4096 locations. Each field is subdivided into 32 pages, each containing 128 locations. The pages within a field do not correspond to any physical separation within memory. The computer has no way of recognizing on which page of memory it is currently executing instructions. Whenever a variable is addressed, it must be defined on the page where the program is currently being executed. When programming in an assembly language like PAL-8, it is the programmer's responsibility to insure that variables are stored on the correct page of memory.

The operating system used during the initial stages of this work was OS/8 version 3C. The updated version 3D became available during the last portion and was adopted, since it eliminated several bugs in the earlier version and provided the system user with an extended set of Keyboard Monitor commands. The five main software components of the operating system are: a keyboard monitor for communications to and from the terminal, device handlers for data transfer to peripherals, a user-service routine for controlling directory operations in addition to opening, closing and chaining to files, a command decoder for communication to system library programs; and, finally, a library of system programs.

The utility programs contain several powerful editing and debugging routines as well as file transfer routines. There are three assemblers available: PAL8, SABR, and RALF. BASIC, FORTRAN II and FORTRAN IV are the three higher level languages available on this system (103).

B. Choice of a Programming Language

Notz (30) developed an extensive library of routines for the operation of the stopped-flow system in our laboratory. These routines had been written in PAL8, and, although they served the purpose that they were written for, they proved to have several disadvantages. The most important disadvantage was the difficulty of modifying the PAL8 programs. Each minor modification to a PAL8 program, which requires new instructions to be inserted on a particular page, requires extensive modification of the entire program to correct for the page-to-page movement of instructions. This problem, coupled with the burden of lengthy routines for simple calculations, and for input and output in assembly language, prompted the change from PAL8 to a higher level language.

1. BASIC, FORTRAN II and FORTRAN IV

Both FORTRAN IV and BASIC are more sophisticated languages than FORTRAN II. They have many extra capabilities designed into their compilers. However, the best programming language for a particular function is not always the language which appears to be the most powerful. The decision must be based on what the program must accomplish as well as how the different programming languages can accomplish this task.

The tasks required of the stopped-flow program include: 1) operation of the valve sequencing interface, 2) operation of the data acquisition interface, 3) ratioing, 4) averaging, 5) calculating absorbances; and 6) displaying the data in a convenient form for interpretation. The most complex calculations performed are logarithms and square roots. Since all of the high level languages mentioned have library routines for these functions, this was not a prime consideration.

An important consideration for a program of this complexity is program size. A program in a higher level language can result in extra core memory being required to contain the program. However, writing inefficiently in assembly language can result in even more inefficient use of memory. Since a higher level language was chosen, it is instructive to compare the memory expansion capabilities of each language.

The computer has a fixed 16K of core memory. This is the maximum size that any program can occupy. However, this size can be increased by storing programs on a mass storage device and swapping these programs into the core memory of the computer. The succession of swapping new programs into core looks and operates as one large program. Using this technique, the effective size of a program can be increased to 300K.

FORTRAN IV incorporates an overlay structure to accomplish this task. Eight separate levels of overlays are allowed with up to 16 overlays per level. An overlay is a set of subroutines stored on a mass storage device and a level is a two block multiple portion of memory set aside for a specific set of overlays. The main overlay is loaded into level 0 and remains there throughout execution. When a subroutine from a particular overlay is called, the overlay containing the subroutine is read into the block of memory reserved for the overlay. This process involves writing over any other overlay which may have previously occupied this level. Since only the main overlay and one overlay of a given level are core resident at a given time, this is the size restriction for the program. Obviously, it is to the programmer's advantage to make the main overlay as small as possible so that the other overlays can be larger. Unfortunately, the main overlay must contain not only the main program, but also all library routines, all RALF assembly language routines, as well as all COMMON sections. If large blocks of data are stored in COMMON, and there are many assembly language routines, this will severely limit the size of the other overlays. This can be circumvented by outputing data into a file on the mass storage device and reading this file whenever the required data are needed. The latter, however, will increase the complexity of the program and increase the execution time.

FORTRAN II and BASIC employ the CHAIN command instead of the overlay structure of FORTRAN IV to increase program size. The CHAIN command encountered in a BASIC language source file reads the named program from the specified device, compiles this program and begins execution. If the chain command is used in a BASIC core image file, it calls another core image file on the system device and begins execution. After execution, the original program is swapped back into core. The FORTRAN II command always reads a core image program from the system device and begins execution of that program. After execution, the original program is not swapped back into core. This process rewrites the chained program over the program that called it. The COMMON area, however, is not disturbed. Each core image file can consist of a main program with as many as eight subroutines. This permits an additional savings in core space if no I/O statements are used in a particular program segment since the I/O conversion routines are not loaded in that segment. This allows over 1K of additional storage area for that segment. Even though any one FORTRAN II program or subprogram must be able to fit into 4K of core, the virtual size of an executable program formed by individual programs and subprograms chained together is limited only by the mass storage limitations of the system device.

All three languages allow sufficient core expansion capabilities to operate large routines effectively. As previously mentioned, large blocks of COMMON data and assembly language routines limit the value of the FORTRAN IV overlay feature compared to the value of the chaining feature in FORTRAN II and BASIC.

The device independent I/O capabilities of BASIC, FORTRAN II and FORTRAN IV also differ. Both FORTRAN IV and BASIC allow up to four different I/O files to be open simultaneously, whereas FORTRAN II restricts the user to one open file at any given time. In FORTRAN IV, however, all of the files used must be defined for the FORTRAN Run-Time System (FRTS) before program execution. This is limited to a maximum of six files. More files can be written but they will not be closed, rendering them useless for data storage. Both BASIC and FORTRAN II incorporate file open and file close statements, allowing an unlimited number of files to be opened and closed during the course of one program. This enables the user to change the names of files during program execution. Each stopped flow run generates a large amount of data in a short period of time, and it is convenient to store these data in files whose names convey the contents. Both BASIC and FORTRAN II are more conducive to this type of file storage than FORTRAN IV.

The most significant difference between the three languages appears when mixing assembly language instructions with the high level language. FORTRAN IV and BASIC both require all assembly language instructions to reside in subroutines separate from the main program. In contrast, FORTRAN II allows the insertion of assembly level instructions directly into the FORTRAN II coding. It also allows direct transfer of variables from FORTRAN II to the assembly language SABR and vice versa. This procedure simplifies the mixing of a higher level language and assembly language and resulted in the choice of FORTRAN II for the language used in the stopped-flow programs.

C. Data Acquisition

This section provides an overview of the main program and subprograms required to control data acquisition from the stopped flow system. Branching between the main data acquisition program, RGSFMN, and the subroutines associated with it is illustrated in Figure 11A. A flow chart for this sequence of programs is contained in Appendix 1, and the complete program listings of the main program along with all subroutines is included in Appendix 2.

This sequence of programs can be executed by the following command string:

```
.LO RGSFMN(HO)$*RGTIME
*RGRINS
*RGWAIT
*RGFILL
*RGSTOR(G)
```

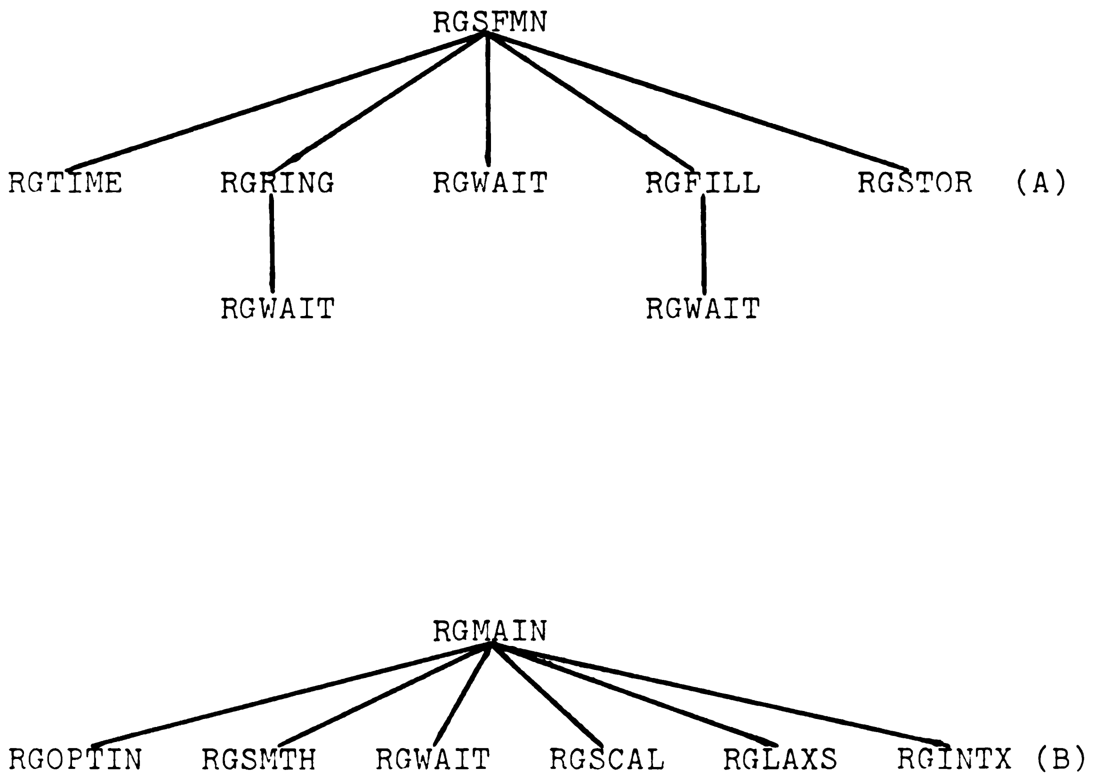

Figure 11. A. Calling sequence for the data acquisition routines. B. Calling sequence for the data analysis routines.

This string of commands loads the relocatable files of all programs and begins execution.

Subroutine RGTIME accepts two variables and passes back two variables from the main program. This subroutine uses the number of data acquisitions to be averaged into one data point and the time, in seconds, between these averaged points to calculate the time period necessary to wait between the data acquisition periods. It passes back the number of clock counts necessary as two different variables to allow data to be acquired over a time period from 0.2 ms to 54 min. These variables are then used by the main program, RGSFMN, to load the clock counters to count down the requested time.

RGWAIT is a general purpose subroutine written to provide an adjustable delay time from 400 ms to 15 min with a single call. It is passed one integer argument which represents the time to be delayed in increments of 0.40 s. The program is used to provide the correct wait period between sequencing of the valves of the stopped flow instrument as well as the correct period for attainment of thermal equilibrium. This routine is called not only from the main program, but also from the subroutines RGRINS and RGFILL.

The subroutine RGRINS operates the stopped flow valve sequencing interface. It is passed the number of rinsing operations desired from the main program. Utilizing IOT instructions and delay intervals created by calling RGWAIT, it sequences the system through the requested number of rinse cycles.

RGFILL utilizes the same IOT instructions and wait loops used in RGRINS. However, it functions to fill the drive syringes, expel the first push and to wait an additional 25 s. The drive syringes are adjusted for slightly less than six pushes per syringe filling to insure complete emptying of the syringes. It was found that the results obtained from the first and last push of the syringes were not consistent with the middle pushes, and, therefore, all data taken ignored the first and last push. The additional 25 s wait period was incorporated after the filling operation to allow the solutions and the stopped flow system to return to thermal equilibrium.

The subroutine RGSTOR takes the raw data from the assembly language routine contained in the main program, converts these data into absorbances, calculates a point-by-point average absorbance value as well as a standard deviation of this value over the number of experimental runs. The maximum number of runs that can be averaged in this manner is eight. The program also calculates the time corresponding to each set of data acquisitions and outputs the time, absorbance and standard deviation to a file on a mass storage device with a file name input by the user at this time.

The main program coordinates all of these programs. It contains five main sections: 1) symbol definition, 2) input options, 3) acquisition and storage of 0% T level, 4) assembly level data acquisition routines and real time clock instructions; and 5) averaging and storage of blank value. After the collection and storage of the data is completed, this program CHAINS to the data analysis portion of the software.

A typical interaction between the operator and the program is illustrated in Figure 12. There are two modes of data acquisition available with this program. The first mode has only one time period over which data are acquired. The second mode allows data collection over two different time periods with a maximum possible delay of 25 min between these time periods. Each time period and delay has its own specifications. This allows data to be acquired rapidly during the initial portion of a reaction and slower later on in the reaction. This proved to be convenient for the phosphate and silicate mixtures in which the phosphate reaction was essentially complete in 2 s, while the silicate was still reacting. In this case, data were acquired rapidly during the first 2 s and then more slowly as the silicate reacted. The user chooses the mode in which he wishes to operate. In the illustration in Figure 12, the one time period mode was chosen.

```
1 = 1 TIME PERIOD, 2 = 2 TIME PERIODS+DELAY: 1
# OF POINTS PER AVERAGE (14 FORMAT):  30
# OF AVERAGES(14 FORMAT):  100
THE TIME BETWEEN POINTS IN SECONDS(E13.6):  .02

SET STOPPED-FLOW FOR ZERO PERCENT T AND HIT RETURN

BLANK(0) OR SAMPLE(1) RUN:  0
# OF SYRINGE FILLINGS PER RUN(1-8):  2
# OF DATA PUSHES PER SYRINGE FILLING(1-5):  4
# OF RINSINGS(0-8):  4

BLANK(0) OR SAMPLE(1) RUN:  1
# OF SYRINGE FILLINGS PER RUN(1-8):  2
# OF DATA PUSHES PER SYRINGE FILLING(1-5):  4
# OF RINSINGS(0-8):  4

FILE NAME= RGPMB6
```

Figure 12. Dialog with data acquisition program.

The next three questions that the user is required to answer all relate to the data acquisition specifications for a single experiment. Data are acquired at a fixed rate of one point every 0.2 ms. These individual data acquisitions are averaged together to form one data point. Averaging 30 points would mean that the averaged result would have been obtained over a span of 6 ms. The response to the question about the number of averages in Figure 12 indicates that an averaged set of 30 data acquisitions will be taken 100 times. The time between those each of those 100 sets of data acquisitions is 0.02 s. The result is 100 data averages taken over the course of 2 s.

The next statement in Figure 12 instructs the user to occlude the light path of the reference PMT. The instruction is printed on the terminal along with a bell sound to inform the user of the fact that human intervention is required. When the light path is interrupted, the user responds with a carriage return. The program then proceeds to acquire 100 A/D conversions at a 100 Hz rate, averages these values and stores the average in one location for future use.

The next response indicates that a blank will be run. The syringes, which are set for 6 pushes, are filled twice, and have the first and last push ignored. This results in 8 separate runs averaged to represent the final blank value. The following section of dialog requires similar information to be entered for the sample run. The last entry that the user is required to supply is the file name under which this entire data set is to be stored.

Execution of the program can be terminated at this point, if no data analysis is desired at this time. If the routine is not terminated, the program automatically calls the data analysis program, which is swapped into core and executed.

D. Data Analysis

This section describes the routines involved in the data analysis programs. The calling sequence of these routines is illustrated in Figure 11B. In addition to the programs shown in Figure 11B, this program uses a DECUS subroutine library called TEKLIB for plotting on a Tektronix terminal.

This program sequence can be executed independently of the data acquisition package by the following command string:

```
.LO RGMAIN(TH)$*TEKLIB(L)
*RGOPTN
*RGSMTH
*RGWAIT
*RGSCAL
*RGLAXS
*RGINTX(G)
```

The main program, RGMAIN, serves as a coordinator for the other subprograms. It consists of calls to the various subroutines described in this section. RGOPTN is a subroutine which displays the options regarding the manner in which the data can be displayed for the user on the Tektronix terminal.

Subroutine RGSMTH performs a 5, 7, 9, or 11 point first derivative, quadratic, Savitsky and Golay smooth on the absorbance-versus-time data. The subroutine is passed the absorbance data array, the time between the data points along with an integer number representing the number of points to be used in the smoothing routine. The subroutine returns a smoothed rate data array.

The subroutine RGSCAL performs two vital functions. The first function is to scale the data array so that it fills the entire plotting surface and insures maximum plotting resolution. The second function of this subroutine is to plot the data array. It is called once for each data array to be plotted.

RGLAXS labels the axes inside the plotting area to maintain maximum resolution on the plotting surface. The maximum and minimum for each variable plotted are also listed.

The final subroutine, RGINTX, is a modification of an interactive routine developed by Holler. Since an extensive discussion of the basics of its operation can be found in Holler's thesis (86), only a brief discussion of the operation and recent modifications to the program will be discussed here.

The Tektronix terminal is not equipped with a cursor so a moving software cursor point was developed. Using keyboard commands, the user can move the cursor forward, backward or halt its movement along the plotted points. The index of any specific point can be passed back to the calling routine by typing an integer from 1 to 4. This feature allows the user to pick a specific region of the plot interactively for further analysis. A complete summary of these commands can be found in Appendix 2 in the comment section of RGINTX. In order to notify the user that he is entering the interactive mode of the plotting package, the terminal bell is rung until the user responds by typing any character on the keyboard. Once in the interactive mode, the number of interactive points that can be defined has been increased to eight to allow more regions of the curve to be investigated. A new function has been added which has proven useful for fixed time studies: the user types a "P" followed by the index of a point. The cursor then moves immediately to that specified point bypassing all intermediate points. A statistical package has been added to the end of the subroutine to permit averages and standard deviations to be calculated over the ranges specified in the interactive mode.

A typical user interaction is found in Figure 13.

```
FILE NAME = RGPMB6

ABSORB(PTS)       = 1       ABSORB(LINE)      = 4
RATE(PTS          = 2       RATE(LINE         = 5
ABS + RATE(PTS)   = 3       ABS + RATE(LINE   = 6
ABS(LINE) + RATE(PTS)   = 7
ABS(PTS) + RATE(LINE)   = 8
OPTION 7 FOR PTS 1-100  = 9
CALC. AVERAGES          = 10   CALL ANOTHER FILE= 11

WHICH OPTION?  9




DO YOU HAVE INTERACTIVE POINTS?  1=YES,  0=NO   1

INPUT THE COORDINATES OF 1 PAIR(1,2)  12

FOR THE POINTS 34 THROUGH 65
THE AVERAGE= 0.138462E-01 WITH STAND. DEV.=0.293709E-03

DO YOU HAVE INTERACTIVE POINTS?  1=YES,  0=NO   1

INPUT THE COORDINATES OF 1 PAIR(1,2)  34

FOR THE POINTS 29 THROUGH 75
THE AVERAGE= 0.136522E-01 WITH STAND. DEV. = 0.388546E-03
```

Figure 13. Dialog with data analysis program.

The user initially specifies the file name containing the absorbance data. The plotting options are then listed for the user to choose from. It was found that a plot of absorbance using lines and a simultaneous plot of rate with points over the entire data set gave the most useful initial information, so option 9 was designed to produce this. Figure 14 illustrates the type of resolution capable with this system. Also, in Figure 13, it can be seen that points 1 through 4 were defined during the interactive mode. The lower half of Figure 13 depicts the results obtained from the curve shown in Figure 14. For the coordinate pair of interactive points 1 and 2, the program returns the index of the points, the average of all the points between and including these points and finally the standard deviation of these points. This process is repeated for points 3 and 4. For a fixed-time study, the user can bypass the interactive mode and input the indices of the points corresponding to the times of interest.

Since these programs were written with the use of independent subroutines, future program modifications should prove to be a simple task. Only the particular subroutine of interest will need to be modified rather than the entire system. Another advantage is that new programs can be created to perform other functions using these subroutines as building blocks. A program to

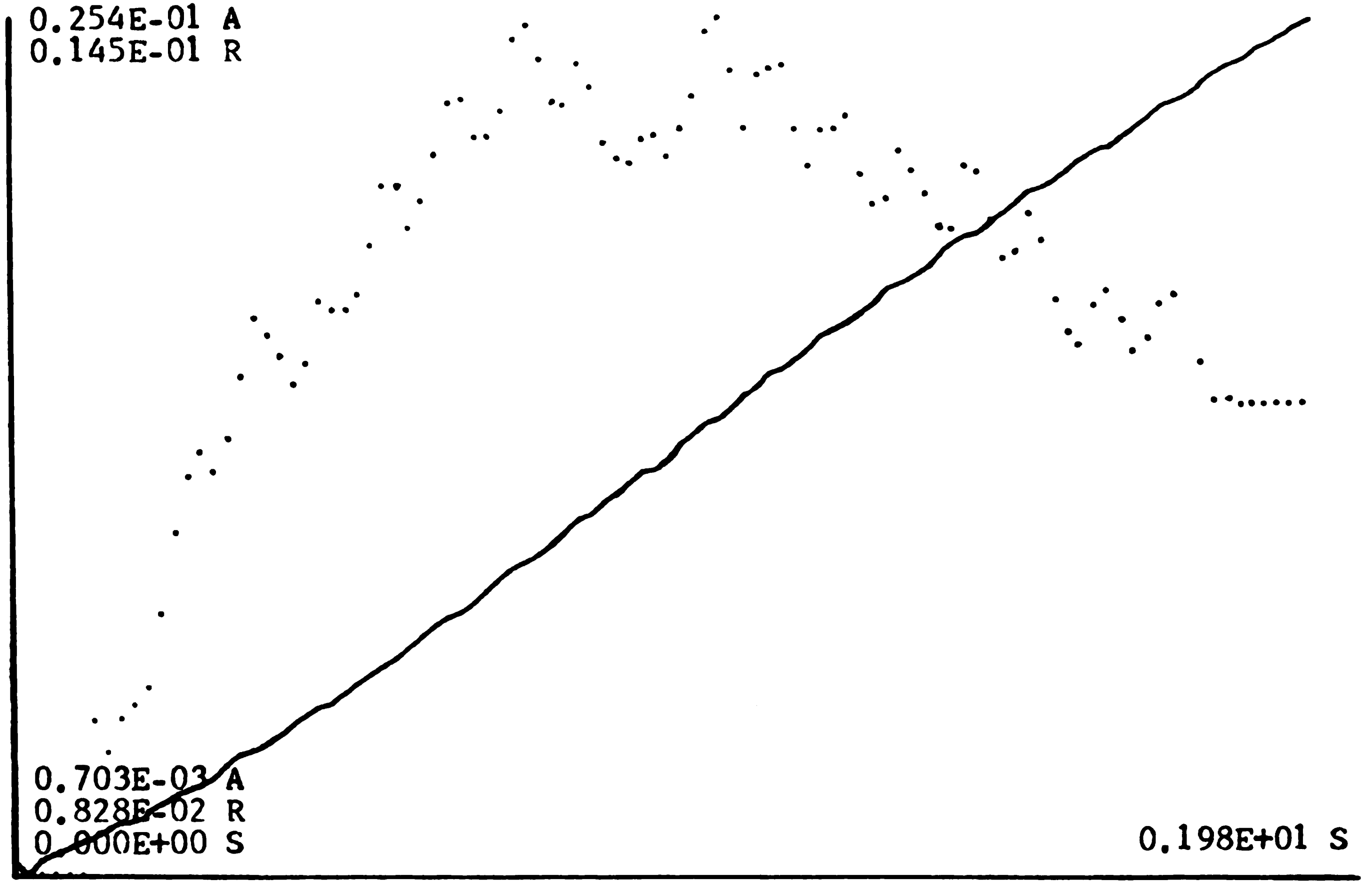

Figure 14. Interactive graphics output.

rinse the observation cell repeatedly was created by merely including a call to RGRINS. The delay program RGWAIT was used by both program packages for various functions. RGSCAL, the scale and plot subroutine, can be added to any program to display the data in a graphical form on the Tektronix terminal. The sophisticated data collection and analysis provided by these programs increases both the precision and accuracy of the rate measurements obtained with the stopped flow system.

CHAPTER V

KINETICS OF 12 MOLYBDOPHOSPHORIC ACID FORMATION

The 12-MPA anion is usually formed in strong mineral acid solutions such as hydrochloric, sulfuric or nitric acid. This chapter examines the kinetics of the 12-MPA formation reaction in nitric acid. The range of acid and molybdate concentrations used as well as other experimental procedures and data are also presented.

The kinetics of the formation of 12-MPA have been studied by previous workers in this laboratory (29,30,59). Beckwith, et al. (29) conducted an extensive study of the formation of 12-MPA in several strong mineral acid solutions. This study used the analytical concentrations of the acids in solution to determine the rate law; there was no correction made for the change in free acid concentration caused by reaction with Mo(VI). This problem and the fact that the ionic strength of the solutions was not controlled led Notz (30) to repeat the initial rate analysis of the 12-MPA system under more rigorous conditions. Notz studied the molybdate-acid equilibrium to determine the number of protons consumed by molybdenum in acidic solutions. He also conducted his initial rate studies at a constant ionic strength. The work done by Notz developed a rate expression which had an average ninth and an inverse first order dependence on acid concentration. This was in disagreement with the previous study which developed a rate law with more complex terms than Notz's rate law and with a different dependence on the acid concentration (the exact form of both rate expressions can be found in Chapter 2). Notz did not vary the molybdenum concentration in his studies. This fact cast doubt on the validity of the rate law he determined since molybdate and molybdate-acid interactions were ignored. A complete study of the formation of the 12-MPA system was undertaken to determine the best rate law under controlled conditions (constant ionic strength, correction for acid consumption).

A. Experimental Conditions

There were two factors which limited the range of investigation. The first was that the molybdate concentration should be present in a 100-fold excess in comparison to the phosphate concentration in order to prevent the formation of unsaturated heteropoly compounds. This puts a lower limit of 0.1 M on the molybdenum concentration for the 1 x 10^{-4} M phosphate solution used in this study. The second factor was that the free acid-to-molybdate ratio should be kept above 10 to 20 to prevent the formation of unreactive Mo(VI) species (30).

The solutions were prepared so that the free acid concentration of the molybdate and phosphate solutions were the same. Since the stopped flow system dilutes each solution in a 1:1 ratio with the other solution used, the lowest molybdate concentration prepared was 0.02 M. This put a lower limit of about 0.3 M on the acid concentration. The solutions were prepared based upon a Mo(VI) and acid study (30) which concluded that each mole of Mo(VI) consumes an average of 2.5 moles of hydrogen ions in forming the reactive cationic Mo(VI) species, presumably by the following reaction

$$2MoO_4^{-2} + 5H^+ = HMo_2O_6^+ + 2H_2O$$

Thus, all equilibrium concentrations of H^+ were calculated from analytical concentrations of nitric acid and corrected for the above reaction. All references to acid concentrations in molybdate solutions are to the free acid concentration based on this calculation. All references to acid concentrations in phosphate solutions are to the analytical concentration. Since the phosphate is present in such a small quantity (10^{-4} M) the analytical concentration is the same as the free acid concentration.

Analytical reagent grade or reagent grade chemicals were used in the preparation of all solutions. Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) was used for the molybdenum solutions and potassium dihydrogen phosphate (KH_2PO_4) was used for the phosphate standards. All solutions were prepared by dilution from a stock solution. Concentrated nitric acid was used as the acid stock solution. The ionic strength of the phosphate solution was adjusted to 2.0 M with sodium nitrate. In this case only the analytical concentration of the acid in the solution was used since the phosphate concentration was negligible. The molybdate solutions were also adjusted to an ionic strength of 2.0 M with sodium nitrate. The free acid concentration and the molybdate concentration (assumed to be in the form of a protonated dimer) were both included in the ionic strength calculations for solution preparation. The acidified molybdate solutions were allowed to equilibrate for 48 hours before use. This was necessary since there is a stabilization period required in order for the solutions to give reproducible kinetics (30,59).

Both 12-MPA and acidified molybdate solutions display an appreciable absorbance in the ultraviolet region of the spectrum. These strong absorption bands tail off into the visible region. The 12-MPA absorbance band extends further into the visible region than the acidified molybdate solution. There is no appreciable absorbance from acidified molybdate at wavelengths longer than 430 nm. However, in order to obtain a reasonable absorbance change for the 12-MPA formation reaction the wavelength used in this study was 400 nm. There is a large excess of acidified molybdate compared to the amount of 12-MPA formed during the first 5% of the reaction. This has a low molar absorptivity and does not change much during the time of the analysis. Therefore, the acidified molybdate does not contribute to the change in absorbance (the parameter monitored to determine the initial rate of reaction) determined in this region. Other researchers have used a wavelength of 350 nm without a large excess of molybdenum for the rate study of these compounds. This could introduce an error since the 12-MPA and the acidified molybdate both have significant molar absorptivities in this region. The observed absorbance change would be due to the decrease in the background absorbance as well as the increase due to the formation of 12-MPA.

The data were acquired using the programs discussed in Chapter 4. Figure 14, in Chapter 4 is a plot of the data acquired for a 0.01 M molybdate solution and a 1.0×10^{-4} M phosphate solution. Both solutions were made 0.3 M in nitric acid and were adjusted to an ionic strength of 2.0 M. The line which consists of 100 plotted points represents the actual absorbance data. Each point on the line represents a time average over 6 ms (the mean of 30 data points acquired at a 0.2 ms interval) and a mean of eight experimental runs. The total time span of the run is 6 s. The points plotted in Figure 14 represent the smoothed rate data. Through the interactive package described in Chapter 4, the average slope of the zero order region (with respect to time) was measured to obtain the average initial rate of reaction.

B. Kinfit Analysis

Table 2 reports the initial rate of formation of 12-MPA under varying conditions. These data were analyzed using KINFIT, a general purpose curve-fitting and equation solving program (105).

The reaction orders for various limiting forms of the rate law were estimated from log-log plots similar to those in Figures 15 and 16. These estimates were used as a guide in choosing different expressions for the rate law. These rate laws were then fit to the data by using KINFIT. The best fit rate law obtained for this data was

$$\frac{d[\text{12-MPA}]}{dt} = \frac{K_1[\text{Mo(VI)}_t][\text{PO}_t^3]}{K_2\frac{[\text{H}^+]^8}{[\text{Mo(VI)}_t]^5} + \frac{K_3[\text{H}^+]^4}{[\text{Mo(VI)}_t]^4} + K_4[\text{H}^+]^2 + 1}$$

$K_1 = 1.1 \times 10^1 \text{ l mol}^{-1} \text{ s}^{-1} \quad \pm \quad 7 \text{ l mol}^{-1} \text{ s}^{-1}$

$K_2 = 2.0 \times 10^{-8} \text{ l}^3 \text{ mol}^{-3} \quad \pm \quad 7 \times 10^{-9} \text{ l}^3 \text{ mol}^{-3}$

$K_3 = 1.2 \times 10^{-7} \quad \pm \quad 5 \times 10^{-8}$

$K_4 = 3.2 \text{ l}^2 \text{ mol}^{-2} \quad \pm \quad 4 \times 10^{-1} \text{ l}^2 \text{ mol}^{-2}$

In order to convert the change in absorbance to a rate

Table 2. Initial Rate of Formation of 12-MPA.

Ionic strength = 2.0 M

$[PO_4^{3-}]$ = 1.00×10^{-4} M

Temperature = 25 ± 0.2 °C

HNO_3 M	Mo(VI) M x 10^2	Initial Rate A/s x 10^3	Std. Dev. of Initial Rate x 10^4
0.30	1.00	6.0	1.9
0.35	1.00	5.1	1.5
0.40	1.00	4.1	1.5
0.45	1.00	3.3	8.3
0.50	1.00	2.5	0.3
0.55	1.00	1.8	0.9
0.60	1.00	1.1	1.0
0.35	1.50	8.9	1.5
0.40	1.50	7.3	1.8
0.45	1.50	6.6	1.3
0.50	1.50	5.7	2.1
0.55	1.50	4.8	1.2
0.60	1.50	3.9	1.3
0.45	2.00	9.0	2.3
0.50	2.00	8.8	2.1
0.55	2.00	7.8	1.4
0.60	2.00	6.9	1.4
0.50	2.50	11.3	3.5
0.55	2.50	10.3	8.5
0.60	2.50	9.4	2.2
0.50	3.00	13.6	3.2
0.50	3.50	16.6	4.4
0.50	4.00	18.2	6.7
0.50	4.50	20.4	2.8
0.50	5.00	21.8	3.0

of reaction a path length of 1.94 cm (the path length of the stopped flow observation cell) and a molar absorptivity of 770 $1.mol^{-1}s^{-1}$ were used. Both of these parameters were determined by Notz (30). Figure 15 is a plot of -log initial rate versus $-\log[H^+]$ at a constant molybdate concentration of 0.01 M. Figure 16 is a plot of the -log initial rate versus the $-\log[Mo(VI)_t]$ at a constant acid concentration of 0.5 M. The asterisks represent experimental data points, and the solid lines are derived from the best fit rate law.

This rate law seems to be in disagreement with the rate law determined by Notz (30). However, it was found that the rate law of Notz fit the experimental data in this study when the Mo(VI) concentration was held constant at 0.01 M. Notz's rate law was not applicable over the entire data set. The curve fitting program either did not converge or converged on negative constants when attempting to fit Notz's rate law at other molybdate concentrations.

The rate law determined in this work is, however, in agreement with that found by Beckwith, et al. (59). The constants determined for the best fit rate law differ from those obtained by Beckwith et al. (59). Table 3 compares the constants determined by Beckwith et al. to those determined in the present study. The small differences are attributed to several factors. First,

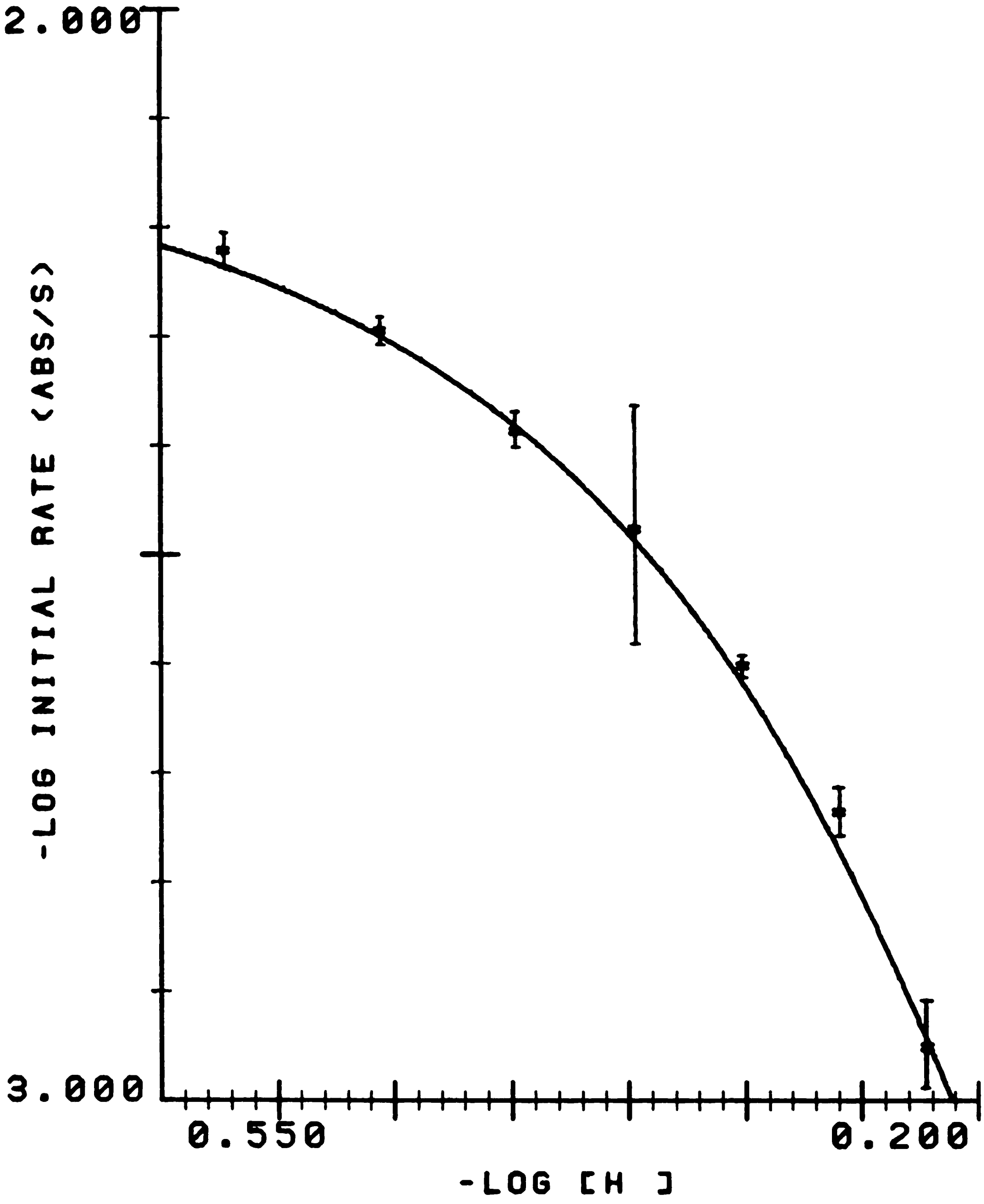

Figure 15. Acid dependence of 12-MPA formation.
Ionic strength = 2.0 M
[Mo(VI)] = 0.01 M
$[PO_4^{3-}]$ = 1.0×10^{-4} M

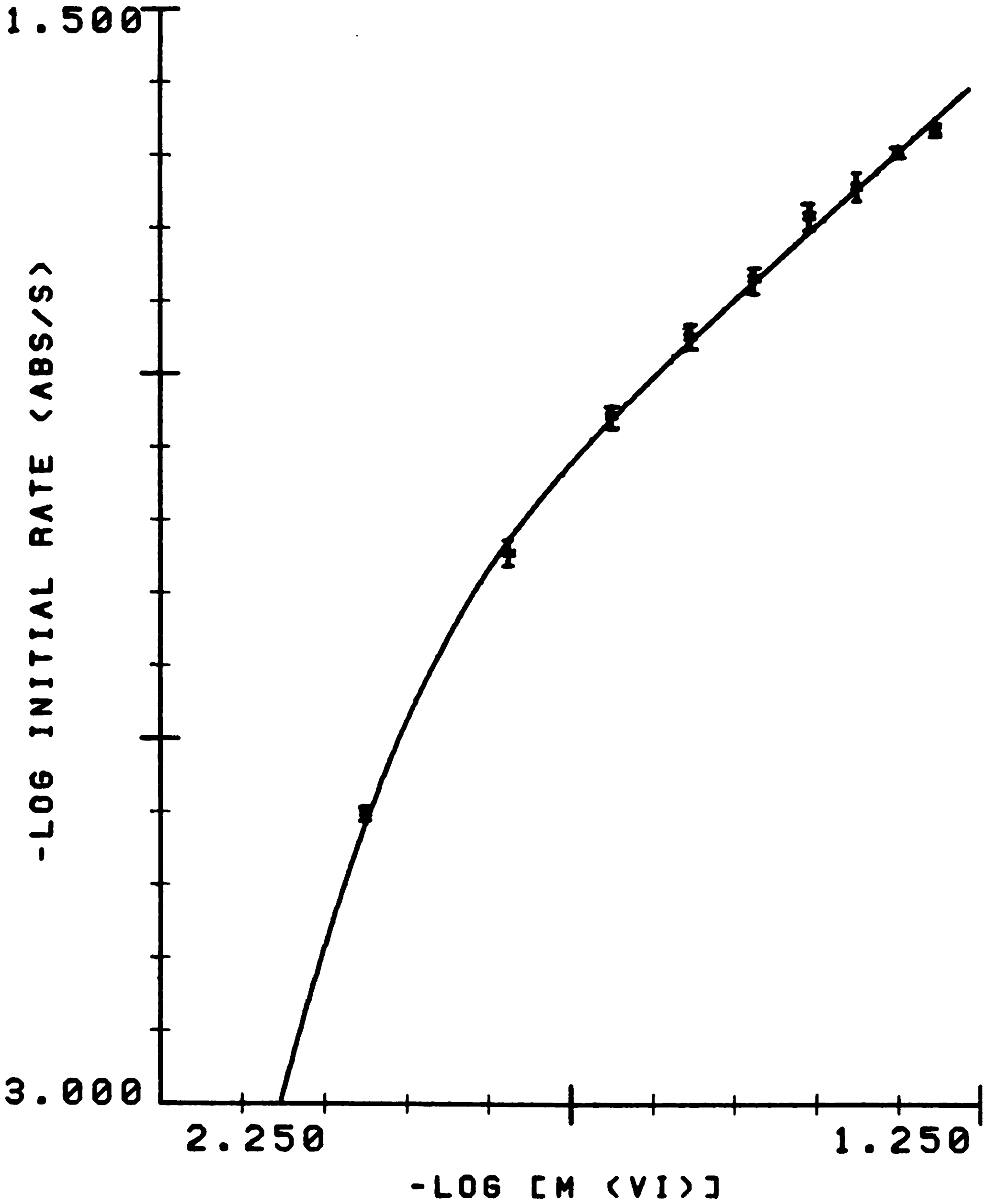

Figure 16. Molybdate dependence of the 12-MPA reaction.

Ionic strength = 2.0 M
$[HNO_3]$ = 0.50 M
$[PO_4^{3-}]$ = 1.0×10^{-4} M

Table 3. A Comparison of the Best Fit Constants for 12-MPA Formation in Nitric Acid.

	Beckwith *et al.*	Present Study
K_1	4.8×10^{1} l mol^{-1} s^{-1}	1.1×10^{1} l mol^{-1} s^{-1}
K_2	4.9×10^{-8} l^{3} mol^{-3}	2.0×10^{-8} l^{3} mol^{-3}
K_3	3.1×10^{-7}	1.2×10^{-7}
K_4	2.8 l^{2} mol^{-2}	3.2 l^{2} mol^{-2}

the data acquisition and analysis procedures used in this study were greatly improved over those used in the previous study. In the previous study, the change in absorbance was displayed on an oscilloscope, photographed and finally analyzed by hand. The completely computerized process used in this study permits the averaging of several runs and reduces the noise due to source flicker both of which result in improved precision. The interactive graphics routine improves the data analysis by reducing human error in the determination of the slope of the absorbance-time curve. Second, Beckwith, *et al.*, used the analytical acid concentration when fitting the data to the rate law. The present study, however, included corrections for acid consumption by molybdate. This would also cause a deviation in the rate constants that were determined in the two studies. Third, the ionic strength of the solutions used in this study was kept at 2.0 M by the addition of sodium nitrate. In the study conducted by Beckwith, the ionic strength was not controlled. It was observed that solutions with a high ionic strength and a high acid-to-molybdate ratio exhibited a decrease in the initial rate of reaction. This indicates that under these conditions some intermediate steps in the mechanism for the reaction involve the reaction of charged species. It could also account for some of the deviation in the rate constants determined for the best fit rate law.

The evidence found in this study supports a rate equation of the same form as was proposed by Beckwith *et al*. (59). Although the rate constants determined in this study do not agree with the rate constants given in the previous study, this in no way contradicts the proposed mechanism. Because of the improved data acquisition and analysis procedures, the correction for acid consumption and the use of constant ionic strength conditions, it is felt that the rate constants presented here should be more accurate than those previously determined.

CHAPTER VI

KINETICS OF 12-MOLYBDOSILICIC ACID FORMATION

The formation of 12-MSA is a well known reaction in that it has been used for years in the determination of silicates. In 1952 Strickland (73-75) pointed out the existence of two forms of the acid. Since that time, the literature has abounded with equilibrium-based methods that utilize the formation of either the α or β isomer or some combination of the two for the determination of silicates.

This chapter presents a basic analysis of the kinetics of the 12-MSA formation reaction. The system was first examined over a wide range of acid concentrations. Then, the reaction was studied in detail over the same range of conditions that were used in the study of the 12-MPA formation reaction. This combined information was used to optimize the rate method for the simultaneous determination of phosphate and silicate. This procedure is explained in detail in Chapter 7.

A. Experimental Conditions

The conditions were chosen so that a mixture of α and β isomers would not form. Below a pH of 1.8 only the β isomer forms (35). The formation of 12-MSA was studied in 0.47-0.002 M nitric acid solution, which corresponds to a pH range of 0.33 to 2.7. The major emphasis of this study was placed on the region where only 12-MSA forms.

The silicate stock solution was prepared by dissolving sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) in water and adding nitric acid until a pH of 3.0 was reached, as measured with a pH meter. This stock solution was 4.00×10^{-3} M in silicate and was volumetrically diluted to obtain the remaining silicate solutions used in this study.

Monomeric silicon units in concentrated solutions are most stable between the pH ranges of 1 to 3 and above 13 (106). However, in dilute solutions (about 5×10^{-3} M) the monomeric molecule $Si(OH)_4$ is stable over the pH range of 1 to 9. At pH values greater than 9 the silicate ion $Si(OH)_3^-$ forms. In solutions more concentrated than 5.0×10^{-3} M, SiO_2 polymerization occurs (107). In all of the experiments carried out, the silicon concentration was at or below 4.0×10^{-3} M.

The ionic strengths of both the acidified molybdate solutions and the silicate solutions were adjusted to 2.0 M using sodium nitrate. The assumption that molybdenum reacts with 2.5 moles of hydrogen ions per mole of molybdenum did not apply over the entire range of acid concentrations that was used in this study. Free acid concentrations measured with a pH meter indicated that the number of protons consumed by molybdenum in acidified solutions varied from 1.5 at the low acid end to above 2.5 at the high acid end. Therefore the acidity of each molybdate solution was measured using a pH meter and compared to standard acid solutions at the same ionic strength. This measurement was made 48 hours after solution preparation in order to allow sufficient time for the acid-molybdate reaction to reach equilibrium. Successive pH determinations were stable over a period of at least two weeks. This long equilibration period did not easily allow the preparation of a series of solutions at a constant acid concentration and varying molybdate concentrations. Therefore a plot of the molybdate dependence of the reaction at a constant pH is not presented. All references to acid concentrations are to concentrations measured with a pH meter, uncorrected for activity coefficient effects. The pH of the silicate solutions was adjusted to 2.76 using nitric acid. The error introduced by the heat of dilution caused by mixing the two solutions of nitric acid (at different concentrations) together should be negligible since less than a 0.1°C change in temperature is expected.

B. Experimental Results

Table 4 presents the initial rate of formation of 12-MSA obtained when the molybdate and acid concentrations were varied. A portion of these data is plotted in Figures 17 and 18. Figure 17 shows a plot of -log (initial rate of formation) versus the pH for a solution which is 0.01 M in Mo(VI). Figure 18 is the same type of plot for a solution which is 0.02 M in Mo(VI). Both curves exhibit the same general shape. In the region between pH 0.3 and 0.8, the rate of formation of 12-MSA shows an inverse seventh order dependence on the acid concentration. The region between pH 0.8 and 1.1 shows a third order dependence and the region from 1.1 to 1.6 exhibits a zero order dependence on the acid concentration. The portion of the curve above pH 1.8 is in the region where both the α and β modifications of 12-MSA form. It is also in this region where the molybdate solutions reacted with less than 2.5 moles of acid per mole of molybdenum.

The silicate concentration was 1.00×10^{-3} M which indicates that it should exist in a monomeric form throughout the entire range of acidities used. Table 5 lists the results of a linearity study for the determination of silicates. The table lists the initial rate of formation as a function of the silicate and acid concentration for 0.01 M Mo(VI) solutions. Figure 19 is a plot of the

Table 4. Initial Rate of Formation of 12-MSA.

Ionic strength = 2.0 M

$Si(OH)_4$ = 1.00×10^{-4} M

Temperature = 25 ± 0.2°C

HNO_3 M x 10^2	Mo(VI) M x 10^2	Initial Rate A/s x 10^3	Std. Dev. of Initial Rate x 10^4
0.2	1.00	0.68	0.3
1.9	1.00	1.4	0.9
2.2	1.00	1.7	1.6
3.9	1.00	2.2	4.8
4.9	1.00	2.2	4.4
7.2	1.00	2.2	3.9
9.1	1.00	2.2	1.8
10.	1.00	2.5	4.3
11.	1.0	3.0	2.5
13.	1.00	3.5	1.4
15.	1.00	3.8	2.2
16.	1.00	4.0	2.2
19.	1.00	4.3	6.7
22	1.00	2.5	3.7
26.	1.00	1.3	1.3
30.	1.00	0.62	0.7
34.	1.00	0.31	0.4
37.	1.00	0.19	0.3
43.	1.00	0.10	0.3
47.	1.00	0.06	0.4
6.3	1.50	2.7	0.7
9.1	1.50	3.0	1.0
13.	1.50	3.9	1.4
4.0	2.00	3.0	4.4

Table 4. Continued.

HNO_3 M x 10^2	Mo(VI) M x 10^2	Initial Rate A/s x 10^3	Std. Dev. of Initial Rate x 10^4
13.	2.00	3.3	1.5
19.	2.00	6.4	1.7
26.	2.00	5.8	0.3
33.	2.00	1.7	0.4
41.	2.00	0.5	0.6
47.	2.00	0.1	0.5
3.7	2.50	4.0	4.6
6.5	2.50	3.3	0.8
9.5	2.50	3.5	3.3.

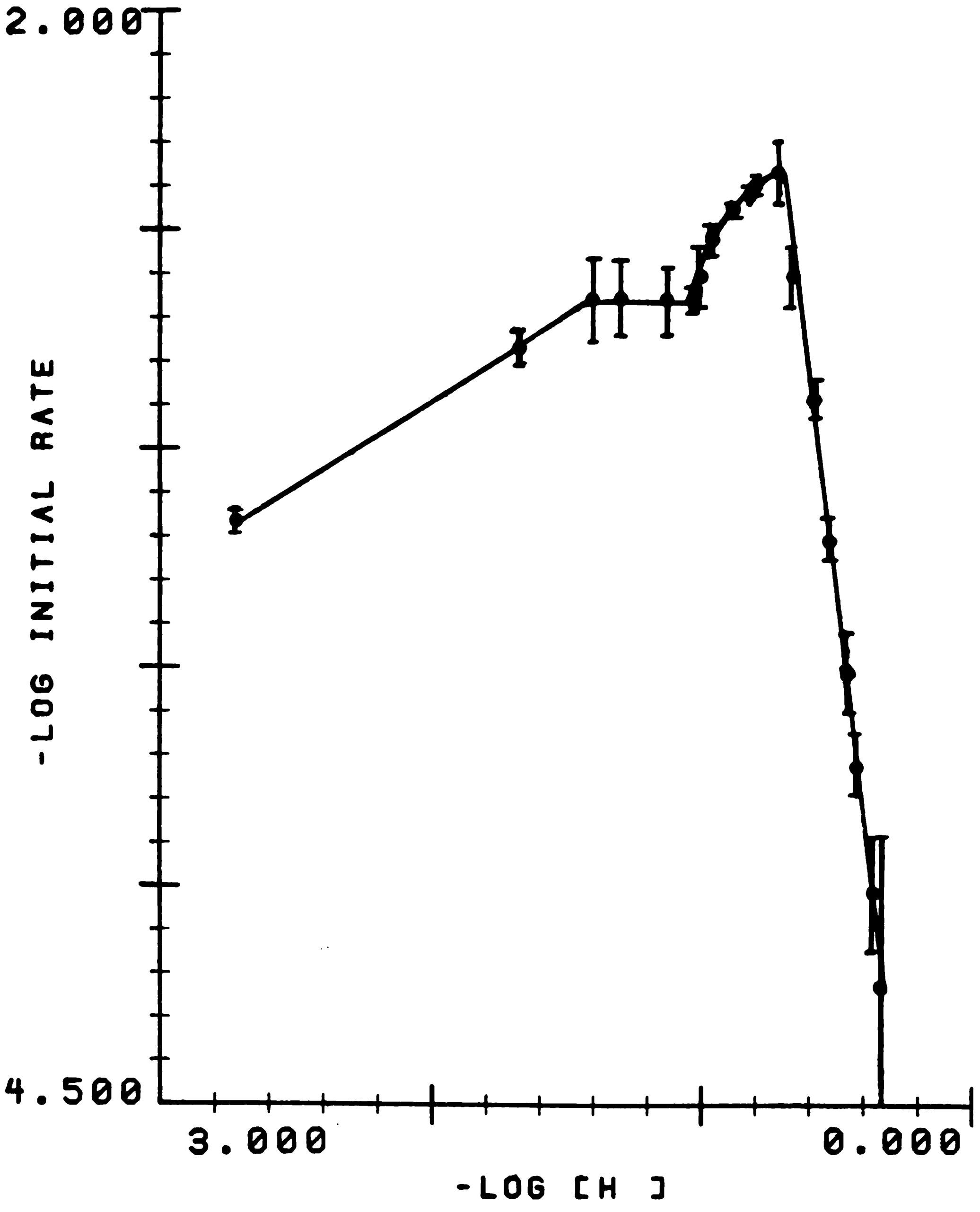

Figure 17. HNO_3 dependence of the 12-MSA formation reaction.
Ionic strength = 2.0 M
[Mo(VI)] = 0.01 M
$[Si(OH)_4]$ = 1.0×10^{-4} M

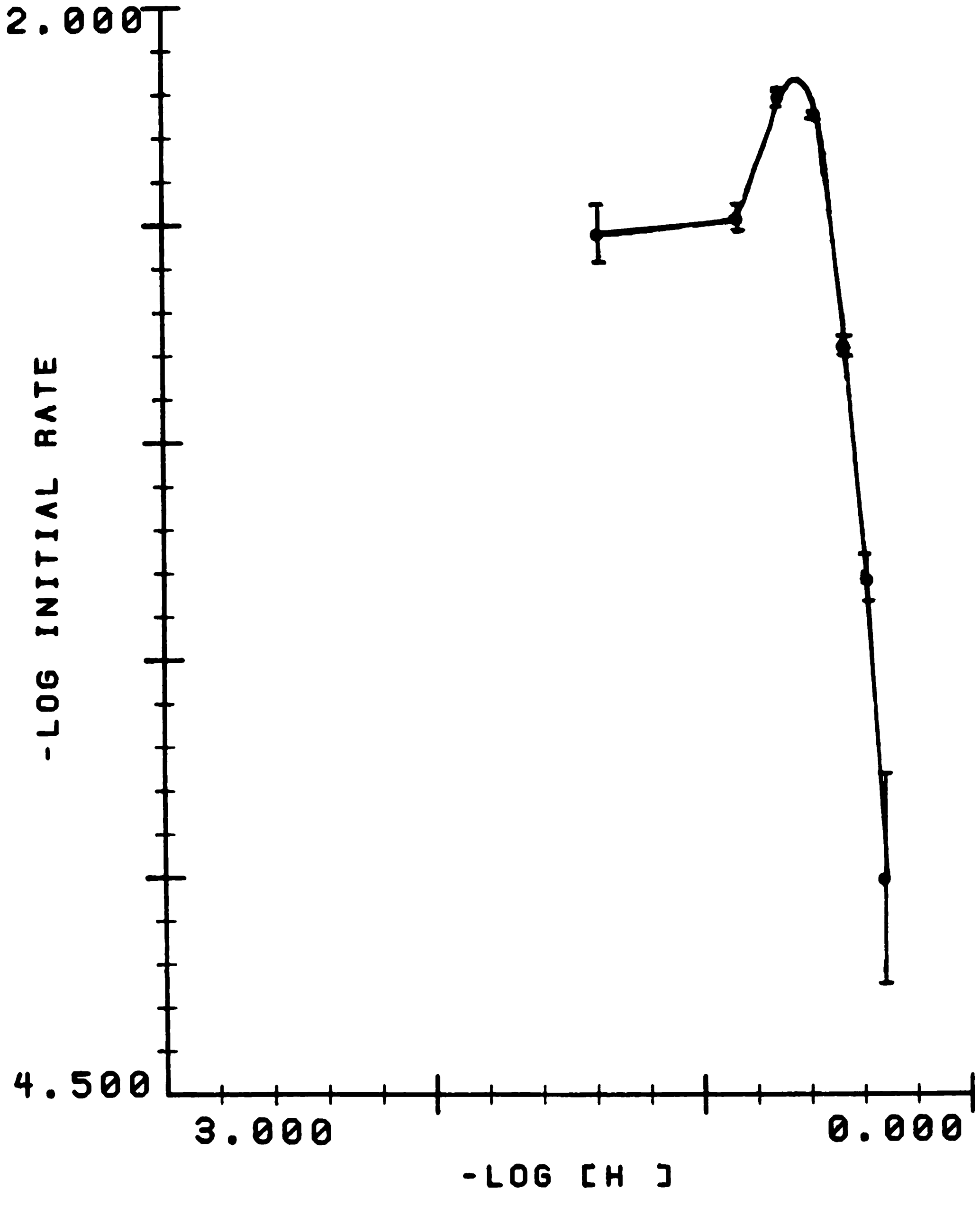

Figure 18. HNO_3 dependence of the 12-MSA formation reaction.
Ionic strength = 2.0 M
[Mo(VI)] = 0.02 M
$[Si(OH)_4]$ = 1.0×10^{-4} M

Table 5. Silicate Dependence of 12-MSA Formation

[Mo(VI)] = 0.01 M

Si M x 10^4	HNO_3 M	Initial Rate A/s x 10^3	Std. Dev. x 10^4
0.05	0.03	0.29	0.6
0.50	0.03	0.45	0.3
1.00	0.03	0.65	0.4
2.00	0.03	1.10	0.2
3.00	0.03	1.40	0.3
4.00	0.03	1.75	0.1
0.05	0.3	0.36	0.5
0.50	0.3	0.62	0.1
1.00	0.3	0.69	0.3
2.00	0.3	1.20	0.6
3.00	0.3	1.60	0.4
4.00	0.3	1.86	0.7

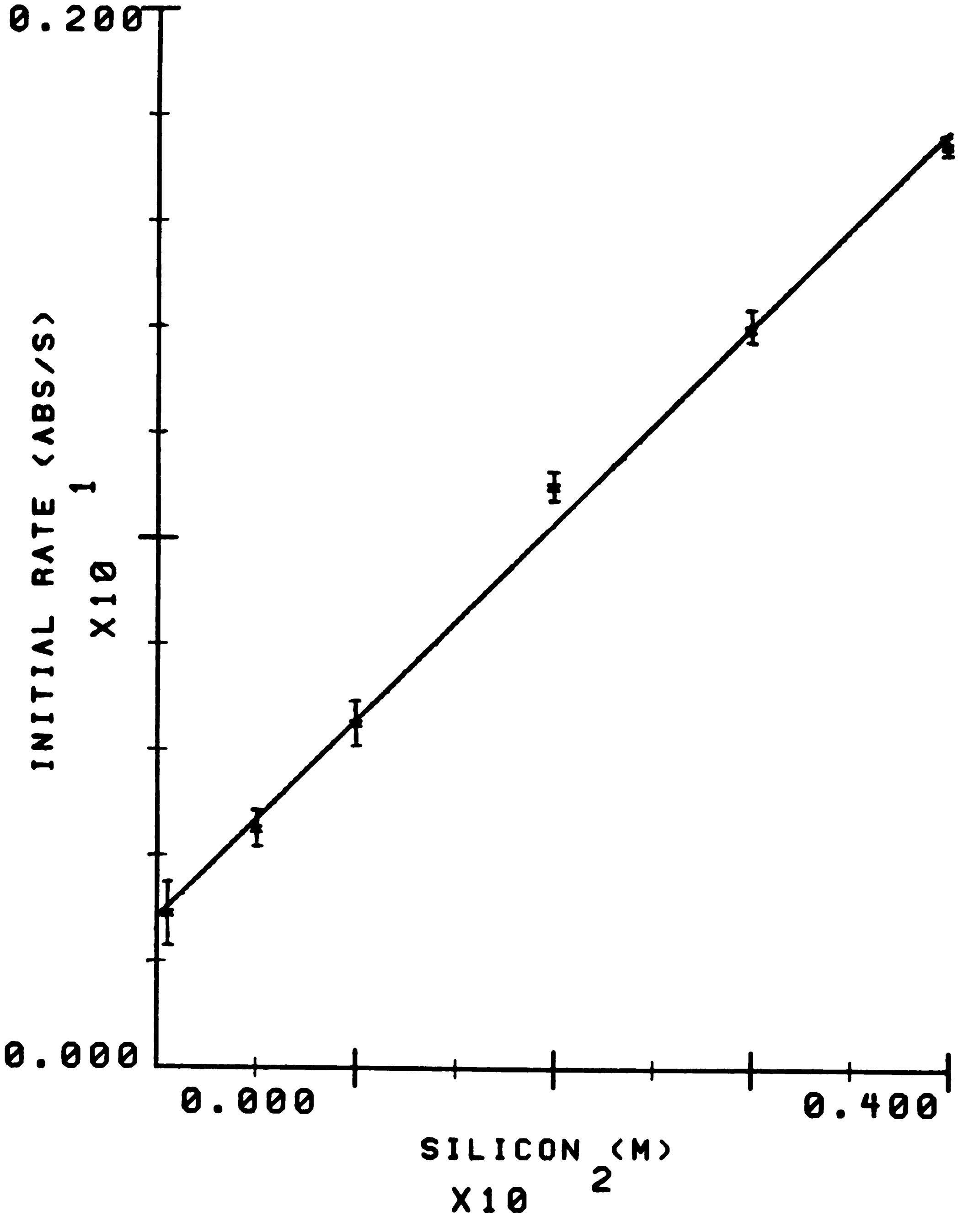

Figure 19. Silicate dependence of the 12-MSA reaction.
Ionic strength = 2.0 M
$[HNO_3]$ = 0.03 M
[Mo(VI)] = 0.01 M

data for a series of solutions with a 0.03 M acid concentration. The plot shows that the reaction is first order with respect to silicate up to a concentration of 4.00×10^{-3} M. It is doubtful that the changes in the initial rate in Figures 17 and 18 are caused by any pH dependence of the silicate unit.

The line in Figure 19 has a positive intercept. There are two possible reasons for this. Maintenance to the stopped flow system may have resulted in imperfections in the flow system where solution forms in a pocket out of the flow stream. This would cause poor rinsing and the next sample would be contaminated by small portions of the previous sample. The other possibility is that there is silicon contamination in the distilled water used or in the stopped flow system itself (the windows of the observation cell are made of quartz). Extensive mixing reduced the blank value, but did not eliminate it entirely.

It is interesting to note that the isoelectric point of Mo(VI); where MoO_3 precipitates out of solution, occurs at pH = 0.9. At hydrogen ion concentrations greater than this Mo(VI) exists predominantely as cationic monomers ($H_3MoO_3^{+}$) and dimers ($H_2Mo_2O_6^{2+}$). At lower acid concentrations Mo(VI) exists as a monomer H_2MoO_4 and several other condensed form such as the heptamer. The changes in initial rate in Figures 17 and 18 appear to correspond to changes in the form of Mo(VI) that exist in solution.

The data over the pH region of 0.3 to 0.8 were fit to a series of rate expressions with KINFIT. The best fit rate equation determined by this method was:

$$\frac{d\ \text{Absorbance}}{dt} = \frac{K_1[\text{Mo(VI)}]^3[\text{Si(OH)}_4]}{K_2\dfrac{[\text{H}^+]^7}{[\text{Mo(VI)}]^2} + \dfrac{K_3[\text{H}^+]^3}{[\text{Mo(VI)}]^2} + 1}$$

$K_1 = 4.6 \times 10^4\ \text{A}^{-1} \pm 4.4 \times 10^4\ \text{A}^{-1}\ \text{s}^{-1}$

$K_2 = 1.8 \times 10^1\ \text{A}^{-5} \pm 1.5 \times 10^1\ \text{A}^{-5}$

$K_3 = 1.2\ \text{A}^{-1} \pm 1.2\ \text{A}^{-1}$

The molar absorptivity of 12-MSA at 400 nm has not been reported in the literature. The constants determined for the rate law are not adjusted for the molar absorptivity of 12-MSA and the path length of the stopped-flow observation cell (1.94 cm). It is possible that other acid and molybdate terms are important in the rate law but were not evident in this study since a rather limited range of concentrations of molybdenum was used. The values for the constants could be refined by fitting a larger data set. The solid line in Figure 20 is a plot of the best fit rate equation while each asterisk represents an experimental data point.

A mechanism which accounts for the overall stoichiometry

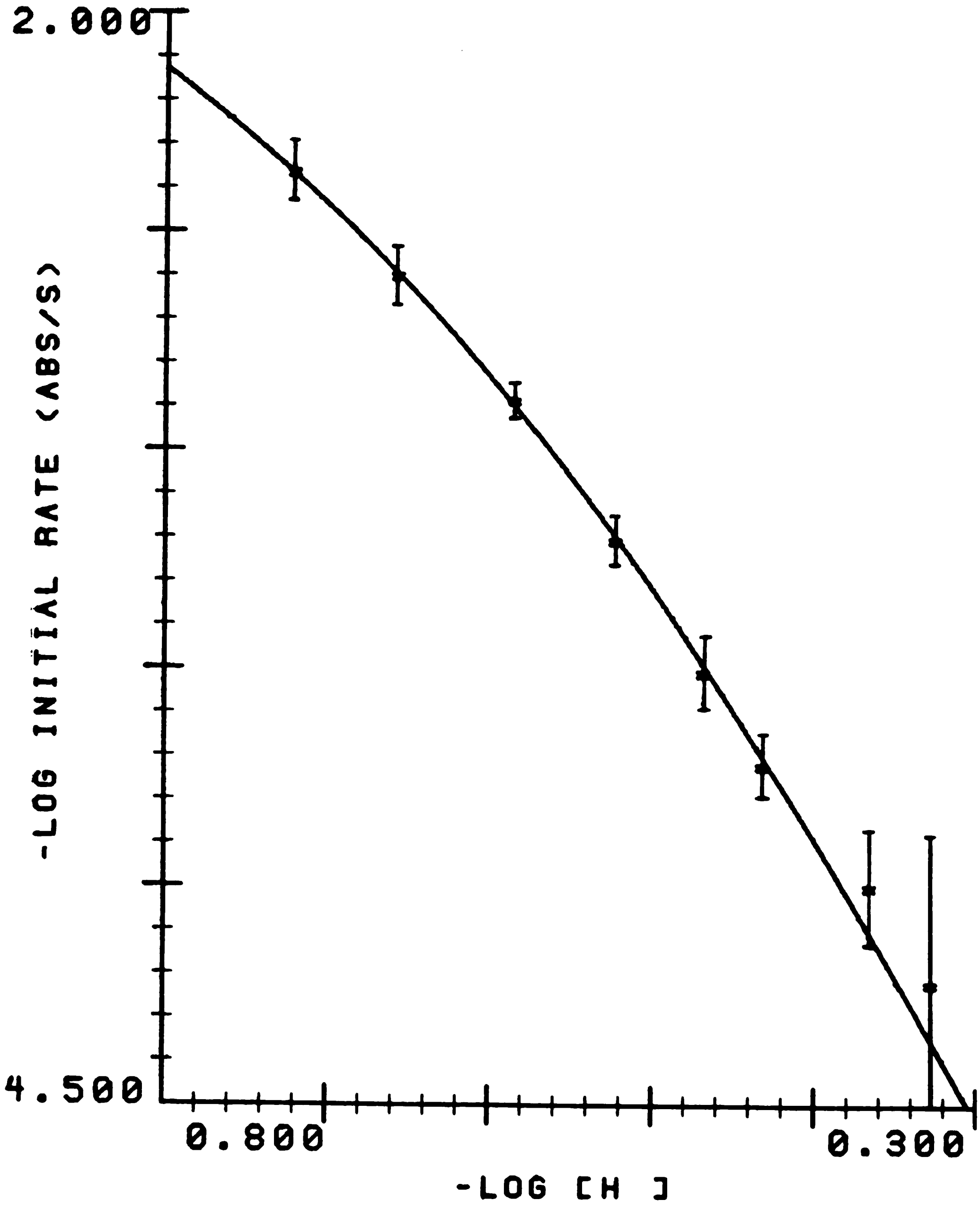

Figure 20. Acid dependence of 12-MSA formation.
Ionic strength = 2.0 M
[Mo(VI)] = 0.01 M
$[Si(OH)_4]$ = 1.0×10^{-4} M

of the reaction and which also accounts for the acid dependence of the rate law is given below:

$$HMo_2^+ + Si(OH)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_2SiMo_2 + 3H^+$$

$$H_2SiMo_2 + 2HMo_2^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} SiMo_6 + 4H^+$$

$$SiMo_6 + 2HMo_2^+ \xrightarrow{k_3} SiMo_{10} + 2H^+$$

$$SiMo_{10} + HMo_2^+ \xrightarrow{\text{rapid}} \text{12-MSA} + H^+$$

where the oxygen atoms in the intermediates have been omitted since their exact forms are unknown. Application of the steady state hypothesis to the intermediates in the above mechanism gives the following rate law:

$$\frac{d[\text{12-MSA}]}{dt} \qquad \frac{K_1[HMo_2^+][Si(OH)_4]}{K_2\frac{[H^+]^7}{[HMo_2^+]^4} + K_3\frac{[H^+]^3}{[HMo_2^+]^2} + 1}$$

where $K_1 = k_1/k_3$

$K_2 = k_{-1}k_{-2}/k_2k_3$

$K_3 = k_{-1}/k_2$

It is obvious that this rate law contains a higher order dependence on molybdenum than was experimentally determined. This could be due to the limited range of molybdenum concentrations used and that higher order dependence was not apparent in the region studied.

In order to clarify the molybdate dependence, it is necessary to include a wider range of molybdenum concentrations in the study. Extending the molybdate concentration to 0.05 M and conducting acid dependence studies in these regions would pinpoint the true molybdate dependence of the reaction.

It is probable that different mechanisms dealing with different species of molybdenum are acting in solutions more basic than pH 0.9. Studies in this area, including studies on the formation of α 12-MSA may give new insights into the differences between the α and β forms of 12-MSA.

CHAPTER VIII

OPTIMIZATION OF THE HETEROPOLYMOLYBDATE RATE METHOD FOR THE DETERMINATION OF PHOSPHATE AND SILICATE

In order to obtain the highest possible sensitivity for a rate method, the conditions are chosen to produce the fastest reaction. The Simplex method was used to determine the conditions under which the rate of formation of both phosphate and silicate is at a maximum. The results of the Simplex optimization along with the experimental results obtained under the optimal experimental conditions are presented.

A. Optimization Techniques

Scientists have tried several different procedures to optimize their experiments. The earliest attempts used a one-factor-at-a-time approach. This approach is based on the assumption that it is necessary to eliminate all but one factor from influencing a particular experiment. All of the variables are held at a low level, and then, the response of the system is determined. The factor being evaluated is then changed to its upper level and the system reevaluated. Fisher (108) proposed factorial designs where all of the factors are simultaneously varied during the experiment. Comparisons are then made between selected experiments to elucidate the main effects as well as the interactions of the factors. These methods, however, did not produce the factor level at which the system response is at an optimum.

Hostelling (107) was one of the first to attack the problem of determining the level of a factor which produces an optimum for a one dimensional or one factor case. Friedman and Savage (110) extended this technique to multifactor optimizations. In this process one factor is varied while all others are held constant. This procedure is then repeated for another factor. This sequential single-factor approach, although one of the most common methods of optimization in analytical chemistry has been shown to fail when the response surface contains a ridge (110). Box points out that it is necessary for factors to be changed together in the direction of the axis of the ridge in order to obtain an optimum (111).

The Evolutionary Operation (EVPO) method proposed by Box is a multifactor response surface design which incorporates factorial designs combined with regression techniques to locate the optimum. This technique requires a large number of complex calculations and is still prone to failure as is pointed out by Lowe (112).

In 1962 Spendly, Hext and Hinsorth (113) introduced the sequential simplex method of optimization. This multifactor method uses an empirical feedback system that does not require the large number of complex calculations of the EVPO methods. In order to describe the simplex method, first consider a function of n variables. The simplex is a geometrical figure formed in the n dimensional space by n+1 points in the space. The n+1 points form the vertices of the general simplex. The function is evaluated at each point and compared to the value of the other points. The point with the lowest response is reflected through the centroid of the opposite face of the simplex (the hyperplane of the remaining points), which forms a new simplex. The function is evaluated at this new point compared to the other responses. The vertex which gives the lowest response is again reflected. The process is continued as the simplex tracks the optimum.

The simplex optimization procedure has been modified by Nelder and Mead (modified simplex) (114) and by Denton (super modified simplex) (115). These modifications have dealt with the expansion and contraction of the simplex figure in order to facilitate the simplex approach and convergence on the optimum. The new vertex is located on a line formed by the vertex with the lowest response and the centroid of the opposite face. The modified simplex allows the new vertex to be one of four points along the line previously described, representing a reflection (the same as in the original simplex method), expansion, contraction and massive contraction. The super modified simplex allows the new vertex to be located anywhere along the line previously described. The distance and direction along the line is determined by a function based on the shape of the response curve in the region of the simplex. The shape is given by a second order polynomial fitted to the responses of the vertex with the lowest response, its reflection and the centroid of the hyperplane of the remaining points. If the curve is concave down, then a contraction occurs to "zero in" on the optimum. In the concave up case, an expansion occurs toward the predicted optimum. The greater the slope (indicating a rapid approach to the optimum), the smaller the expansion and vice versa. This procedure increases the reliability of the simplex method in the presence of noise and the efficiency of conforming to boundary conditions. The simplex algorithm has been applied to both numerical analysis and the optimization of dynamic systems. The application presented here is a combination of both types. The rate equations obtained in Chapters V and VI were based on the dynamic chemical system. These equations were then optimized using the simplex method. There is an extra advantage to having an equation that describes the system - if it is three dimensional or less it is possible to visualize the response surface.

B. Simplex Optimized Phosphate and Silicate Determinations

The Nelder and Mead version of Simplex was used to determine the conditions for the fastest rate of heteropolymolybdate formation. In each case the upper limit on the acid concentration was 0.60 M and the lower limit was 0.02 M. The molybdate concentration was bound between the limits of 0.01-0.08 M. An additional constraint was placed on the system. In order to eliminate solutions in which unreactive Mo(VI) species form, any vertex with an acid-to-molybdate ratio less than 20 was rejected. An undesirable response was associated with any vertex that violated any of the constraints imposed on the parameters. This allows the Simplex to approach the boundary, but not cross it. The Simplex was started with several sets of different vertices to ensure convergence on a global rather than a local optimum.

The subroutine SMPLX2.F4 is a FORTRAN IV program written by Joseph (116) which performs the comparison of responses between vertices and calculates the new vertex of the simplex figure. This general purpose subroutine was used in conjunction with a main program to compute the optimum conditions for the heteropolymolybdate formation reactions. The main program enables the user to enter the starting simplex vertices and the resolution in the parameters that are optimized (acid and molybdate concentration). The function to be optimized (the experimental rate equation) is also contained in the main program. The response of the system is the rate predicted from the rate equation. A set of vertices as well as the responses associated with the vertices is printed out for each simplex move in order to follow the progress of the simplex.

The optimum conditions determined by the simplex method for the reaction-rate measurement for phosphate determinations is a Mo(VI) concentration of 0.02 M and an acid concentration of 0.4 M. The optimum conditions determined by the simplex method for silicate determinations are 0.015 M Mo(VI) and 0.30 M HNO_3. It is necessary to use the same reaction conditions for a simultaneous analysis so a compromise between the two sets of conditions was used (0.02 M Mo(VI) and 0.30 M HNO_3).

C. Experimental Procedure

A series of separate standard solutions of phosphate and silicate were prepared. The initial rate of reaction of these solutions was measured in the manner previously described in Chapter 5. Tables 6 and 7 present the data obtained for the individual phosphate and silicate determinations. Figures 22 and 23 are the analytical curves obtained for these determinations. The phosphate determination is not linear above a phosphate concentration of 1.5×10^{-4}. At this concentration the ratio of molybdenum-to-phosphate is only 65 (5 times the

Table 6. Phosphate Determination.

[Mo(VI)] = 0.02 M

$[HNO_3]$ = 0.30 M

$[PO_4^{3-}]$ M x 10^3	Initial Rate A/s x 10^2	Std. Dev. of Rate x 10^3
0.05	3.1	0.7
0.075	4.5	0.6
0.10	5.8	0.4
0.15	8.2	0.5
0.20	10.1	0.6
0.30	12.9	0.9
0.40	14.2	0.5

Slope = 5.07 x 10^2

Y-intercept = 6.4 x 10^{-3}

Table 7. Silicate Determination

[Mo(VI)] = 0.02 M

[HNO_3] = 0.30 M

[$Si(OH)_4$] M x 10^3	Initial Rate A/s x 10^4	Std. Dev. of Rate x 10^4
0.05	0.4	0.2
0.10	0.8	0.2
0.20	1.7	0.2
0.30	2.5	0.2
0.40	3.2	0.4
0.50	4.3	0.1
1.00	8.6	0.1
2.00	16.7	0.2

Slope = 0.855

Y-intercept = 0.0

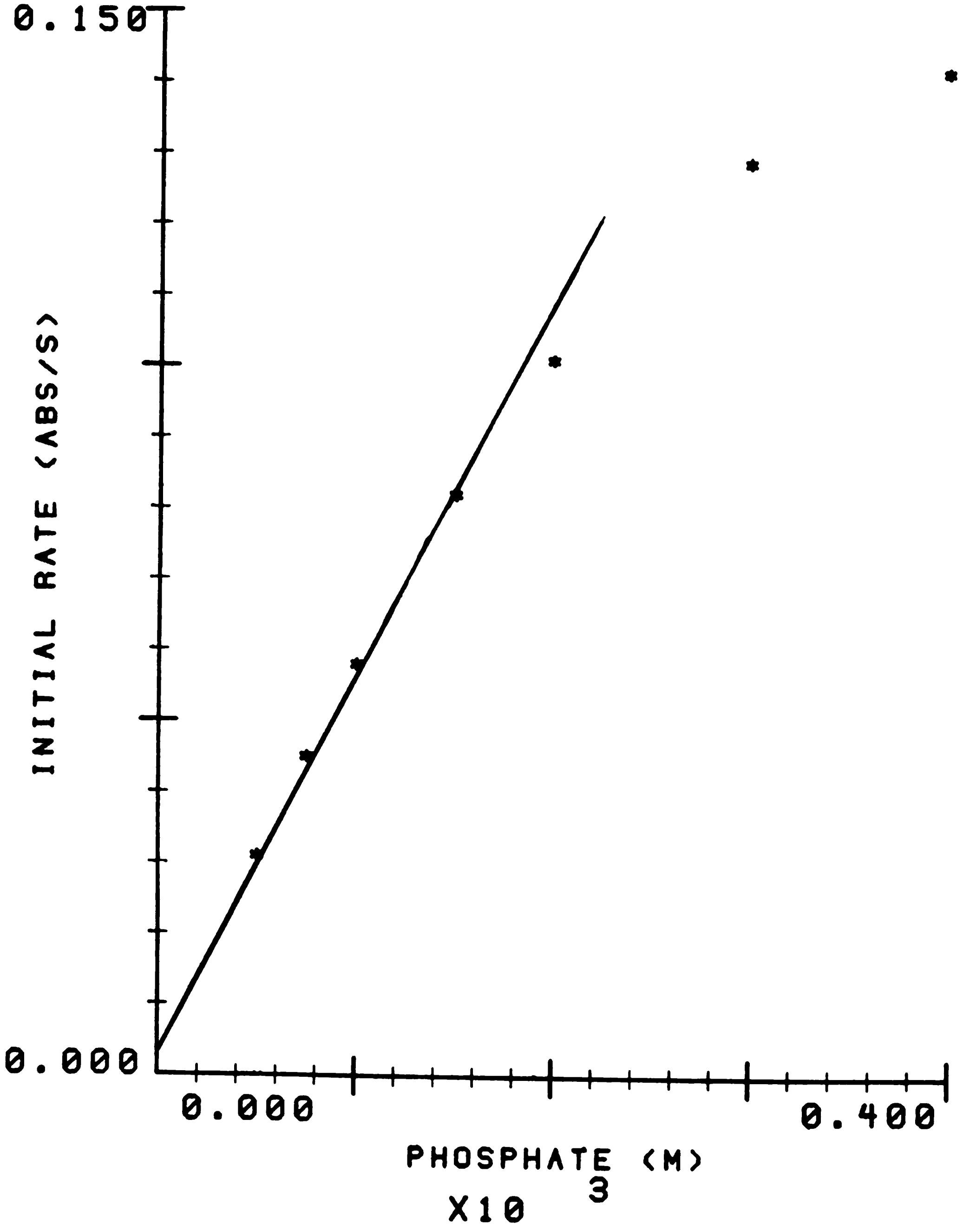

Figure 21. Phosphate determination.

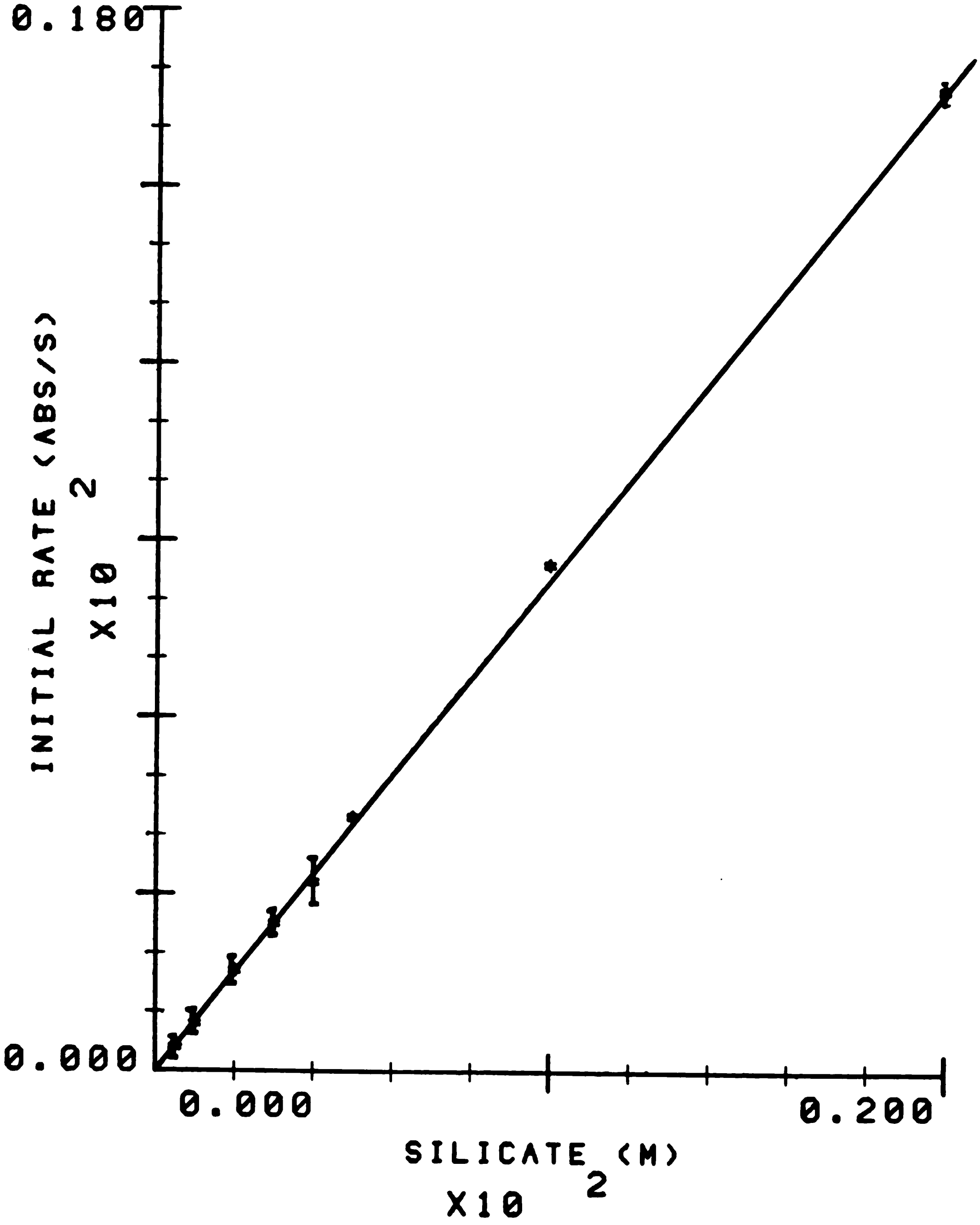

Figure 22. Silicate determination.

stoichiometric ratio). This leads to the formation of unsaturated products and causes the bend off in the analytical curve. In contrast, the silicate determination was linear up to a molybdenum-silicate ratio of 10 which is slightly less than the stoichiometric ratio.

The simultaneous determination of phosphate and silicate was attempted using the analytical curves derived for the individual phosphate and silicate analyses. Standard solutions were prepared with the phosphate and silicate in the same solution. The change in absorbance which occurred upon mixing the standard solutions with the acidified molybdate solution was monitored for 200 s. The resulting data were analyzed during the first 20 s to determine the initial rate of the phosphate reaction. The rate was averaged over the period in which the rate was zero order with respect to time. During this time, there is a very small change in absorbance due to an induction period for the silicate reaction. In all cases observed, the rate of the induction period during the time that the initial rate of the phosphate reaction was measured was less than 2% of the initial rate of the phosphate reaction.

The remaining data were analyzed to determine the initial rate of the silicate reaction. The time at which the initial rate was measured varied because the reaction possesses a concentration dependent induction period. The concentrations of phosphate and silicate were determined from the respective analytical curve determined for the individual analyses.

The results of simultaneous determinations of phosphate and silicate are presented in Table 8. The simultaneous determination of phosphate and silicate with an accuracy of 5% is possible only for solutions with low phosphate concentrations. As the phosphate concentration increases the molybdate concentration is depleted before the silicate reaction starts resulting in an increase in the error of the silicate determination.

D. Conclusion

The linearity of the individual analyses can be improved by using molybdate solutions of higher concentrations. A higher concentration of molybdenum would extend the linear range of analysis for both phosphate and silicate. In addition, it would reduce the interference of high phosphate concentrations on silicate determinations because the molybdate would not be as easily depleted. The rate due to the induction period of the silicate reaction would have to be checked to see if it would cause an interference in the phosphate determination.

The best procedure to follow when optimizing the simultaneous determination is to perform the analyses required by the simplex and optimize the system for the

Table 8. Simultaneous Determination of Phosphate and Silicate.

Mo(VI) = 0.02 M

HNO_3 = 0.30 M

Actual M x 10^3		Experimental M x 10^3		% Relative Error	
$Si(OH)_4$	PO_4^{3-}	$Si(OH)_4$	PO_4^{3-}	$Si(OH)_4$	PO_4^{3-}
1.00	0.050	0.96	0.051	4.	2.
0.50	0.050	0.48	0.051	4.	2.
0.50	0.100	0.47	0.100	6.	0.
0.50	0.150	0.42	0.143	16.	1.

minimum error of analysis. An optimization of this type would take about sixty days unless an automated sample preparation system was used and the molybdenum-acid equilibrium was accelerated. The attainment of equilibrium could probably be hastened by heating the solution. If the equilibration time could be reduced to thirty minutes without affecting the species formed in solution, the entire optimization could probably be done in a single day.

The optimum conditions for the rate determination of phosphate are also applicable to the equilibrium method. The same is not true for the silicate conditions. The β form of 12-MSA decomposes to the α form and a true equilibrium is not reached until complete conversion to the α form. The present study addressed only the rate method of analysis based on the formation of β-12-MSA.

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APPENDICES

APPENDIX 1

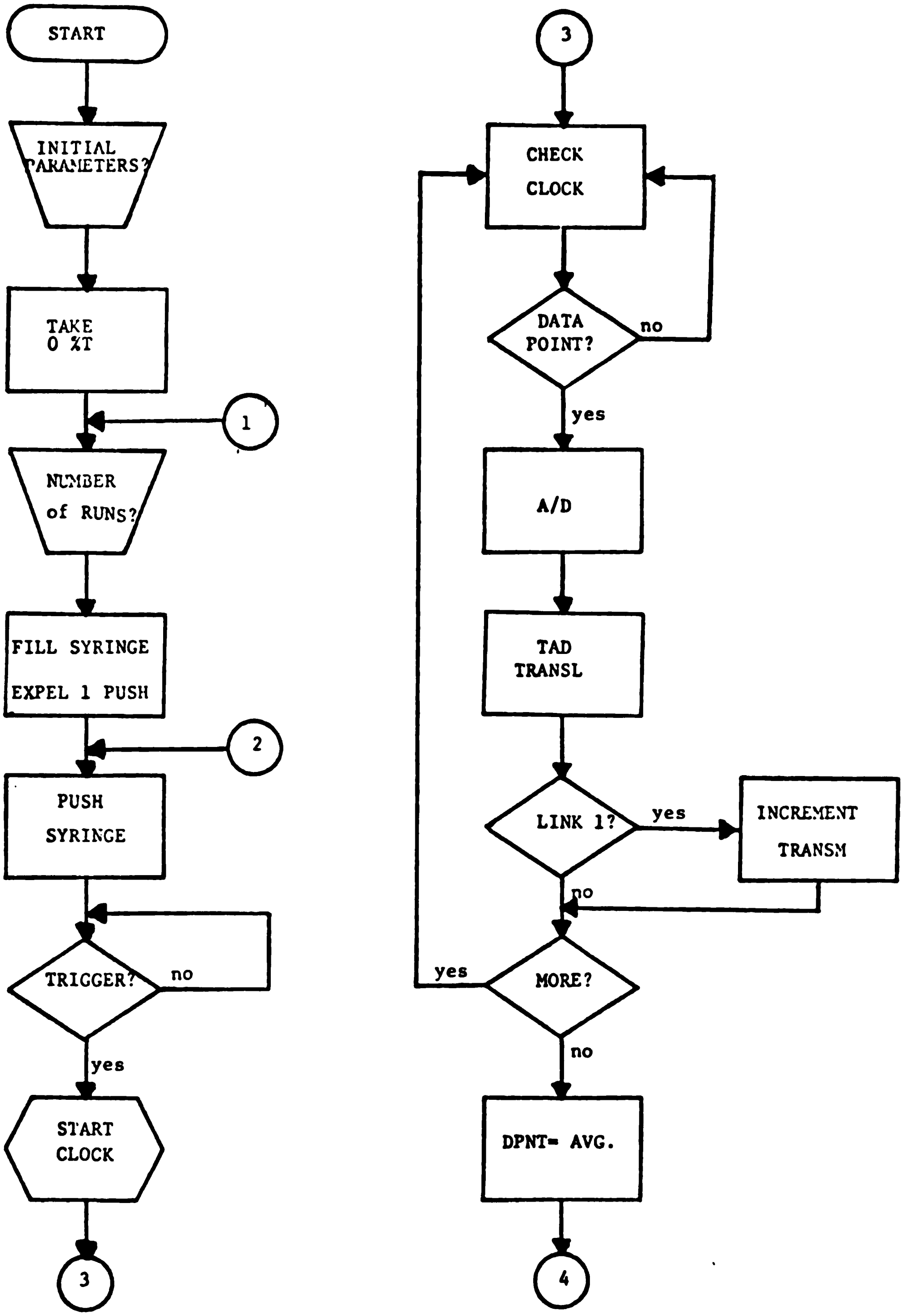

Figure 23. Flowchart for data acquisition and analysis programs.

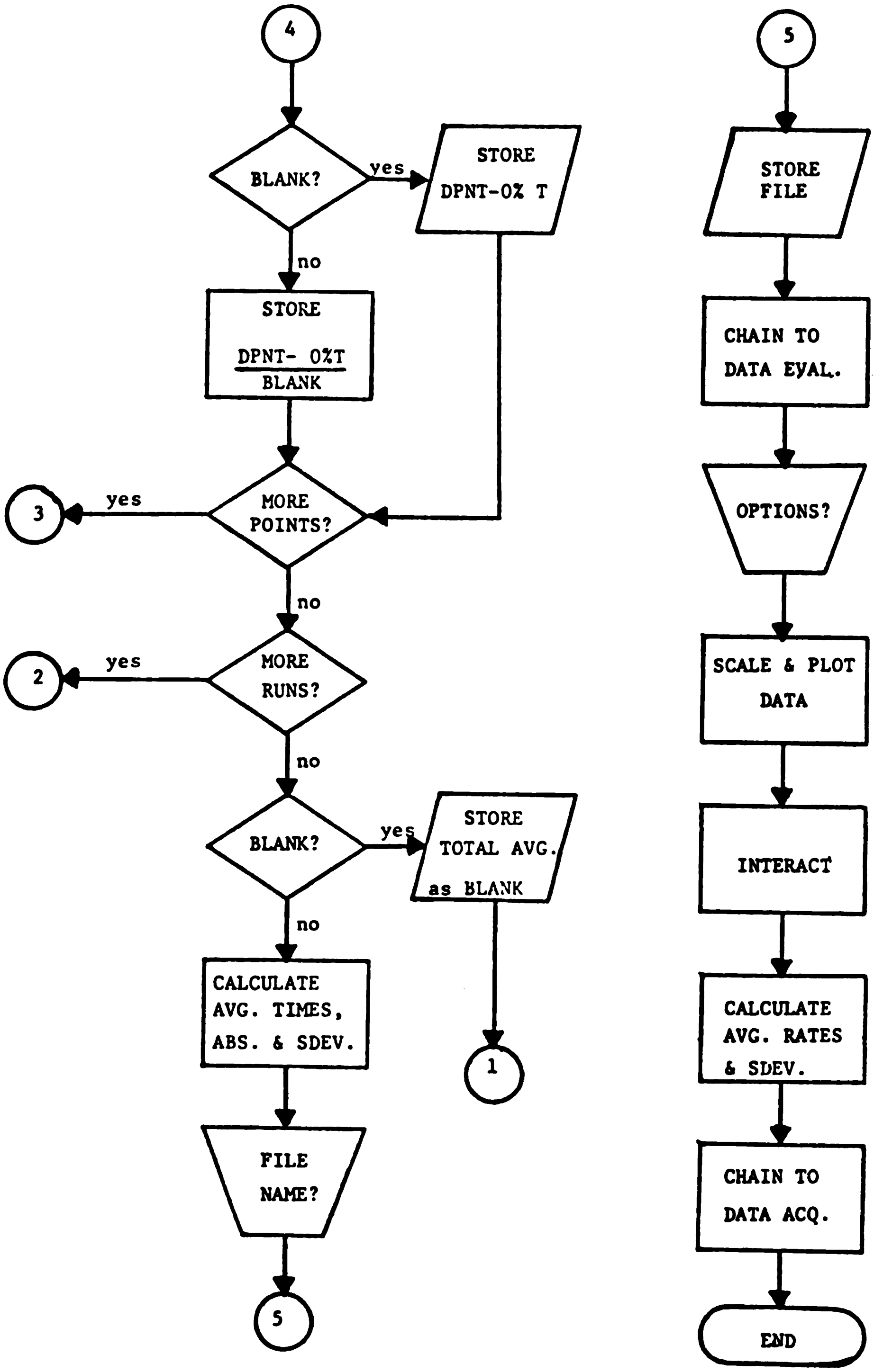

Figure 23. Continued.

APPENDIX 2

SELECTED PROGRAM LISTINGS

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C       PROGRAM RGSFMN.FT                    ROY GALL
C       LOADING SEQUENCE:
C
C       LO RGSFMN,RGTIME,RGWAIT,RGRINS,RGFILL,RGSTOR(HOG)
C
        COMMON IDATA,SDEV,T,AVG
        DIMENSION IDATA(1000), SDEV(100), T(100), AVG(100)
S       ABSYM   AINC    0012    /AUTO INCREMENT REGISTER
S       ABSYM   MNDP1   0161    /-# OF AVERAGES IN TIME PERIOD 1
S       ABSYM   MNCC1   0162    /-# OF CLOCK COUNTS
S       ABSYM   MNAP1   0163    /-# OF DATA ACQUISITIONS PER AVERAGE
S       ABSYM   MNEC1   0134    /-# OF EXTRA CLOCK COUNTS
S       ABSYM   MNCC2   0135    /DELAY PERIOD CLOCK COUNTS
S       ABSYM   MNEC2   0136    /DELAY PERIOD EXTRA CLOCK COUNTS
S       ABSYM   NAP3    0137    /# OF DATA ACQUISITIONS PER AVERAGE
S       ABSYM   MNDP3   0140    /-# OF AVERAGES IN TIME PERIOD 2
S       ABSYM   MNCC3   0141    /-# OF CLOCK COUNTS
S       ABSYM   MNAP3   0142    /-# OF DATA ACQUISITIONS PER AVERAGE
S       ABSYM   MNEC3   0143    /-# OF EXTRA CLOCK COUNTS
S       ABSYM   BLOS    0144    /BLANK(-1) OR SAMPLE(-4)
S       ABSYM   TRNSL   0145    /%T STORAGE
S       ABSYM   TRNSM   0146    /DITTO
S       ABSYM   TMPD    0147    /TIME PERIOD
S       ABSYM   MZERT   0150    /-0%T
S       ABSYM   BLNK    0151    /100%T  BLANK
S       ABSYM   MAP     0152    /=MNAP
S       ABSYM   MNCC    0153    /=MNCC
S       ABSYM   MNEC    0154    /=MNEC
S       ABSYM   DPNT    0155    /TEMPORARY STORAGE FOR DATA POINT
S       OPDEF   TADI    1400    /TAD I
S       OPDEF   DCAI    3400    /DCA I FOR AUTOINCR
S       OPDEF   CLZE    6130    /ONES IN AC CLEAR CLOCK ENABLE REGISTER
S       SKPDF   CLSK    6131    /SKIP IF CLOCK OVERFLOWS OR ST SET
S       OPDEF   CLOE    6132    /ONES IN AC SET CLOCK ENABLE REGISTER
S       OPDEF   CLAB    6133    /AC TO BUFFER PRESET + COUNTER REGISTERS
S       OPDEF   CLSA    6135    /CLOCK STATUS REGISTER TO AC,ONES CLEAR
S       OPDEF   CDF     6201    /CHANGE TO DATA FIELD 0
S       OPDEF   CDF1    6211    /CHANGE TO DATA FIELD 1
S       OPDEF   DEACT   6651    /DEACTIVATE CIRCUIT
S       OPDEF   ACTIV   6652    /ACTIVATE CIRCUIT
S       SKPDF   TRIGR   6654    /SKIP ON SF TRIGGER
S       OPDEF   OVALV   6661    /SET FF1
S       OPDEF   SUCK    6662    /SET FF2
S       OPDEF   PUSH    6664    /SET FF3
S       OPDEF   CVALV   6671    /CLEAR FF1
S       OPDEF   PRESS   6672    /CLEAR FF2
S       OPDEF   WASTE   6674    /CLEAR FF3
S       OPDEF   MQL     7421    /AC TO MQ, 0 TO AC
S       OPDEF   DVI     7407    /DIVIDE
S       OPDEF   SWBA    7447    /SWITCH FROM MODE B TO A
S       OPDEF   CLASWP  7721    /LOAD MQ TO AC, CLEAR MQ
```

```
C
C   INITIALIZE CIRCUITRY FOR COMPUTER CONTROLLED STOPPED FLOW OPERATION
C
S       CLA CLL
S       6521            /SET MUX TO CHANNEL 0
S       NOP
S       NOP
S       CLA CLL
S       TAD (0177
S       DCA AINC
S       CVALV
S       PRESS
S       WASTE
S       ACTIV
S       SWBA
S       CLA CLL
        IZERO=0
        IBLOS=2
        IPB=0
        NAVE3=0
C
C       READ EXPERIMENTAL CONDITIONS FROM TERMINAL
C
23      READ(1,1)ISAME
1       FORMAT('0=ALL PARAMETERS SAME AS BEFORE, 1=CHANGE PARAMETERS',I1)
        IF(ISAME)210,200,7
7       READ(1,2)NTMPD
        NTMPD=((NTMPD-1)*3+1)*-1
2       FORMAT('1=1 TIME PERIOD, 2=2 TIME PERIODS + DELAY',I1)
        READ(1,6)NPTS1,NAVE1,TMBT1
6       FORMAT('# OF POINTS PER AVERAGE (I4 FORMAT):',I4,/,'# OF AVERAGES
      1 (I4 FORMAT):',I4,/,'TIME BETWEEN POINTS IN SECONDS
      1 (E13.6):',E13.6)
        CALL RGTM(TMBT1,NPTS1,ICNT1,ITLP1)
        NAVE3=0
        IF(NTMPD+2)13,100,100
13      READ(1,4)TMBT2
4       FORMAT('ENTER LENGTH OF DELAY BETWEEN DATA TAKING PERIODS IN
     1 SECONDS(E13.6 FORMAT):',E13.6)
        CALL RGTM(TMBT2,0,ICNT2,ITLP2)
12      READ(1,5)NPTS3,NAVE3,TMBT3
5       FORMAT('# OF POINTS PER AVERAGE (I4 FORMAT):',I4,/,'# OF AVERAGES
     1 (I4 FORMAT):',I4,/,'TIME BETWEEN POINTS IN SECONDS (E13.6 FORMAT)
     1 ',E13.6)
        CALL RGTM(TMBT3,NPTS3,ICNT3,ITLP3)
```

```
C
C        -0% T STORED
C
100      READ(1,101)IUYTR
101      FORMAT('SET STOPPED FLOW FOR ZERO PERCENT T AND HIT RETURN',I1)
S        PAGE
S        LAP
S        CLA CLL
S        DCA ZTL
S        DCA ZTM
S        TAD (-144
S        DCA CNT
S        CLA CMA          /SET AC=-1
S        CLZE             /CLEAR CLOCK ENABLE REGISTER
S        CLA
S        TAD (-144
S        CLAB             /-100 TO CLOCK BUFFER AND CLOCK COUNTER
S        CLA CLL
S        TAD (5400
S        CLOE             /SET CLOCK ENABLE
S        CLSA             /CLOCK STATUS TO AC
SDONE1,  CLSK             /SKIP ON CLOCK INTERRUPT
S        JMP DONE1
S        CLSA             /CLOCK STATUS TO AC
S        CLA CLL
S        6531             /CLEAR FLAG AND CONVERT
SDONE2,  6532             /SKIP ON FLAG
S        JMP DONE2
S        6534             /DRIVE DATA INTO AC
S        TAD (4000        /CONVERT TO POSITIVE BINARY
S        CLL
S        TAD ZTL
S        DCA ZTL
S        SZL              /SKIP IF NO OVERFLOW IN ZTL
S        ISZ ZTM          /CARRY 1 TO ZTM
S        CLL
S        ISZ CNT          /SKIP IF FINISHED 100 LOOPS
S        JMP DONE1
S        CMA
S        CLZE             /CLEAR CLOCK ENABLE REGISTER
S        CLA
S        TAD ZTL
S        MQL              /LOAD MQ FROM AC AND CLEAR AC
S        TAD ZTM
S        DVI              /EAE DIVIDE BY 100
S        144
S        7721             /LOAD AC FROM MQ THEN CLEAR MQ
S        CIA
S        DCA I ZERL
S        CLA CLL
S        TAD (207
SBELL,   TSF
S        JMP BELL
S        TLS
S        CLA CLL
S        TAD MZERT
S        DCA \IPB
S        CLA CLL
         WRITE(1,756)IPB
         IPB=0
S        JMP \200
SZTL,    0
SZTM,    0
SCNT,    0
SZERL,   MZERT
```

```
S       EAP
S       PAGE
S       CLA CLL
200     READ(1,3)IBLOS,NSYFL,NDAPU,NRINS
3       FORMAT('BLANK(0) OR SAMPLE(1) RUN:',I1,/,'# OF SYRINGE
      1 FILLINGS PER RUN(1-8):',I1,/,'# OF DATA PUSHES PER SYRINGE
      1 FILLING(1-5):',I1,/,'# OF RINSINGS(0-8):',I1)
        NDAPQ=NDAPU
        NEXPU=5-NDAPU
        NSFL=NSYFL
        WRITE(1,756)NSFL
        CALL RGRIN(NRINS)
        CALL RGFIL
210     CONTINUE
S       CLL CLA
S       TAD \IBLOS
S       DCA BLOS
S       TAD \NAVE1
S       DCA I NP10
S       TAD \NAVE1
S       CIA
S       DCA MNDP1
S       DCA TRNSM
S       DCA TRNSL
S       TAD \ICNT1
S       TAD \ICNT1
S       CIA
S       DCA MNCC1
S       TAD \NPTS1
S       CIA
S       DCA MNAP1
S       TAD \ITLP1
S       TAD \ITLP1
S       CIA
S       DCA MNEC1
S       TAD \ICNT2
S       TAD \ICNT2
S       CIA
S       DCA MNCC2
S       TAD \ITLP2
S       TAD \ITLP2
S       CIA
S       DCA MNEC2
S       TAD \NAVE3
S       DCA NAP3
S       TAD \NAVE3
S       CIA
S       DCA MNDP3
S       TAD \ICNT3
S       TAD \ICNT3
S       CIA
S       DCA MNCC3
S       TAD \NPTS3
S       CIA
S       DCA MNAP3
S       TAD \ITLP3
S       TAD \ITLP3
S       CIA
S       DCA MNEC3
S       TAD \NTMPD
S       DCA TMPD
S       TAD (-2            /CLOCK COUNTER = .2 MSEC
S       CLAB               /AC TO CLOCK COUNTER
S       PUSH
STR,    TRIGR
S       JMP TR
S       CLA CLL
S       TAD (5400
S       CLOE               /START CLOCK
S       CLSA               /CLEAR CLOCK FLAG
S       JMP GO
SNP10,  NAP1
```

```
S       PAGE
S       LAP
SGO,    CLA CLL
SAGN,   TAD MNAP1
S       DCA MAP
SDATAP, CLSK            /SKIP ON CLOCK INTERRUPT
S       JMP DATAP
S       CLSA            /CLEAR CLOCK FLAG
S       CLL CLA
S       6531            /CLEAR FLAG AND CONVERT A TO D
SDONEP, 6532            /SKIP ON FLAG
S       JMP DONEP
S       6534            /DRIVE DATA INTO AC
S       TAD (4000       /CONVERT TO POSITIVE BINARY
S       CLL
S       TAD TRNSL       /SUMMATION OF
S       DCA TRNSL       /ANALOG POINTS
S       SZL
S       ISZ TRNSM       /CARRY OF 1 IN ADDITION
S       CLL
S       ISZ MAP         /CHECK FOR MORE AVERAGES
S       JMP DATAP       /PER DATA POINT
S       TAD TRNSL       /EAE DIVISION OF THE
S       MQL             /SUMMATION OF ANALOG
S       TAD TRNSM       /POINTS BY THE NO. OF
S       DVI             /POINTS AVERAGED TO YIELD
SNAP1,  0               /ONE DATA POINT
S       7721            /LOAD AC FROM MQ THEN CLEAR MQ
S       DCA DPNT        /DATA POINT STORAGE LOCATION
S       DCA TRNSL       /CLEAR STORAGE LOCATIONS
S       DCA TRNSM
S       TAD BLOS        /BLANK(0) OR SAMPLE(1)
S       SNA
S       JMP BLK         /BLANK STORAGE
S       CLA
S       TAD BLNK        /GET BLANK
S       DCA DBLNK
S       TAD DPNT        /GET DATA POINT
S       TAD MZERT       /SUBTRACT 0%T LEVEL
S       DVI             /EAE DIVIDE BY
SDBLNK, 0               /AVERAGE BLANK VALUE
S       7721            /LOAD AC FROM MQ THEN CLEAR MQ
S       SZL
S       JMP ERR         /SAMPLE %T > BLANK %T
S       JMP STORE
SBLK,   TAD DPNT
SSTORE, CDF1            /STORE DATA IN FIELD 1
S       DCAI AINC       /AUTO INCREMENTED DATA LOCATION
S       CDF             /CHANGE TO FIELD 0
```

```
S       CLA CLL
S       TAD MNCC1
S       DCA MNCC
S       TAD MNEC1
S       DCA MNEC
S       ISZ MNDP1
S       JMP MOPTS
S       JMP TIMUP
SMOPTS, TAD MNCC
S       SZA
S       JMP WAIT
S       JMP EXTRA
SWAIT,  CLA CLL
S       CLSK
S       JMP WAIT
S       CLSA
S       CLA CLL
S       ISZ MNCC          /CHECK CLOCK COUNTER
S       JMP MOPTS         /TAKE MORE POINTS
SEXTRA, TAD MNEC          /CHECK EXTRA WAITING LOOP
S       SNA               /NOT FINISHED YET
S       JMP AGN
S       CLL CLA
S       TAD (1            /LOAD CLOCK COUNTER FOR 4096 COUNTS
S       DCA MNCC
S       JMP MOPTS         /WAIT ANOTHER .4096 SEC
STIMUP, ISZ TMPD          /MORE THAN 1 TIME PERIOD?
S       JMP DELAY         /GO TO DELAY PERIOD
S       JMP MORE          /FINISHED ONE RUN
SDELAY, ISZ TMPD
S       JMP DEL2
SDEL3,  TAD MNCC3         /RESET CLOCK COUNTERS FOR SECOND DATA PERIOD
S       DCA MNCC1
S       TAD MNEC3
S       DCA MNEC1
S       TAD MNAP3
S       DCA MNAP1
S       TAD NAP3
S       DCA NAP1
S       TAD MNDP3
S       DCA MNDP1
S       TAD (-1
S       DCA TMPD
S       JMP AGN
SDEL2,  TAD MNCC2         /RESET CLOCK COUNTERS FOR DELAY PERIOD
S       DCA MNCC
S       TAD MNEC2
S       DCA MNEC
S       JMP MOPTS
SERR,   7721              /CLEAR AC,LINK,MQ
S       TAD BLNK
S       JMP STORE
S       EAP
S       PAGE
SMORE,  WASTE             /FINISHED ONE RUN
S       CLA CLL
        ILONG=-4
        CALL RGWAT(ILONG)
311     NDAPQ=NDAPQ-1
C*************************
756     FORMAT(I8)
C****************************
```

```
        IF(NDAPQ)310,310,210
310     DO 340 LM=1,NEXPU
S       PUSH
S       CLA CLL
        ILONG=-3
        CALL RGWAT(ILONG)
320     CONTINUE
S       WASTE
S       CLA CLL
        ILONG=-3
        CALL RGWAT(ILONG)
330     CONTINUE
340     CONTINUE
        NSYFL=NSYFL-1
        IF(NSYFL)350,350,600
600     CALL RGFIL
350     IF (IBLOS)360,360,380
C
C       STORE BLANK VALUE  (100%T)
C
SMNPT,  0
SBLNKL, 0
SBLNKM, 0
360     CONTINUE
S       CLA CLL
S       TAD (-177
S       TAD AINC
S       DCA NPT
S       TAD NPT
S       CIA
S       DCA MNPT
S       DCA BLNKL
S       DCA BLNKM
S       TAD (177
S       DCA AINC
S       CLL
SBKA,   CDF1             /CHANGE TO FIELD 1
S       TADI AINC        /GET ONE BLANK POINT
S       CDF              /CHANGE BACK TO FIELD 0
S       TAD BLNKL
S       DCA BLNKL
S       SZL
S       ISZ BLNKM        /CARRY OF 1 ON ADDITION
S       CLL
S       ISZ MNPT         /GET MORE POINTS
S       JMP BKA
S       CLA CLL
S       TAD BLNKL        /SET UP EAE FOR DIVISION
S       MQL              /OF THE SUMMATION OF ALL
S       TAD BLNKM        /THE BLANK POINTS BY THE
S       DVI              /NUMBER OF BLANK POINTS
SNPT,   0                /TO YIELD THE AVERAGE BLANK
S       7721
S       TAD MZERT        /SUBTRACT 0%T
S       DCA BLNK         /STORE IN LOCATION BLNK
S       TAD (177         /RESET AINC FOR SAMPLE STORAGE
S       DCA AINC
S       CLA CLL
S       TAD BLNK
S       DCA \IPB
S       CLA CLL
        WRITE(1,756)IPB
        GO TO 200
380     NDAPU=NDAPU*NSFL
381     CALL RGSTO(NPTS1,NPTS3,NAVE1,NAVE3,ITLP1,ITLP2,ITLP3,ICNT1,ICNT2,
     6  ICNT3,NSFL,NDAPU,NTMPD)
998     CONTINUE
S       DEACT
S       CLA CLL
        CALL CHAIN('RGMAIN')
999     END
```

```
C       PROGRAM RGRINS.FT                    ROY GALL
C
        SUBROUTINE RGRIN(NRINS)
C
C       THIS SUBROUTINE RINSES THE STOPPED FLOW SYRINGES THE
C       SPECIFIED (NRINS) NUMBER OF TIMES
C
S       OPDEF   OVALV   6661    /SET FF1
S       OPDEF   SUCK    6662    /SET FF2
S       OPDEF   PUSH    6664    /SET FF3
S       OPDEF   CVALV   6671    /CLEAR FF1
S       OPDEF   PRESS   6672    /CLEAR FF2
S       OPDEF   WASTE   6674    /CLEAR FF3
S       CVALV
S       PRESS
S       WASTE
S       CLA CLL
        DO 20 J=1,NRINS
S       OVALV
S       CLA CLL
        CALL RGWAT(-4)
S       SUCK
S       CLA CLL
        CALL RGWAT(-10)
S       CVALV
S       CLA CLL
        CALL RGWAT(-4)
S       PRESS
S       CLA CLL
        CALL RGWAT(-4)
        DO 20 K=1,6
S       PUSH
S       CLA CLL
        CALL RGWAT(-3)
S       WASTE
        CALL RGWAT(-3)
20      CONTINUE
        RETURN
        END
```

```
C       PROGRAM RGSTOR.FT                  ROY GALL
C
C       THIS PROGRAM CALCULATES THE AVERAGE ABSORBANCE AS WELL AS
C       THE STANDARD DEVIATION OF THE ABSORBANCE VALUES
C       THESE THREE PARAMETERS ARE THEN STORED IN THE SPECIFIED
C       FILENAME ON FLP2
C
        SUBROUTINE RGSTO(NPTS1,NPTS3,NAVE1,NAVE3,ITLP1,ITLP2,ITLP3,ICNT1,ICNT2,
     6  ICNT3,NDAPU,NTMPD)
        COMMON IDATA,SDEV,T,AVG
        DIMENSION IDATA(1000),SDEV(100),T(100),AVG(100)
380     READ(1,390)FNAME
S       CLA CLL CML RAR
S       DCA \IPB
S       CLA CLL
390     FORMAT('ABSORBANCE DATA FILENAME (6 CHARACTERS) =',A6)
        CALL OOPEN('FLP2',FNAME)
        APT=FLOAT(NPTS1)
        T(1)=APT*.0001+.0002
        DO 395 LT=2,NAVE1
        LTM1=LT-1
        T(LT)=T(LTM1)+1.6384*FLOAT(ITLP1)+.0004*FLOAT(ICNT1)
395     CONTINUE
        IF(NTMPD+1)400,450,400
400     BPT=FLOAT(NPTS3)
        IP2=NAVE1+1
        IP4=NAVE1+NAVE3
        IP3=IP2+1
        T(IP2)=T(NAVE1)+1.6384*FLOAT(ITLP2)+.0004*FLOAT(ICNT2)+BPT*.0001
        DO 410 LT=IP3,IP4
        LTM1=LT-1
        T(LT)=T(LTM1)+1.6384*FLOAT(ITLP3)+.0004*FLOAT(ICNT3)
410     CONTINUE
450     ITPNT=NAVE1+NAVE3
        NDPSH=NDAPU
        DO 490 I=1,ITPNT
        SUM=0.
        SUM2=0.
        DO 470 J=1,NDPSH
        JM1=J-1
        INDEX=I+ITPNT*(JM1)
        IX=IDATA(INDEX)+IPB
        WRITE(1,492)INDEX
        WRITE(1,492)IDATA(INDEX)
        X=IX
        AB=-ALOG((X+2048.)/4096.)/2.3026
        SUM=SUM+AB
        SUM2=SUM2+AB*AB
470     CONTINUE
        DPSH=FLOAT(NDPSH)
        AVG(I)=SUM/DPSH
        VAR=ABS(SUM2-SUM*SUM/DPSH)/(DPSH-1.)
        SDEV(I)=SQRT(VAR)
490     CONTINUE
        WRITE(4,491)(T(I),AVG(I),SDEV(I), I=1,ITPNT)
491     FORMAT(3E13.6)
492     FORMAT(3I6)
        CALL OCLOSE
        RETURN
        END
```

```
C       PROGRAM RGFILL.FT                     ROY GALL
C
        SUBROUTINE RGFIL
C
C       THIS SUBROUTINE FILLS THE SYRINGES OF THE STOPPED FLOW
C       THEN CYCLES THROUGH ONE RUN
C
S       OPDEF   OVALV   6661    /SET FF1
S       OPDEF   SUCK    6662    /SET FF2
S       OPDEF   PUSH    6664    /SET FF3
S       OPDEF   CVALV   6671    /CLEAR FF1
S       OPDEF   PRESS   6672    /CLEAR FF2
S       OPDEF   WASTE   6674    /CLEAR FF3
S       OVALV
S       CLA CLL
        CALL RGWAT(-4)
S       SUCK
S       CLA CLL
        CALL RGWAT(-10)
S       CVALV
S       CLA CLL
        CALL RGWAT(-4)
S       PRESS
S       CLA CLL
        CALL RGWAT(-4)
S       PUSH
S       CLA CLL
        CALL RGWAT(-3)
S       WASTE
S       CLA CLL
        CALL RGWAT(-40)
        RETURN
        END
```

```
C       PROGRAM RGTIME                        ROY GALL
C
        SUBROUTINE RGTM(TMBT,NPTS,MNC,MNE)
        DPTS=FLOAT(NPTS)
        TMBTS=TMBT-DPTS*.0002
        MNE=IFIX(TMBTS/1.6384)
        FMNE=2.*FLOAT(MNE)
        MNC=IFIX((TMBT-FMNE*.8192)*2500.)
        RETURN
        END
```

```
          SUBROUTINE RGWAT( ILONG)
C         THIS SUBROUTINE DELAYS FOR .4 SEC FOR EACH STEP OF ILONG
S         OPDEF   CLZE    6130    /ONES IN AC CLEAR CLOCK ENABLE REGISTER
S         SKPDF   CLSK    6131    /SKIP IF CLOCK OVERFLOWS OR ST SET
S         OPDEF   CLOE    6132    /ONES IN AC SET CLOCK ENABLE REGISTER
S         OPDEF   CLAB    6133    /AC TO BUFFER PRESET + COUNTER REGISTERS
S         OPDEF   CLSA    6135    /CLOCK STATUS REGISTER TO AC, ONES CLEAR
S         CLA CLL CMA
S         CLZE
S         CLA
S         CLAB
S         TAD I \ILONG
S         DCA MC1
S         TAD (5400
S         CLOE
S         CLSA
SCF1,     CLSK
S         JMP CF1
S         CLSA
S         ISZ MC1
S         JMP CF1
S         CLA CLL CMA
S         CLZE
S         CLA
S         JMP \666
SMC1,     0000
666       RETURN
          END
```

```
C        PROGRAM RGMAIN  ROY CALL
C        THIS IS THE MAIN PROGRAM FOR THE INTERACTIVE DATA
C        ANALYSIS FOR THE STOPPED FLOW SYSTEM
C
C        LOADING SEQUENCE
C
C        LO RGMAIN(I),RGOPTN,RGSMTH,RGSCAL,RGLAXS,RGNRXS,RGWAIT0*TEKLIB(LG)
C
C        DATA FILES MUST BE WRITTEN IN 3E13.6 AND BE 100 ENTRIES LONG
C        THE DATA IS ASSUMED TO BE WRITTEN IN THE FORM (X,Y,STD. DEV.)
C
         COMMON T,A,R,SDA
         DIMENSION T(100), A(100), SDA(100), R(100)
         CALL ERASE
         CALL RGWAT(-1)
         CALL FDIS(0,500,675)
         CALL FDIS(1,600,475)
         CALL FDIS(1,900,475)
         CALL FDIS(1,668,345)
         CALL FDIS(1,800,75)
         CALL FDIS(1,500,245)
         CALL FDIS(1,200,75)
         CALL FDIS(1,332,345)
         CALL FDIS(1,100,475)
         CALL FDIS(1,400,475)
         CALL FDIS(1,500,675)
         CALL ALPHA
         CALL HOME
         WRITE(1,100)
100      FORMAT('EVIL ROYS FANTASTIC STOPPED FLOW DATA EVALUATOR')
11       READ(1,101)FLN
101      FORMAT('FILENAME = ',A6)
         READ(1,12)IGES
12       FORMAT('IS FILENAME CORRECT? 1=YES  2=NO',I2)
         IF(IGES-1)11,13,11
13       CALL RGOPT(ICHOS,IF,IL)
         IF(ICHOS-11)183,11,183
183      CALL IOPEN('FLP2',FLN)
         READ(4,102)(T(I),A(I),SDA(I),I=1,100)
102      FORMAT(3E13.6)
         TINC=T(2)-T(1)
         CALL RGSMT(A,R,1,TINC)
747      CONTINUE
         GO TO(1,2,3,4,5,6,7,8,7,10,11),ICHOS
1        IT=-1
18       CALL ERASE
         CALL RGWAT(-1)
         CALL RGSCL(A,IF,IL,AMAX,AMIN,IT,IXSCAL,YSCALE)
         CALL RGLAX(AMAX,AMIN,0,0,T(IF),T(IL),1)
         CALL RGNRX(A,IF,IL,IXSCAL,YSCALE,AMIN)
         CALL RGOPT(ICHOS,IF,IL)
         GO TO 747
4        IT=20
         GO TO 18
2        IT=-1
28       CALL ERASE
         CALL RGWAT(-1)
         CALL RGSCL(R,IF,IL,RMAX,RMIN,IT,IXSCAL,YSCALE)
         CALL RGLAX(0,0,RMAX,RMIN,T(IF),T(IL),2)
         CALL RGNRX(R,IF,IL,IXSCAL,YSCALE,RMIN)
         CALL RGOPT(ICHOS,IF,IL)
         GO TO 747
5        IT=-1
         GO TO 28
3        IT=-1
         IV=-1
```

```
38        CALL ERASE
          CALL RGWAT(-1)
          CALL RGSCL(A,IF,IL,AMAX,AMIN,IT,IXSCAL,YSCALE)
          CALL RGSCL(R,IF,IL,RMAX,RMIN,IV,IXSCAL,YSCALE)
          CALL RGLAX(AMAX,AMIN,RMAX,RMIN,T(IF),T(IL),3)
          CALL RGNRX(R,IF,IL,IXSCAL,YSCALE,RMIN)
          CALL RGOPT(ICHOS,IF,IL)
          GO TO 747
6         IT=1
          IV=1
          GO TO 38
7         IT=1
          IV=-1
          GO TO 38
8         IT=-1
          IV=1
          GO TO 38
10        CONTINUE
          END
```

```
C       PROGRAM RGOPTN.FT       ROY GALL
C
C
C       PROGRAM FOR OPTIONS POSSIBLE IN RGMAIN.FT
C
C
        SUBROUTINE RGOPT(IOPT,IF,IL)
        WRITE(1,1)
1       FORMAT('ABSORB. (PTS.) =    1',10X,'ABSORB. (LINE) =    4')
        WRITE(1,2)
2       FORMAT('RATE (PTS.) =    2',13X,'RATE (LINE) =    5')
        WRITE(1,3)
3       FORMAT('ABS. + RATE (PTS.) =    3',6X,'ABS + RATE (LINE) =    6')
        WRITE(1,4)
4       FORMAT('ABS. (LINE) + RATE (PTS.) =    7')
        WRITE(1,5)
5       FORMAT('ABS. (PTS.) + RATE (LINE) =    8')
        WRITE(1,6)
6       FORMAT('OPTION 7 FOR POINTS 1-100  =    9')
        WRITE(1,7)
7       FORMAT('CALC AVERAGES =    10',10X,'CALL ANOTHER FILE =    11')
        READ(1,82) IOPT
82      FORMAT('WHICH OPTION ?',I2)
        GO TO (8,8,8,8,8,8,8,8,9,8,11),IOPT
8       READ(1,100) IF,IL
100     FORMAT('INDEX  OF FIRST POINT = ',I3,' LAST POINT = ',I3)
        IF(IL-IF) 10,10,11
10      WRITE(1,101)
101     FORMAT('FIRST POINT HAS TO BE LESS THAN SECOND POINT')
        GO TO 8
9       IF=1
        IL=100
11      RETURN
        END
```

```
C       PROGRAM RCSMTH.FT        ROY GALL
C
C
C       BASED ON AN ARTICLE BY A. SAVITZKY AND M. GOLAY IN
C       ANALYTICAL CHEMISTRY VOL.36,NO.8,JULY 1964 P.1627
C       THIS PROGRAM DOES A FIRST DERIVATIVE QUADRATIC SMOOTH
C       ON THE DATA BASED ON 5,7,9 OR 11 POINTS
C
C       A     =NAME OF DATA ARRAY
C       R     =NAME OF SMOOTHED FIRST DERIVATIVE ARRAY
C       TINC  =INCREMENT IN THE X AXIS
C       INO   =1 GIVES AN 11 POINT SMOOTH
C              2 GIVES A 9 POINT SMOOTH
C              3 GIVES A 7 POINT SMOOTH
C              4 GIVES A 5 POINT SMOOTH
C
C
        SUBROUTINE RCSMT(A,R,INO,TINC)
        DIMENSION A(100),R(100)
        WRITE(1,137)
137     FORMAT('HERS')
        GO TO (1,2,3,4),INO
1       CONTINUE
        DO 10 I=6,95
        PART=(A(I+5)-A(I-5))*5.+(A(I+4)-A(I-4))*4.+(A(I+3)-A(I-3))*3.
        R(I)=(PART+(A(I+2)-A(I-2))*2.+A(I+1)-A(I-1))/(TINC*110.)
10      CONTINUE
        R(1)=R(6)
        R(2)=R(6)
        R(3)=R(6)
        R(4)=R(6)
        R(5)=R(6)
        R(96)=R(95)
        R(97)=R(95)
        R(98)=R(95)
        R(99)=R(95)
        R(100)=R(95)
        RETURN
2       CONTINUE
        DO 20 I=5,96
        PART=(A(I+4)-A(I-4))*4.+(A(I+3)-A(I-3))*3.+(A(I+2)-A(I-2))*2.
        R(I)=(PART+A(I+1)-A(I-1))/(TINC*60.)
20      CONTINUE
        R(1)=R(5)
        R(2)=R(5)
        R(3)=R(5)
        R(4)=R(5)
        R(97)=R(96)
        R(98)=R(96)
        R(99)=R(96)
        R(100)=R(96)
        RETURN
3       CONTINUE
        DO 30 I=4,97
        PART=(A(I+3)-A(I-3))*3.+(A(I+2)-A(I-2))*2.+A(I+1)-A(I-1)
        R(I)=PART/(TINC*28.)
30      CONTINUE
        R(1)=R(4)
        R(2)=R(4)
        R(3)=R(4)
        R(98)=R(97)
        R(99)=R(97)
        R(100)=R(97)
        RETURN
4       CONTINUE
```

```
      DO 40 I=3,98
      R(I)=((A(I+2)-A(I-2))*2.+A(I+1)-A(I-1))/(TINC*10.)
40    CONTINUE
      R(1)=R(3)
      R(2)=R(3)
      R(99)=R(98)
      R(100)=R(98)
      RETURN
      END
```

```
C     PROGRAM RGSCAL.FT       ROY CALL
C
C     THIS PROGRAM SCALES THE DATA AND PLOTS THE DATA
C
C     D     =THE DATA ARRAY
C     IF    =THE FIRST POINT TO BE PLOTTED
C     IL    =THE LAST POINT TO BE PLOTTED
C     DMAX  =THE MAXIMUM BETWEEN IF AND IL
C     DMIN  =THE MINIMUM BETWEEN IF AND IL
C     IXSCAL=THE SCALING FACTOR FOR THE X AXIS
C     YSCALE=THE SCALING FACTOR FOR THE Y AXIS
C     IT    =>0     PLOTS A VECTOR
C            =0     PLOTS A DARK VECTOR
C            <0     PLOTS A POINT
C
C     SUBROUTINES CALLED:
C
C     FDIS:  PLOTTING SUBROUTINE
C     ALPHA: PUTS TEK INTO ALPHA MODE
C     HOME:  RETURNS CURSOR TO HOME POSITION
C
C
      SUBROUTINE RGSCL(D,IF,IL,DMAX,DMIN,IT,IXSCAL,YSCALE)
      DIMENSION D(100)
      DMAX=D(IF)
      DMIN=D(IF)
      DO 40 J=IF,IL
      IF(D(J)-DMIN) 10,20,20
10    DMIN=D(J)
20    IF(DMAX-D(J)) 30,40,40
30    DMAX=D(J)
40    CONTINUE
      YSCALE=ABS(768./(DMAX-DMIN))
      IXSCAL=1024/(IL-IF)
      IX=-IXSCAL
      KL=(D(IF)-DMIN)*YSCALE
      IF(KL-768)50,60,50
50    CALL FDIS(0,0,768)
      GO TO 70
60    CALL FDIS(0,0,0)
70    DO 19 I=IF,IL
      IX=IX+IXSCAL
      IY=(D(I)-DMIN)*YSCALE
      CALL FDIS(IT,IX,IY)
19    CONTINUE
      CALL ALPHA
      CALL HOME
      RETURN
      END
```

```
C       PROGRAM RGLAXS.FT        ROY GALL
C
C
C       THIS PROGRAM LABELS THE AXIS INSIDE THE PLOTTING AREA
C       SO THAT NO RESOLUTION IS LOST
C
C
        SUBROUTINE RGLAX(AMAX,AMIN,RMAX,RMIN,TMIN,TMAX,IMODE)
        CALL FDIS(0,0,768)
        CALL FDIS(1,0,0)
        CALL FDIS(1,1024,0)
        CALL FDIS(0,0,768)
        CALL ALPHA
        CALL HOME
        GO TO ( 10,20,30), IMODE
10      CONTINUE
        WRITE( 1,100) AMAX
100     FORMAT( 1X,E10.3,' ABS')
        CALL FDIS(0,0,40)
        CALL ALPHA
        WRITE( 1,101) AMIN,TMIN,TMAX
101     FORMAT( 1X,E10.3,' ABS',/,1X,E10.3,' S',47X,E10.3,' S')
        CALL BELL
        RETURN
20      CONTINUE
        WRITE( 1,200) RMAX
200     FORMAT( 1X,E10.3,' RATE')
        CALL FDIS(0,0,40)
        CALL ALPHA
        WRITE( 1,201) RMIN,TMIN,TMAX
201     FORMAT( 1X,E10.3,' RATE',/,1X,E10.3,' S',47X,E10.3,' S')
        CALL BELL
        RETURN
30      CONTINUE
        WRITE( 1,300) AMAX,RMAX
300     FORMAT( 1X,E10.3,' A',/,1X,E10.3,' R')
        CALL FDIS(0,0,60)
        CALL ALPHA
        WRITE( 1,302) AMIN
302     FORMAT( 1X,E10.3,' A')
        CALL FDIS(0,0,40)
        CALL ALPHA
        WRITE( 1,303)RMIN,TMIN,TMAX
303     FORMAT( 1X,E10.3,' R',/,1X,E10.3,' S',47X,E10.3,' S')
        CALL BELL
        RETURN
        END
```

```
C        PROGRAM: RGNRXS.FT       ROY GALL
C
C        DATA  =THE NAME OF THE DATA ARRAY
C        JSKP  =THE INDEX OF THE FIRST POINT TO BE PLOTTED
C        J     =THE INDEX OF THE LAST POINT TO BE PLOTTED
C        INCX  =THE SCALED INCREMENT ON THE X AXIS
C        YSCALE=THE SCALE FACTOR FOR FULL SCALE ON THE Y AXIS
C        AMIN  =MINIMUM Y VALUE IN PORTION OF DATA ARRAY PLOTTED
C
C
C
C        CHARACTERS RECOGNIZED BY THE INTERACTIVE ROUTINE
C
C        F=PLOT FORWARD  CNTRL/F=PLOT 1 POINT FORWARD
C        R=PLOT REVERSE  CNTRL/R=PLOT 1 POINT REVERSE
C        1,2,3,4,5,6,7,8=STORE INDEX OF POINT 1,2,3,4,5,6,7,8
C        S=STOP AND BLINK
C        P=PLOT POINT OF ENTERED INDEX
C        CNTRL/G=GO TO DATA ANALYSIS
C
C        CALLS FDIS:A PLOTTING ROUTINE FOR THE TEK TERMINAL
C              BELL:A SUBROUTINE FOR RINGING THE TERMINAL BELL
C              HOME:A SUBROUTINE TO PUT THE CURSOR IN THE HOME POSITION
C              RGWAT:A SUBROUTINE INTRODUCED TO PROVIDE A DELAY
C              ALPHA:A SUBROUTINE TO RETURN THE TERMINAL TO THE ALPHA MODE
C
         SUBROUTINE RGNRX(DATA,JSKP,J,INCX,YSCALE,AMIN)
         DIMENSION DATA(400)
C
C        INITIALIZE
C
         I1=0
         I2=0
         I3=0
         I4=0
         I5=0
         I6=0
         I7=0
         I8=0
         IPTS=J-JSKP+1
         DO 717 I=1,500
C
C        THIS RINGS THE BELL 500 TIMES OR STOPS WHEN
C        ANY CHARACTER ON THE KEYBOARD IS HIT
C
         CALL RGWAT(-2)
S        KSF
S        JMP F63
S        JMP F18
S F63,   CLL
717      CALL BELL
S F18,   CLL
```

```
S \12,  CLA CLL
S       TAD I \JSKP
S       DCA I COUNT     /STORE IT
S       TAD ("S         /BRING IN AN "S"
S       DCA CHAR        /REPLACE THE OLD CHARACTER WITH IT
S       JMP STOP        /START PLOTTING
S \13,  CLA CLL         /GET RID OF GARBAGE
S       KSF             /CHECK THE KEYBOARD
S       JMP GOON        /GO ON
S       KRB             /READ IT
S       DCA CHAR        /STORE IT
S GOON, TAD CHAR        /GET IT AGAIN
S       TAD (-206       /IS IT A CNTRL F?
S       SNA CLA
S       JMP FORW1
S       TAD CHAR        /GET IT AGAIN
S       TAD (-"F                /IS IT AN F? (306)
S       SNA CLA         /NOPE
S       JMP FORW        /YES, INCREMENT AND PLOT
S       TAD CHAR        /GET IT AGAIN
S       TAD (-222       /IS IT CNTRL R?
S       SNA CLA
S       JMP REVER1
S       TAD CHAR        /GET IT AGAIN
S       TAD (-"R                /IS IT AN R? (322)
S       SNA CLA         /NOPE
S       JMP REVER       /YES, DECREMENT AND PLOT
S       TAD CHAR        /GET IT AGAIN
S       TAD (-207               /IS IT A CONTROL G? (207)
S       SNA CLA         /NOPE
S       JMP F15         /RETURN
S       TAD CHAR        /GET IT AGAIN
S       TAD (-320               /IS IT A P
S       SNA CLA         /NOPE
S       JMP F22         /YES
S       TAD CHAR        /GET IT AGAIN
S       TAD (-323               /IS IT AN S?
S       SNA CLA         /SKIP IF IT ISN'T
S       JMP F14         /MUST BE S, PLOT THEN GO LOOK FOR NUMBERS 1-4
S       JMP STOP        /MUST BE 1-4, GO CHECK
S FORW1,TAD ("S
S       DCA CHAR
S FORW, TAD \IPTS       /MAKE SURE IPTS NOT EXCEEDED
S       CIA     /NEGATE IT
S       TAD I COUNT     /ADD # POINTS
S       SMA CLA         /SKIP IF IPTS.LE.COUNT
S       JMP LIMIT       /GO MAKE BLIPS IF IPTS.EQ.COUNT
S       ISZ I COUNT     /INCREMENT THE COUNTER
S       JMP F17         /GO PLOT THE POINT
S LIMIT,TAD ("S         /323
S       DCA CHAR        /STORE "S" FOR STOP
S       JMP F14         /GO BLIP
SREVER1,TAD ("S
S       DCA CHAR
S REVER,STA             /MAKE THE AC -1
S       TAD I COUNT     /ADD TO THE COUNTER
S       SPA SNA         /IS COUNTER > 0?
S       JMP F14         /NO, GET ANOTHER CHARACTER
S       DCA I COUNT     /NET EFFECT:DECREMENTS COUNTER
S       JMP F17         /GO PLOT
S STOP, TAD CHAR        /CHECK FOR CHARACTER
S       AND (0007       /GET RID OF BITS 0-8
```

```
S       SNA
S       JMP LOC8
S       TAD MINUS1      /ADD -1
S       SNA
S       JMP LOC1
S       TAD MINUS1
S       SNA
S       JMP LOC2
S       TAD MINUS1
S       SNA
S       JMP LOC3
S       TAD MINUS1
S       SNA
S       JMP LOC4
S       TAD MINUS1
S       SNA
S       JMP LOC5
S       TAD MINUS1
S       SNA
S       JMP LOC6
S       TAD MINUS1
S       SNA CLA
S       JMP LOC7
S       JMP F14         /TRY IT AGAIN
S LOC1, CLA CLL
S       TAD I COUNT
S       DCA \I1
S       JMP F14
S LOC2, CLA CLL
S       TAD I COUNT
S       DCA \I2
S       JMP F14
S LOC3, CLA CLL
S       TAD I COUNT
S       DCA \I3
S       JMP F14
S LOC4, CLA CLL
S       TAD I COUNT
S       DCA \I4
S       JMP F14
SLOC5,  CLA CLL
S       TAD I COUNT
S       DCA \I5
S       JMP F14
SLOC6,  CLA CLL
S       TAD I COUNT
S       DCA \I6
S       JMP F14
SLOC7,  CLA CLL
S       TAD I COUNT
S       DCA \I7
S       JMP F14
SLOC8,  CLA CLL
S       TAD I COUNT
S       DCA \I8
S       JMP F14
SCOUNT,\ICOUN           /COUNTER
S CHAR, 0000            /CHARACTER HOLDER
S F14,  CLL             /CLEAR THE LINK LOCATION BEFORE
S       JMP \14         /GOING TO FORTRAN
S F15,  CLL             /DITTO
S       JMP \15
S F17,  CLL
S       JMP \17
S F22,  CLL
S       JMP \22
SMINUS1,7777            /-1
```

```
C
C
22      CALL FDIS(0,1000,760)
        READ(1,23)ICOUT
23      FORMAT(I3)
S       CLA CLL
S       TAD (-323
S       DCA CHAR
        IF(ICOUT-JSKP)27,25,25
25      IF(ICOUT-J)26,26,27
26      ICOUN=ICOUT
        GO TO 14
27      CALL BELL
14      CONTINUE
17      IX=(ICOUN-JSKP)*INCX
        IY=(DATA(ICOUN)-AMIN)*YSCALE
        CALL FDIS(-1,IX,IY)
        CALL ALPHA
        GO TO 13
15      CALL HOME
16      READ(1,100)IDEC
100     FORMAT('DO YOU HAVE INTERACTIVE POINTS? 1=YES 0=N0',I1)
        IF(IDEC)200,200,101
101     READ(1,102)IFI,ILI
102     FORMAT('INPUT THE COORDINATES OF ONE PAIR (1,2)',2I1)
        GO TO(81,82,83,84,85,86,87,88),IFI
81      IF=I1
        GO TO 90
82      IF=I2
        GO TO 90
83      IF=I3
        GO TO 90
84      IF=I4
        GO TO 90
85      IF=I5
        GO TO 90
86      IF=I6
        GO TO 90
87      IF=I7
        GO TO 90
88      IF=I8
        GO TO 90
90      GO TO(91,92,93,94,95,96,97,98),ILI
91      IL=I1
        GO TO 300
92      IL=I2
        GO TO 300
93      IL=I3
        GO TO 300
94      IL=I4
        GO TO 300
95      IL=I5
        GO TO 300
96      IL=I6
        GO TO 300
97      IL=I7
        GO TO 300
98      IL=I8
        GO TO 300
```

```
300     EN=IL-IF
        SUM=0.
        SUM2=0.
        DO 173 L=IF,IL
        SUM=SUM+DATA(L)
        SUM2=SUM2+DATA(L)*DATA(L)
173     CONTINUE
        AVG=SUM/(EN+1.)
        VAR=ABS(SUM2-SUM*SUM/(EN+1.))/EN
        SDEV=SQRT(VAR)
        WRITE(1,500)IF,IL
500     FORMAT('FOR THE POINTS ',I2,' THROUGH ',I3)
        WRITE(1,501)AVG,SDEV
501     FORMAT('THE AVERAGE = ',E13.6,' WITH STAND. DEV. = ',E13.6)
        IF(IDEC)200,200,16
200     READ(1,201)IDEC
201     FORMAT('NON INTERACTIVE PAIRS? 0=YES 1=NO',I1)
        IF(IDEC)202,202,400
202     READ(1,203)IF,IL
203     FORMAT('FIRST COORD (I2)',I2,'SECOND COORD (I3)',I3)
        GO TO 300
400     RETURN
        END
```