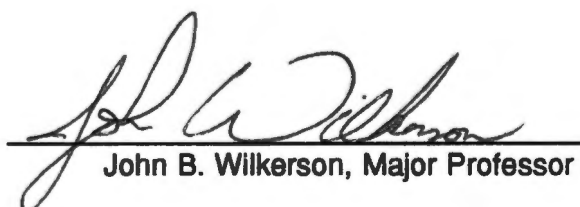
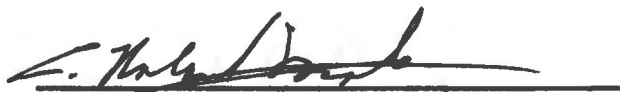
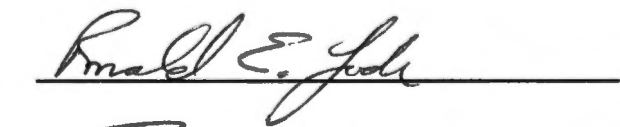


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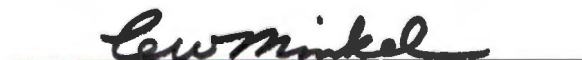
I am submitting herewith a thesis written by Kenneth John Hurley entitled "Evaluation of a Continuous, Flow-Proportional Real-Time Streamflow Sampler Using a Computer-Controlled Hydrograph Generator." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agricultural Engineering.


John B. Wilkerson, Major Professor

We have read this thesis and
recommend its acceptance:


Accepted for the Council:


Associate Vice Chancellor
and Dean of the Graduate School

**Evaluation of a Continuous Flow-Proportional
Real-Time Streamflow Sampler Using a
Computer Controlled Hydrograph Generator**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Kenneth John Hurley

May 1996

DEDICATION

This thesis is dedicated in the memory of my father John William Hurley, and to my mother Dorothy Maxine Harrison whose love and encouragement guided me in my pursuit of an education.

ACKNOWLEDGMENTS

I would like to thank my major professor, Dr. John B. Wilkerson, for his guidance and patience. I would also like to thank my other committee members, Dr. Daniel Yoder, Dr. Ronald Yoder, and Dr. C. Roland Mote for their comments and assistance during this study. I would also like to thank Paul Elliot, Walker Garner, and Craig Wagoner for their technical assistance and excellent workmanship in constructing the experimental equipment. Appreciation is also expressed to Joe Kirby, whose assistance in the development of the system electronics contributed to the project's success. I would also like to thank David Johnson, Ray Maynard, and Brian Corwin for their many contributions to the study. Thanks also to Julie Hicks for the many hours of technical editing.

Compliments are extended to the staff and graduate students in the Agricultural Engineering Department for providing a friendly and professional place to work. Finally, I thank my family for the love and kindness that inspired me to succeed in my education and career.

ABSTRACT

This study investigated the problems with current streamflow sampling techniques and resulted in the design and evaluation of a continuous, flow-proportional, real-time streamflow sampling unit. The sampling unit was evaluated against a commercially available pumping type sampler to determine which sampler more accurately represented both constituent mass movement and the timing of constituent movement. The samples were taken from test streams produced by a computer-controlled hydrograph generator. Potassium bromide was injected into these streams with both constant and dynamic feed rates. Samples taken by each sampler were analyzed for bromide concentrations using a selective ion probe.

Results of this study indicated that a sampling unit that continuously extracts a flow proportioned sample and stores the sample in a discrete container provided more accurate information on both constituent mass movement and timing of movement than a sampler that took discrete samples at fixed time intervals. The sampler that collected samples at timed intervals was susceptible to missing sudden spikes in concentration and in over estimating the actual characteristics of the test stream when a sudden spike in concentration was detected. The continuous real-time sampler extracted a sample that was representative of the actual constituent characteristics of the test streams.

Results of this study indicated that continuous, flow-proportional, real-time sampling is an effective method of acquiring water quality data. This type of sampling provides the ability to obtain high quality information on total constituent mass movement as well as when the movement actually occurred.

PREFACE

This document is composed of four independent parts. Part 1 is styled as a general introduction and overview of the study. Part 2 describes the design and evaluation of a computer-controlled hydrograph generator, and Part 3 describes the design and evaluation of a continuous, flow-proportional, real-time streamflow sampling unit. Part 4 is a summary of Parts 2 and 3. Due to the four independent parts, some repetition may be encountered in this document.

Pages are numbered consecutively, and tables and figures are numbered in sequence as they appear in each part of this thesis.

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PART 1: GENERAL INTRODUCTION AND OVERVIEW

INTRODUCTION

Public interest and research emphasis on water quality has led to a demand for high quality information. Relevant and accurate information is essential to quantify the current status of existing stream conditions, and to model expected impacts from management or regulatory changes. During the last few years, it has become evident that there is a lack of water quality data for Tennessee streams. Of the 19,124 miles of rivers and streams within Tennessee, only about 20% are classified as being "monitored", leaving 80% of Tennessee's streams with no water quality data less than 5 years old (Tennessee Department of Health and Environment, 1990). Monitoring efforts have often operated under severe budget and manpower restrictions, leading to poor equipment placement and monitoring strategies. For this reason, obtaining the highest quality of information on stream characteristics at low operating costs is an important consideration in today's monitoring systems.

RATIONALE: WHY DEVELOP A CONTINUOUS, FLOW-PROPORTIONAL, REAL-TIME STREAMFLOW SAMPLING UNIT?

To collect high quality sampling information, current sampling techniques must be addressed. The first question is whether to collect samples at discrete times or to

sample continuously. Discrete sampling is simply the removal of a sample from a stream at a specific time, with the time of sample withdrawal usually very short in comparison to the time between samples. This is the form of sampling provided by the current generation of commercially available automated pumping samplers.

Continuous sampling involves the continuous withdrawal of a known portion of a stream. Continuous samplers have been around for a long time, but have gotten very limited use recently due to the mechanization and accuracy of discrete sampling techniques.

In general, discrete samples are very easy to use and give information on constituent concentrations at specific times. Continuous samples, on the other hand, do not give specific time information, but ensure that sudden spikes in concentration will not be missed.

The second question is whether to withdraw a set sample volume, or to make the sample volume proportional to the measured flow rate. The set volume sample is usually much easier to withdraw, as it makes no attempt to link the sampling process to the measurement of flow rate. The flow proportional method, on the other hand, tries to use flow information to change the sample size or sampling rate, thereby including within the sample itself some information on the flow rate. The flow proportional method makes calculating total constituent mass movement much less complicated, with fewer assumptions, than other sample withdrawal techniques.

Finally, the issue of handling the sample after extraction must be addressed. Should the sample be stored in individual containers (with the sample in each container representing a specific time period of the flow), or should samples be stored in a single large container, giving a composite sample whose chemical constituents will be some

average of the entire sampling period? Samples combined into a single composite are much easier and cheaper to analyze, but all information regarding the change of concentration with respect to time is lost. This may not be important if all that is desired is total mass movement, but it is critical when modelling chemical movement patterns or when monitoring for concentration thresholds.

Questions concerning sample extraction, volume, and handling can be combined in any of the eight possible combinations as shown in Table 1. The abbreviations shown in the inner boxes (for example, DFI stands for discrete, flow proportional, individual) are used to minimize complexity.

Table 1. Possible Combination of Sample Collection and Storage Methods

Sample Volume	Sample Interval		Sample Handling
	Discrete	Continuous	
Set	DSI	CSI	Individual
	DSC	CSC	Composite
Flow Proportional	DFI	CFI	Individual
	DFC	CFC	Composite

NOTES:

- DSI = Discrete, set time intervals, individual
- DSC = Discrete, set time intervals, composite
- DFI = Discrete, flow proportional, individual
- DFC = Discrete, flow proportional, composite
- CSI = Continuous, set time intervals, individual
- CSC = Continuous, set time intervals, composite
- CFI = Continuous, flow proportional, individual
- CFC = Continuous, flow proportional, composite

Several of these possible combinations are already covered by existing samplers. For example, the most standard way of using modern automated samplers is with discrete set volumes taken at regular intervals and stored individually (DSI) or composited (DSC). The chemical concentration in the sample is multiplied by the average flow rate, as measured by a weir or flume, over the sampling period to determine the constituent mass movement. These samplers can also be set to take samples after specific volumes of flow pass through a flow measurement device. The samples can then be stored individually (DFI) or in a composite container (DFC), depending on whether the timing of constituent movement is important. If the samples are composited, the sample constituent concentration should reflect that of the total stream during that period. Some examples of how these various systems operate are displayed in Figure 1.

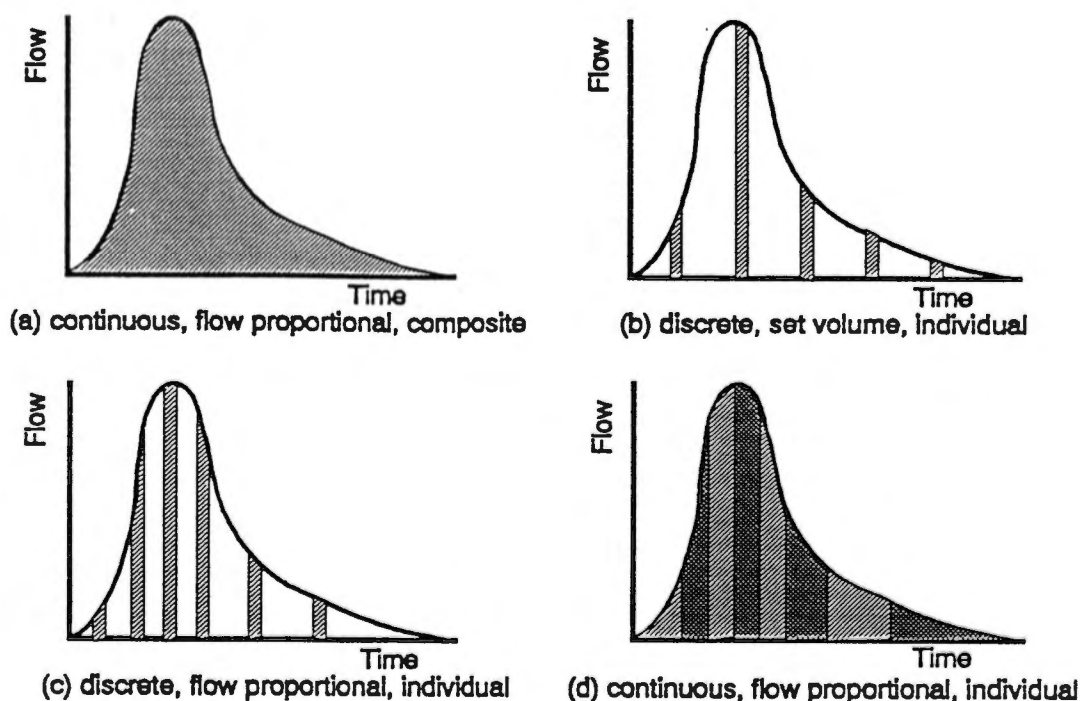


Figure 1. Examples of Sampling Strategies

Figure 1(a) shows the results of a continuous, flow proportional, composite sample (CFC). CFC samples give a good indication of total constituent mass movement, but provide no indication on the timing of the movement. This method normally encompasses the use of a flow divisor of some sort. Figure 1(b) shows the sampling curve for a commercially-available pumped sampler that withdraws samples at regular intervals (discrete, set volume, individual storage, or DSI). This method would provide timing information at the points that the samples are taken, but nothing in between samples. Total constituent mass movement can only be determined by linking the sample information to flow data. Most commercial samplers provide the flexibility to change the timing sequence to take samples at regular flow increments, making them flow proportional [Figure 1(c)]. If stored individually (DFI), the samples give information on both total constituent movement and on timing of movement, but still yield no information about the periods between sample extractions. If stored together (DFC), the resulting sample yields only information about total constituent movement. Finally, the option that this study will pursue will allow for a continuous, flow proportional, individually stored sample (CFI), as shown in Figure 1(d). This method of sampling covers the entire time so as to not miss peaks or valleys in concentrations, yields total constituent mass, and provides information on the timing of constituent movement.

As mentioned previously, grab sampling techniques share a weakness inherent in discrete sample extraction; it cannot be guaranteed that the discrete sampling points will catch sudden peaks or valleys in the concentration. This problem is solved by continuous sampling techniques, but there are difficulties in both extracting and handling these types of samples. Examples of the continuous technique include the

Geib type flow divisor and the Coshocton wheel, both of which can be labeled as CFC devices. As with all compositing techniques, these devices share the weaknesses of not giving information on concentration changes with time and both techniques require large amounts of sample storage space.

There is currently no commercially available method for the CSI, CSC, nor CFI sampling techniques, so there is no method to combine the advantages of continuous flow sampling with individual storage to provide both an adequate measure of constituent mass movement and a record of concentration changes with time.

OVERVIEW OF STUDY

The purpose of this study was to design and automate a continuous, flow proportional, real-time stream flow sampling unit, and to evaluate the sampler against a current commercially available pumping type sampler. The evaluation involved determining the ability of the samplers to define the total constituent mass and the timing of bromide tracers injected into synthesized streams with varying flow rates and flow shapes. To provide the synthesized streams in a laboratory setting, a computer-controlled device known as a hydrograph generator was designed and installed.

Part 2 of this thesis describes the design of the hydrograph generator, and provides an indication of accuracy for the device in producing flow rates from pre-programmed hydrographs. Part 3 describes the design, testing, and evaluation of

the continuous, flow-proportional, real-time sampling unit. Finally, Part 4 provides a summary of all the work involved in completing this study.

PART 2: DESIGN OF A COMPUTER-CONTROLLED HYDROGRAPH GENERATOR

INTRODUCTION

Background Information

Chow (1959) defines a hydrograph as the curve obtained by plotting the discharge of runoff against time for a specified period of time. The shape of a hydrograph follows a somewhat predictable pattern. This pattern consists of a period of increasing discharge that culminates in a peak or crest. Following the peak is a period of decreasing discharge known as the recession limb of the hydrograph. Figure 2 displays the three primary segments of a hydrograph.

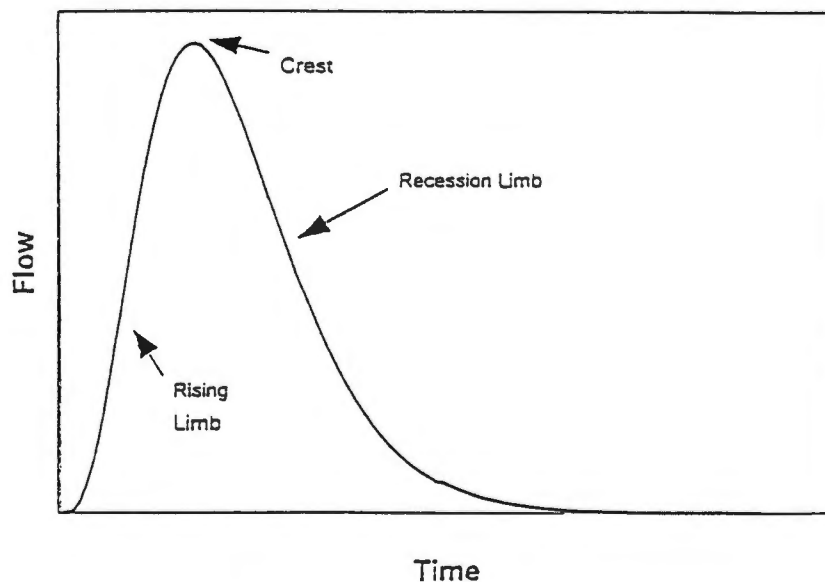


Figure 2. Segments of a Hydrograph

The rising limb of a hydrograph extends from the beginning of surface runoff to the first inflection point on the hydrograph. The rising limb represents the increase in discharge from a watershed.

The crest segment includes the part of the hydrograph from the inflection point on the rising limb to a corresponding point on the recession limb. The maximum instantaneous discharge rate, or hydrograph peak, occurs within this time interval.

The recession limb includes the remaining part of the hydrograph. This section of a hydrograph may or may not decrease to zero discharge depending on the amount of baseflow or groundwater flow. The recession limb represents the withdrawal of water from storage after excess rainfall has ceased (Gray, 1970).

Many researchers have studied methods of hydrograph synthesis. The United States Department of Agriculture, Soil Conservation Service employs an average dimensionless hydrograph developed from an analysis of a large number of natural unit graphs for watersheds varying widely in size. This dimensionless hydrograph has its ordinate values expressed as the dimensionless ratio, Q/Q_p , and its abscissa values as the dimensionless ratio, t/P_r , where Q is the discharge at any time (t), and P_r is the period of rise. For a given watershed, once the values of Q_p and P_r are defined, the unit graph can be constructed (Schwab et al., 1966).

A device capable of producing both constant and dynamic flow rates in a laboratory environment would be a useful research tool. This device would allow the evaluation of how flow measurement devices, such as weirs and flumes, respond to dynamic flow rates found in natural streams. It would also be practical in producing streams to test the effectiveness of water sampling equipment.

Current technologies for producing controllable flow rates use tanks with a retracting sluice gate. As the sluice gate moves up and down, flow from the tank varies. The problems with this type of system is the amount of space required to produce flows over an extended period of time. Another disadvantage is that only a small range of flow rates can be produced with this device. No literature on a flow controllable device was found during a thorough literature review.

Objectives

The objectives for this phase of the project were:

1. To design and construct a computer-controlled hydrograph generator that would produce and maintain sensitive dynamic flow control over a wide range of flow rates (0.03 to 1100 L/min).
2. Develop a control program that would allow this device to generate a stream from a user-defined data file, such as the Soil Conservation Service's dimensionless unit hydrograph.

DESIGN OF HYDROGRAPH GENERATOR

Theory of Operation

The hydrograph generator can be described using four major sub-systems: a water pump and associated plumbing, a flow control valve, a flow metering section, and a computer control system. Figure 3 illustrates the basic components of the hydrograph generator.

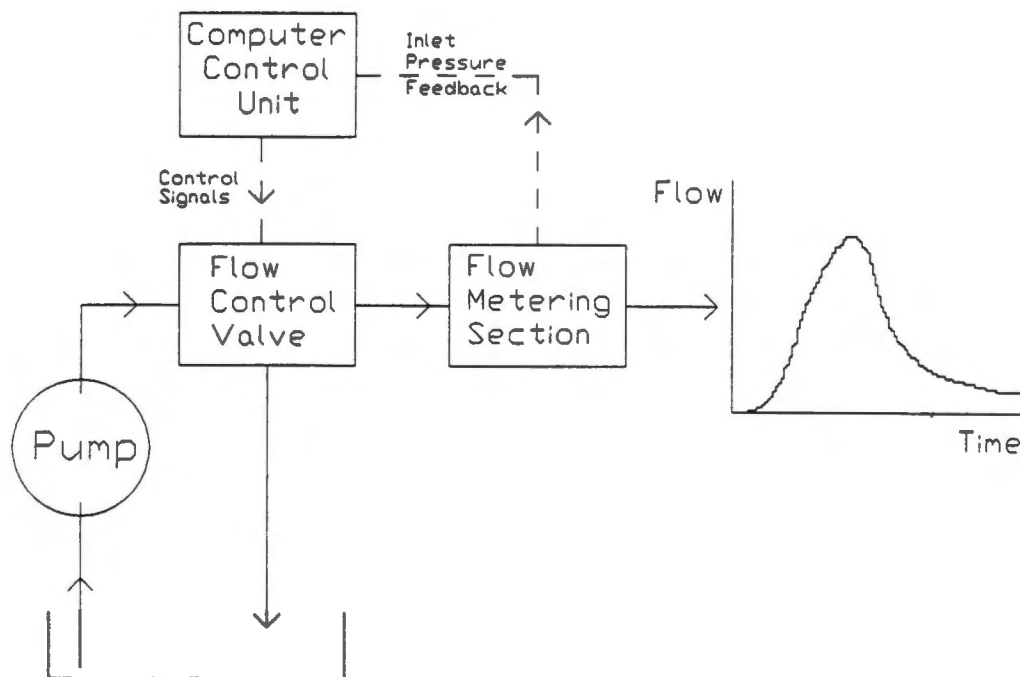


Figure 3. Components of the Hydrograph Generator

A water pump delivers flow under pressure to the flow control valve, which regulates the inlet pressure of the flow metering section. Pressure in the flow metering section is measured and calibrated against the outflow from the section. The computer control unit monitors the inlet pressure from the flow metering section and calculates an error term based on the difference between the desired pressure and actual system pressure. The controller automatically adjusts the flow control valve based on the sign and magnitude of the error signal to achieve the desired flow rate from the system.

Mechanical System

Pump and Associated Plumbing

A centrifugal pump, powered by an 11 kW three-phase motor, is used to deliver the required flow and pressure to the flow control valve. The pump produces flow rates in excess of 1100 L/min for discharge pressures less than 207 kPa. A pressure relief valve was installed between the pump and the flow control valve to prevent pressure in the system from exceeding 207 kPa.

Flow Control Valve

A flow control valve is used to control the water pressure to the inlet of the flow metering section. The flow control valve is powered by an electro-mechanical drive system. Figure 4 is a sketch of the flow control valve.

The flow control valve regulates water pressure to the flow metering section by diverting some of the flow away from that section. Flow is discharged through an orifice located in the needle valve assembly. As the electromechanical drive system lowers the needle valve into the orifice, less area is exposed for the water to discharge, sending more flow to the flow metering section and building pressure throughout the system.

The needle valve is moved vertically through an orifice plate. The needle valve is a 50.8 cm long aluminum cone with a maximum diameter of 8.9 cm tapering to a diameter of 1.3 cm (Figure 4). Attached to the cone of the needle valve is a stainless steel shaft, 1.1 m in length and 2.9 cm in diameter.

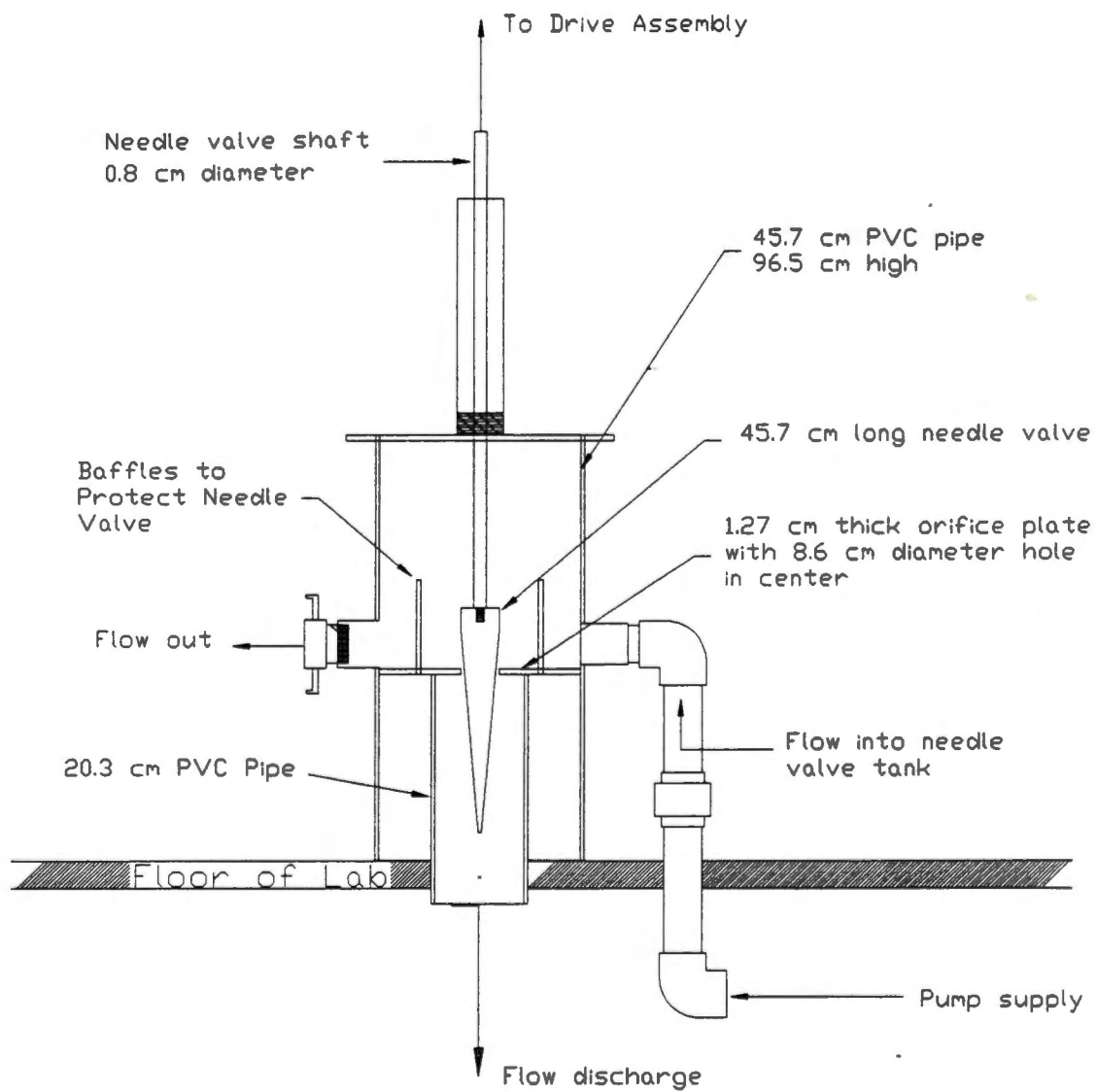


Figure 4. Flow Control Valve

The needle valve and orifice plate are mounted on the inside of a PVC pipe (Schedule 80), 96.5 cm in length with a diameter of 45.7 cm. On one side of the valve housing, a 7.6 cm PVC inlet was installed. This inlet is connected to the pump's discharge outlet. On the opposite side of the housing, an outlet with a quick connect was attached to accommodate a 7.6 cm diameter flexible hose. This outlet serves to carry flow to the flow metering section. Baffles were installed inside the valve housing at the inlets and outlets to protect the needle valve from being damaged by pressurized flow in the system. Attached to the inside of the valve housing beneath the orifice plate is a 20.3 cm diameter section of PVC pipe, 0.8 m in length.

A motor and transmission system are used to provide the linear motion necessary to move the needle valve into and out of the orifice plate. Figure 5 is a sketch of the motor and gear drive system for the flow control valve.

A roller chain connects the needle valve shaft to a 46-tooth drive sprocket located on a 2.5 cm shaft. Attached to one end of the shaft is a drive sprocket with 84 teeth. This sprocket is driven by a 10-tooth sprocket on the motor shaft. This reduces the drive pulley speed and increases the torque by a factor of 8.4.

The maximum torque required to raise the needle was calculated to be 113 N·m based on the maximum pressure inside the valve housing and the maximum diameter of the needle valve. The gear drive ratio reduces the maximum torque required by the motor to 13.45 N·m.

A 90 volt permanent magnet DC gearmotor (Dayton, Model 4Z530A) with a nameplate rating of 6.5 rpm at 56.5 N·m was selected. Control of this motor will be discussed in a later section.

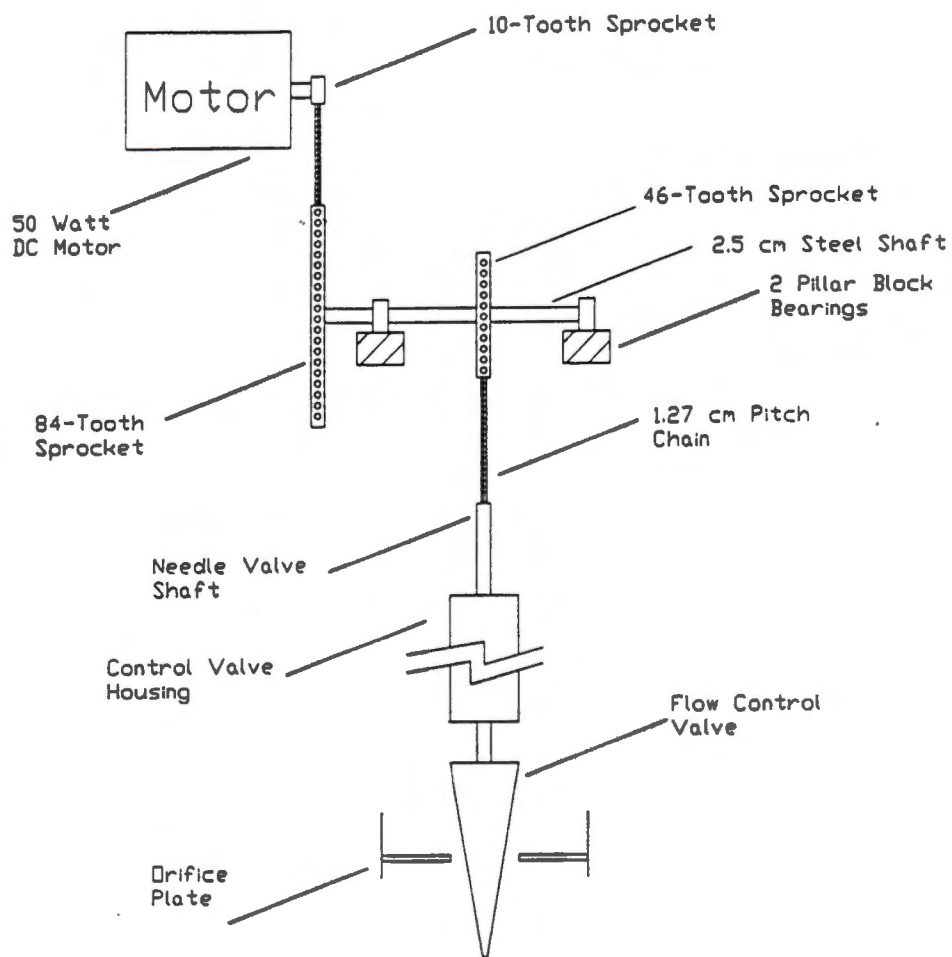


Figure 5. Motor and Gear Drive for Control Valve

Flow Metering Section

The purpose of the flow metering section is to accurately regulate flow based on a known system pressure. The flow metering section acts as a weir at low flows and as an orifice at high flows, thus giving the system increased control sensitivity at both high and low flow rates.

When the needle valve is at its highest position, water enters the flow metering section and rises to a level just below the beginning of a control slit. As the needle moves down, blocking a portion of the orifice opening, the water level rises above the bottom of the control slit, causing water to flow through the slit. As the water level in the control slit rises, flow from the slit increases. Flow from the slit that occurs before the water level reaches the top of the slit is characterized as open channel weir flow. Once the water level reaches the top of the slit, flow from the slit is characterized as orifice flow. Figure 6 is a schematic of the flow metering section.

The flow metering section consists of an inner pipe, an outer pipe, and a support frame for stability. The inner pipe, as discussed previously, has a control slit cut into the side to provide flow control over a wide range of head pressures. The outer pipe is used to carry the flow discharged from the control slit to the section's outlet.

The inner pipe consists of a 1.4 m long section of PVC (Schedule 40), 15.2 cm in diameter, and capped at the top. A diamond shaped slit, 1.0 m in length with a maximum width of 6.3 mm, was machined into a rectangular PVC plate mounted to the side of the inner pipe. A pressure transducer was mounted at the entrance to the inner pipe for the purpose of measuring system pressure.

The outer pipe of the flow metering section consists of a 1.7 m long section of 30.5 cm diameter PVC that connects to a reducer, followed by two 90 degree elbows (Figure 6). The support frame of the flow metering section was made from 5.1 cm and 3.8 cm aluminum angle.

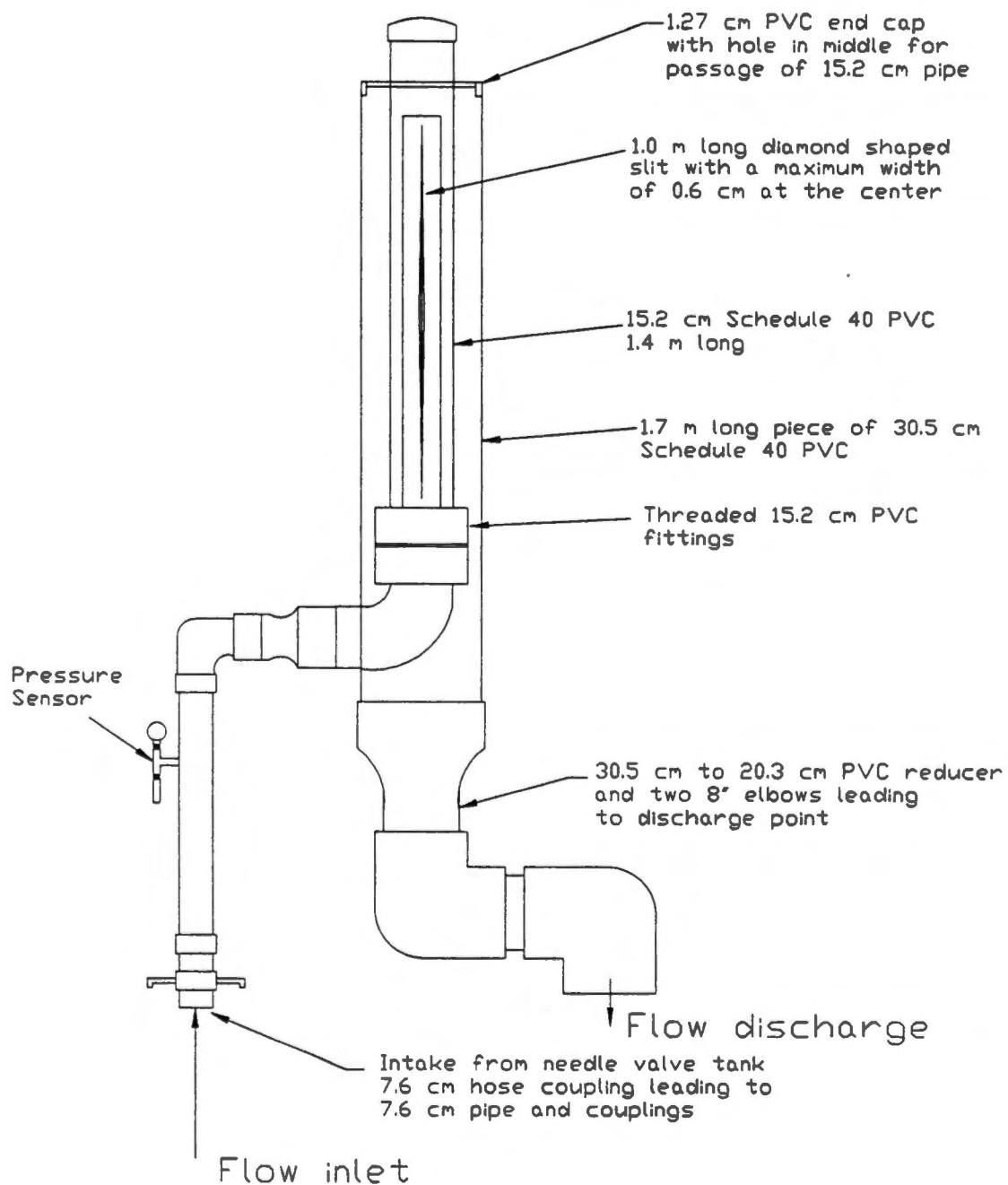


Figure 6. Cut-Away View of Flow Metering Section

Electronic Control System

Theory of Operation

The electronic control system consists of three subsystems: a microcomputer-based controller, a DC motor controller, and a pressure sensor for feedback from the flow metering section. The electronic control system was designed so that the system can be operated manually by switches or automatically with the microcomputer-based controller. This flexibility of control allowed for easy operation and setup of the system.

The microcomputer-based controller was used to automate the entire system. This controller accepts input parameters from a data file and the pressure feedback sensor, then makes decisions on what actions are needed to achieve desired flow rates with varying times. Outputs from the control system control the state and direction of the flow control motor. The pressure feedback sensor measures the actual pressure in the flow metering section. This feedback signal is used to calculate an error term based on the difference between the desired system pressure and the current pressure, and generate a corrective action on the position of the flow control valve. Figure 7 displays the components of the electronic control system.

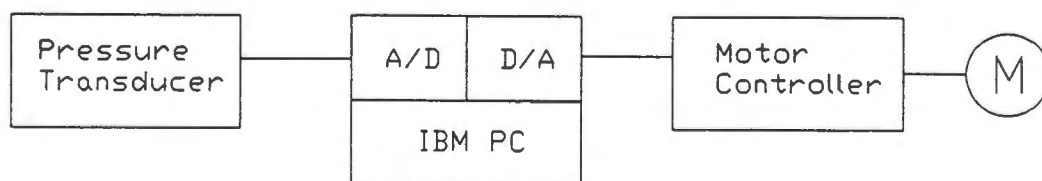


Figure 7. Electronic Control System

Microcomputer-Based Controller

The microcomputer based controller is composed of an IBM PC-XT with analog-to-digital (A/D) and digital-to-analog (D/A) interface cards installed.

A multifunction interface board with a 12-bit A/D (PGA-AD08, Computer Boards, Inc.) is used to convert the analog signal produced by the pressure sensor to a digital format. This interface card also provides digital output ports to turn the motor on and off and to control motor direction.

A 12-bit interface D/A (CIO-DAC02, Computer Boards, Inc.) is used to provide a constant excitation voltage to the pressure sensor, and provides an analog signal used to control the linear speed of the needle valve.

Motor Controller

The motor control system is composed of a variable speed DC motor controller, two solid state relays, two electromechanical relays, and a voltage isolation circuit. Figure 8 shows a schematic of the ladder logic of the motor control electronics.

The variable speed motor controller (125K from Dart Controls, Inc.) is powered by 120 VAC and produces the 0-90 volts required to control the motor.

120 V

Neutral

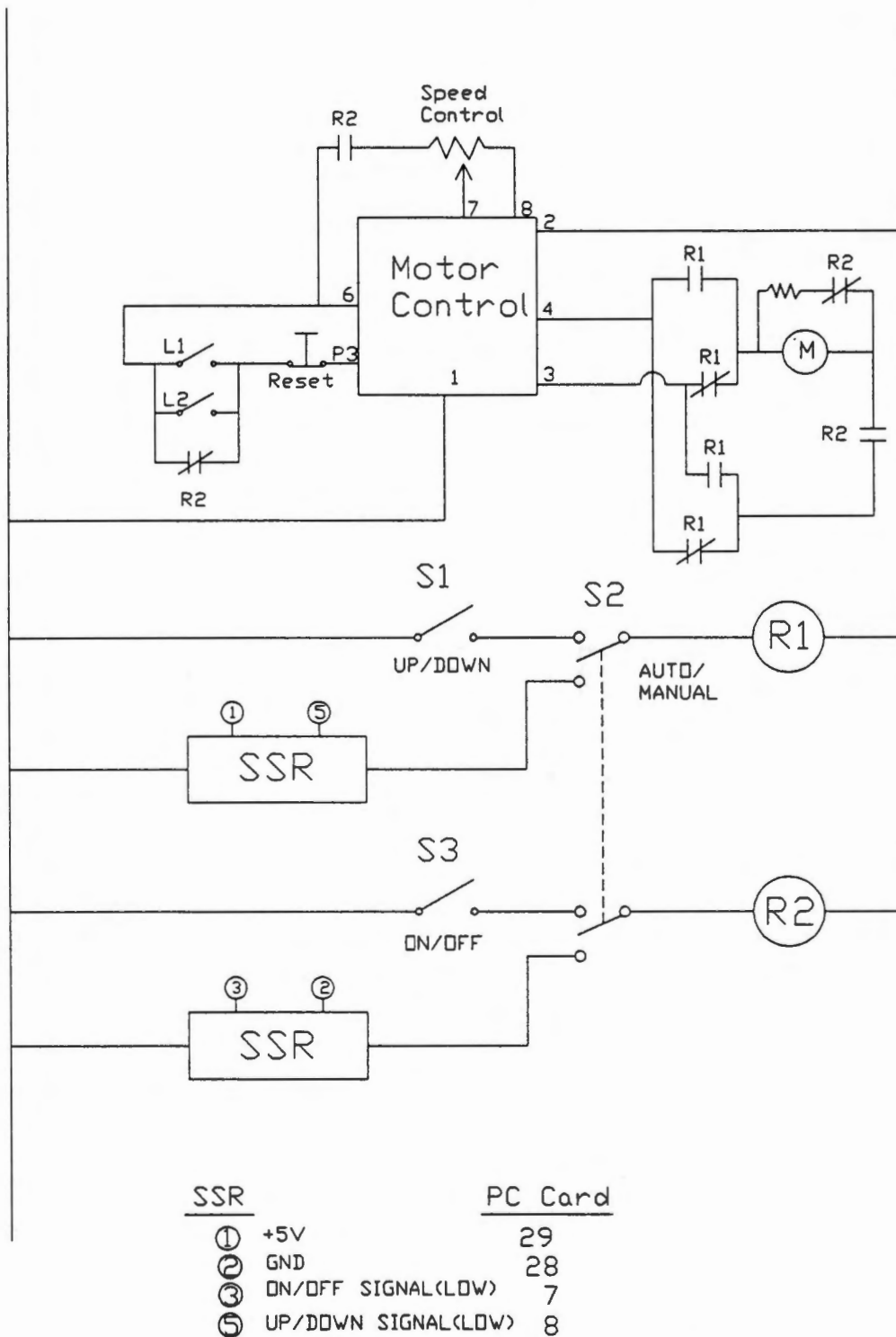


Figure 8. Ladder Logic for Electronic Controller

The flow control valve can either be manually or automatically controlled with the computer. Electromechanical relays control the state and direction of the motor. Motor speed is controlled automatically by connecting the output of the D/A (0-5 volts) to the motor controller. A voltage isolation circuit is used to separate the power return lines of the computer and motor controller. To protect the needle valve from overextending its travel boundaries, two limit switches are used to limit the travel of the needle. One switch is activated when the needle reaches its highest position while the other switch activates when the needle valve seats into the orifice plate.

The limit switches were connected to the "inhibit" pin of the motor controller. When either of the limit switches are activated, power to the motor shuts off. In order for the motor to be reactivated after the limit switches are closed, a manual override switch must be momentarily engaged.

Pressure Feedback Sensor

A pressure transducer is used to translate the pressure at the entrance to the flow metering section to an electrical signal. This pressure measurement is used to model and control the flow rate from the flow metering section.

Originally, a 0-241 kPa transducer was selected to measure the system pressure. However, 35 kPa was the highest pressure measured in the inlet pipe to the flow metering section. To gain better measurement resolution and control accuracy, a 0-35 kPa transducer was purchased (PSI-Tronix, Model PSI-30). This sensor consists of silicon piezoresistive strain gauges mounted on a flat diaphragm arranged in a wheatstone bridge configuration.

Calibration Procedure

The overall objective of the calibration procedure was to develop a known relationship between system pressure and discharge flow rate.

Volumetric Measurements

Two tests procedures were used to measure the flow rate through the hydrograph generator. For low flow rates, a 24 L calibrated bucket was used to catch the volume of water over a specified period of time. For most of the low flow rates, water was collected for 1 minute. A graduated cylinder was used to accurately measure the amount of water collected.

For high flow rates, volumes were measured in a large volumetric tank using a stilling well. A thin rod with a float attached to its bottom was used to determine the change in height in the tank for a specified period of time.

Calibration Program

To take pressure readings while simultaneously measuring flow rates, a program was written to read the pressure transducer and store the readings on the hard drive of the PC. The program averaged 25 pressure readings over an approximate 1 second interval. These average readings were then stored to the hard drive of the computer. To find the average pressure of a corresponding flow rate, the pressure readings taken every second were averaged over the entire flow measurement period.

Calibration Results

The hydrograph generator was found to produce a flow range from 0.1 to 1300 L/min. The corresponding pressure range was 9.3 kPa to just over 34.5 kPa.

TableCurve® (Janson Software Inc.), a curve fitting software program, was used to model the nonlinear relationship between inlet pressure and flow rate. The following equation fit the data best over the desired flow range:

$$Pressure(kPa) = \frac{a+c*\ln[flow(L/min)]}{1+b*\ln[flow(L/min)]}$$

where;

$$a = 8.8465$$

$$b = -0.1191$$

$$c = -0.6106$$

This equation yielded an R² value of 0.998. Figure 9 displays the calibration curve produced from the TableCurve® program. Figure 10 displays the error associated with each flow rate in the calibration equation.

Control Programs

Two automation programs were developed for the hydrograph generator. The first was written to produce a hydrograph derived from a dimensionless unit hydrograph. The second program was developed to produce static flow rates that could be chosen arbitrarily by the operator.

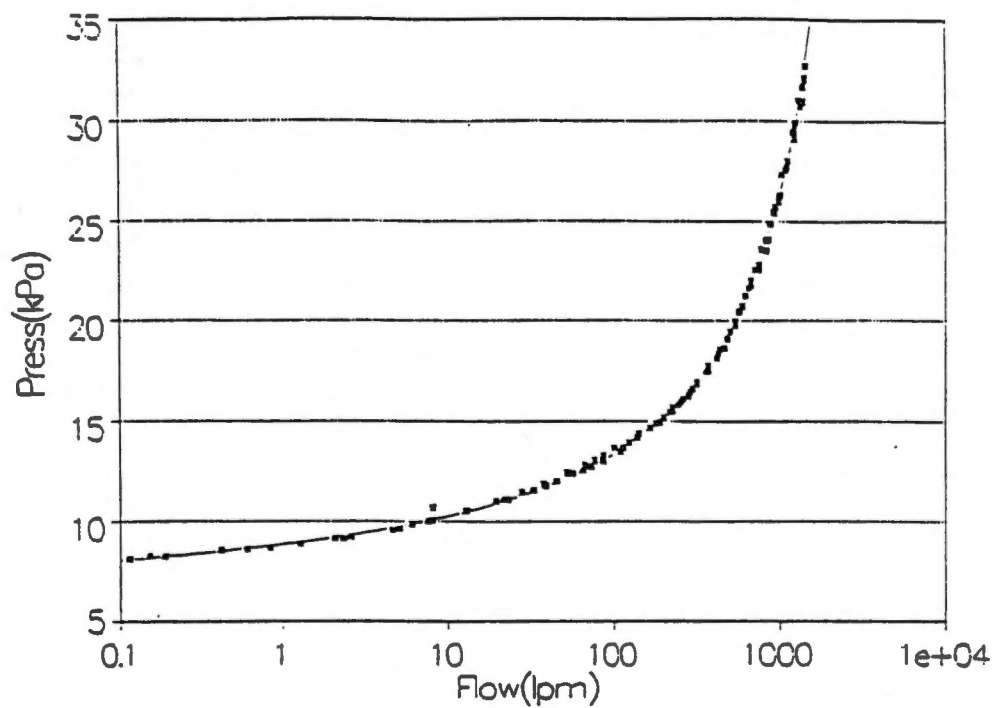


Figure 9. Calibration curve relating flow rate versus pressure for flow metering section

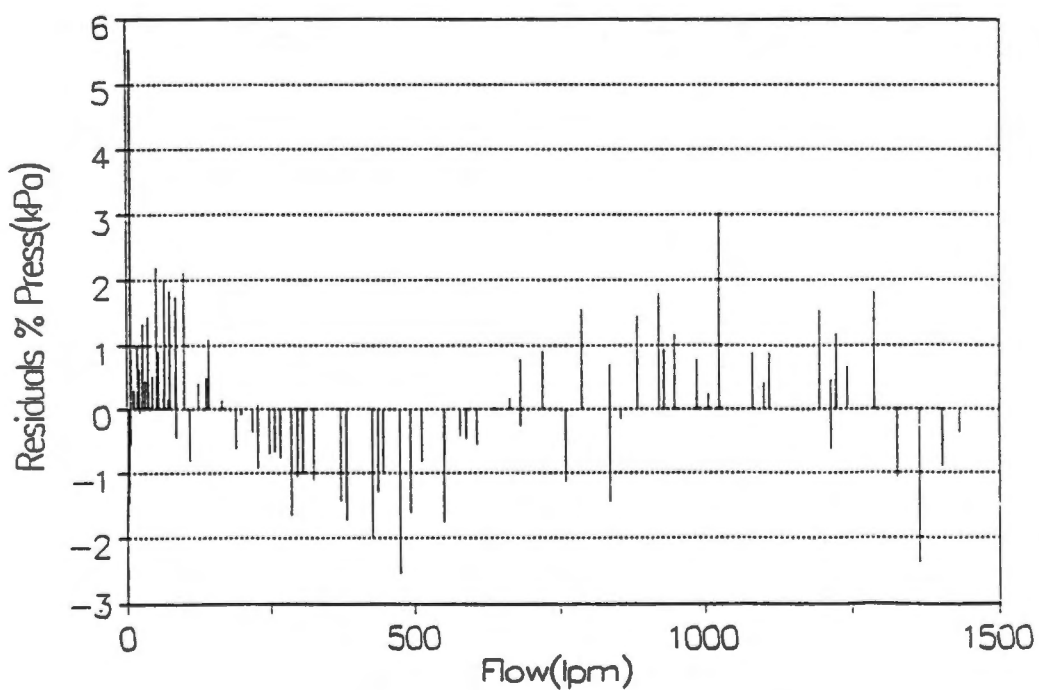


Figure 10. Residual errors plotted versus flow rate

Hydrographs

As discussed earlier, a hydrograph describes the relationship between discharge and time during a runoff event. In order for a computer-based control system to reproduce a hydrograph, a data file was created, containing times and corresponding flow rates. The Soil Conservation Service's dimensionless unit hydrograph was used to define the general hydrograph shape. This unit hydrograph was plotted over 100 arbitrary units of flow and 100 arbitrary units of time to describe the basic hydrograph shape.

The coordinates of the Soil Conservation Service's hydrograph curve were used to fit an equation using TableCurve® software. This equation enabled the production of a hydrograph by inserting the length of the hydrograph and the peak flow rate. Using this equation and a spreadsheet program, flow rates were calculated at short time increments. From this spreadsheet, a data file containing lines of time and flow rate was produced.

The program written to read the data file and produce a simulated hydrograph is shown in algorithm format below:

1. The low-level drivers for the D/A and A/D cards were loaded and initialized. One channel of the D/A was programmed to excite the pressure transducer at 10 volts. All control was initially turned off.
2. The computer then read the desired hydrograph data file stored on disk and transferred each line of data into a program array. An output file was opened to store actual hydrograph flow rates with desired hydrograph data in the same data file.
3. The program set the time to zero and began the timing sequence for the hydrograph.
4. The first line of desired flow rate and time was read from the data array. The computer compared the actual time with that read from the data file. If the actual time was before the data time, the program continued

with the same data values of flow rate and time. If the actual time was later than the data time, then the computer read the next line of flow rate and time information from the data array.

5. The flow rate read from the data file was converted to a corresponding system pressure using the calibration equation. A system pressure reading was then taken from the pressure transducer. The difference between the actual pressure at the flow inlet and the desired pressure was then calculated. This difference was used to calculate an error term used to actuate a corrective action in the positioning of the flow control valve. From the sign of the error signal, the computer determined which direction the needle needed to travel.
6. The computer sent a voltage to the motor controller to control the speed of the needle valve. If the difference between actual and desired pressure was within an acceptable band, the voltage sent to the motor controller was insufficient to actuate the motor. The larger the error term, the greater the corrective action, and the faster the motor would run.
7. During program execution, the program constantly updated the computer screen with important information such as the difference in system pressure and desired pressure, the direction and magnitude of the motor output, and time into a simulated hydrograph. Desired and actual flow rates were also displayed to give the operator the ability to monitor the effectiveness of the system.
8. When all of the data lines had been read, the computer disabled power to the motor controller and ended the program.

Static Flow Rates

The program written to achieve a static flow rate was similar to the hydrograph program. The difference in the two programs was that a data file containing flow rate and time was not needed.

The desired static flow rate was entered through the keyboard of the PC. This flow rate was maintained until the computer was given instructions to change the flow rate or to end the program. Appendix A contains both the programs to produce hydrographs and static flow rates.

RESULTS

The hydrograph generator system produced controllable flow rates from 0.03 to 1300 L/min. The system had the capability of producing either static flow rates or flow rates that followed the shape of a hydrograph as defined from a data file.

Figure 11 shows an example of the system's ability to follow the shape of a hydrograph defined by a data file containing flow rates and time based on the Soil Conservation Service's dimensionless hydrograph.

The average error from individual readings taken and stored throughout the hydrograph simulation was calculated to be 1.80% for this test. Based on the standard deviation of these calculated errors, the error of the system rarely exceeded 5%.

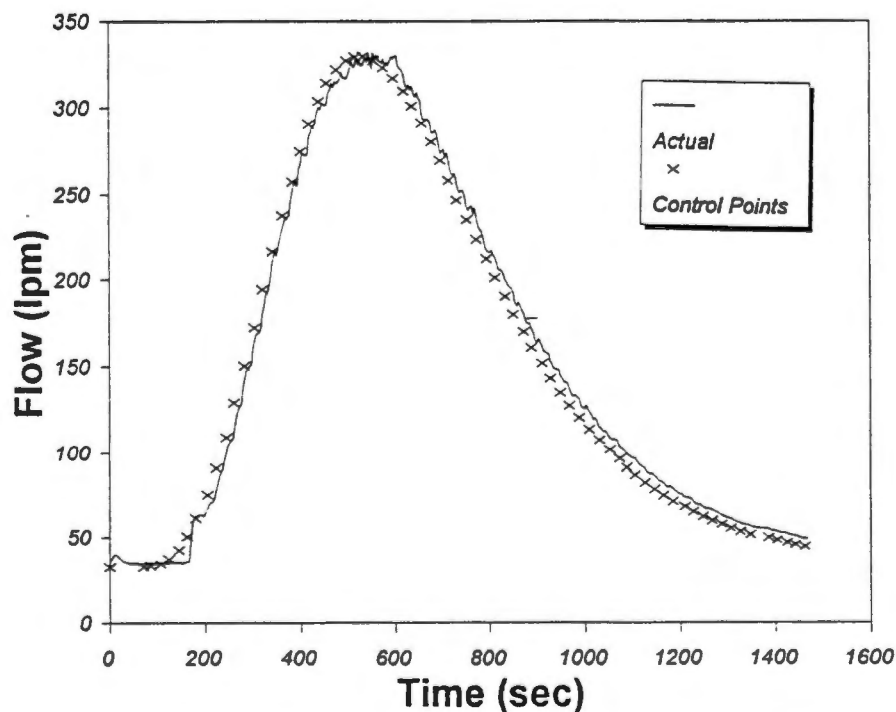


Figure 11. Results From an Actual Hydrograph Run

DISCUSSION

The objective of this study was to design and construct a device with the ability to automatically produce controllable flow rates that follow a predefined hydrograph shape. These objectives were achieved using a design based on the principles of pressure control and system feedback to produce flow rates that rarely exceeded 5% error from the desired rates.

Although this system did not produce the smooth curve of an actual hydrograph, it did a very good job in following the general shape of the curve. For this reason, this system could be used in the laboratory to test the accuracy of flow measurement devices such as weirs and flumes. This system could also be used to test the ability of water sampling equipment in defining the timing and amount of contaminant movement.

Future work involving the design of this system should concentrate on achieving a smoother hydrograph curve. A smooth curve could be produced by providing more data points for the controller to read. The response of the system could also be improved by developing a proportional and integral control for the system. The system used only proportional control principles.

This system required frequent calibration due to system drift. Variations in slit geometry are believed to account for much of the system calibration drift.

PART 3: THE DESIGN AND EVALUATION OF A CONTINUOUS, FLOW-PROPORTIONAL, REAL-TIME STREAMFLOW SAMPLING UNIT

INTRODUCTION

Background

Stream sampling is one of the basic elements of any water quality study. Sampling is required to measure constituents that cannot be measured by in-situ monitoring methods, and is used to describe the chemical composition of a water body and to monitor other characteristics of a stream. Sampling information defines abnormal concentrations of chemical constituents, peaks of constituent discharges, and the mean concentration of constituents in a stream.

The information acquired from stream sampling is a useful tool in modelling constituent movement for future studies of stream characteristics, and in complying with regulatory agencies. The National Pollutant Discharge Elimination System (NPDES), a branch of the Environmental Protection Agency (EPA), uses sampling information to support issuance and revision of permits that allow industries and utilities to discharge wastewaters into streams. Private industries conduct water sampling to acquire proof of compliance with the guidelines of regulatory agencies.

Agricultural runoff is sampled by researchers to provide information for in studies aimed at reducing the amount of erosion and the movement of pesticides and fertilizers into our nation's streams.

Although sampling provides useful information on the characteristics of constituent movement, there are problems with current water sampling methods. Discrete grab samples, commonly used in commercially available sampling equipment, provide information about the characteristics of a stream at a particular instant in time. These samples are merely "snapshots" in time and do not represent the characteristics of the stream for an entire flow period because sudden spikes in constituent concentrations can pass by a sampling station undetected. To calculate mass movement from these types of samples, assumptions are made concerning the periods in-between the collection of samples. Laboratory costs associated with grab sampling are more expensive than for other sampling methods due to the number of samples that must be analyzed.

Composite sampling is used to acquire mass constituent movement information at lower costs than grab sampling. The problem with this method is that it yields no information on the timing of constituent movement because all individual samples are combined into a single composite container.

Continuously extracting a known portion of flow ensures complete streamflow coverage and therefore approximates to a true monitoring system. Unfortunately, this method yields excessively large sample volumes, and because most continuous sampling methods use composite sample bottles, no information on timing is given.

A sampling method that combines the advantages of continuous flow proportional extraction and discrete sample collection will provide a more accurate

monitoring system because information on both constituent timing and mass can be collected. Such a system requires the collection of small sample volumes to reduce both storage requirements and laboratory costs.

Objectives

The objectives of this study were to:

1. Design and automate a prototype sampling unit that combines the advantages of continuous flow proportional extraction and discrete sample collection.
2. Evaluate this prototype sampling unit against a modern commercially available discrete sampler under static and dynamic constituent and flow conditions.

REVIEW OF LITERATURE

Sampling Information

Stream sampling is used to provide information necessary for establishing water quality standards. Sampling is most often used to comply with permits established by the EPA. To assure compliance with the terms and requirements of EPA permits, a discharger of pollutants must consider the following: the amount of effluent, concentration, or other measurement specified in a permit; the volume of effluent discharged from each point source; the proper installation, use, and maintenance of

monitoring equipment; type, amount, and quantity of pollution discharged; and test procedures for the analysis of pollutants.

Sampling Standards and Protocols

The NPDES, a branch of the EPA, requires that all dischargers of pollutants meet guidelines stated in NPDES permits. For streams with a continuous discharge of pollutants, the maximum daily discharge and average monthly discharge must be found to comply with NPDES permits. For streams that have noncontinuous discharges, knowledge of the following parameters are required to comply with NPDES regulations:

1. The frequency of effluent discharges
2. The total mass of pollutants moved during an effluent discharge
3. The maximum rate of effluent discharge
4. Comparisons to limitations on specified pollutants by mass, concentration, or other appropriate measure. For example, a stream should not contain at any time more than 0.1 mg/L or more than 250 g of zinc in any total discharge (BNA, 1989).

To comply with the NPDES, samples must be taken from a rainfall event greater than 2.54 mm at least 72 hours from the last 2.54 mm of rain. The duration and total rainfall should be $\frac{1}{2}$ to $1\frac{1}{2}$ times the average storm for an area. The streamflow data that is required for monitoring includes maximum flow rate, total volume of discharge, and the method of flow measurement for the event (ISCO, 1991).

The American Society For Testing Materials (ASTM) lists three procedures for the collection of water samples (ASTM, 1992). The first of these is the collection of

a grab sample at a specified site representing conditions at the time of sampling. Grab samples are required by the EPA for each hour of discharge, up to a minimum of four grab samples for discharge events of 4 or more hours of duration. EPA requires that grab samples be analyzed for pH, temperature, cyanide, total phenols, residual chlorine, oil and grease, and fecal coliform.

The second ASTM procedure for sampling is the collection of a composite sample consisting of multiple grab samples. EPA requires composite samples for sampling pollutants that do not require grab samples. Composite samples should be a combination of a minimum of eight sample aliquots of at least 100 mL each. Depending on the variability of discharges, 2, 4, 8, 16, or 24-hour composites may be required. For NPDES permit compliance, composites must be proportional to either the streamflow at the time of sampling or to the total stream flow since the collection of the previous sample (BNA, 1989).

The third ASTM procedure for sampling is to provide a continuous flowing sample from one or more sampling sites. The continuously flowing sample is normally composited into a single large container. Sampling continuously prevents errors in monitoring that an instantaneous pulse of pollutants may cause. However, the large sample volumes are not needed. Thus, continuous sampling is rarely practiced.

The NPDES defines two types of samples to be taken during a storm water runoff event. The first is a "first flush grab sample" taken during the first 30 minutes of a storm. The second type is a flow weighted composite sample. Industrial dischargers are required to collect both first flush grab samples and flow weighted composite samples. Municipalities are required to collect only flow weighted composite samples from three storm events, 1 month apart for compliance (EPA, 1988).

Samples should be taken at a site where the flow is well mixed. Sites near a Parshall flume or locations with hydraulic turbulence are excellent sampling points. The sample should be taken in the center of the flow channel where the velocity is highest and the possibility that solids have settled is at a minimum. The mouth of the bottle or the sample inlet should be placed a few inches below the water surface to avoid an excess of floating materials (BNA, 1989).

A sample volume must be obtained that is large enough so that all required analyses can be performed. The minimum volume of a grab sample should be between 1 and 2 L. Composite samples should be composed of individual portions of at least 25 to 100 mL. A total composite sample should be between 2 and 4 L, depending on the frequency of sampling.

The sampling period for a composite sample should not exceed 24 hours. Table 2 is a suggested sampling schedule for both grab and composite samples (BNA, 1989).

Table 2. Suggested Sampling Schedule for Grab and Composite Samples

Characteristic	High Variability	Low Variability
BOD	4 hr	12 hr
COD	2 hr	8 hr
Suspended Solids	8 hr	24 hr
Alkalinity	1 hr grab	8 hr
pH	Continuous	4 hr
Nitrogen	24 hr	24 hr
Heavy Metals	4 hr	24 hr

Sampling Techniques

Grab Samples

A grab sample is an individual sample collected from a single location at a specified time, or at period of time generally not exceeding 15 minutes. Grab samples are taken manually by tipping an open container into a stream so that the mouth of the bottle faces upstream. Sampling devices have been devised that will allow grab sampling at a specified depth in a stream (EPA, 1988).

Grab samples are the least representative of the sampling techniques because they represent only a "snap-shot" in time and often miss sudden spikes in concentration. Grab samples may show abnormally high concentrations in some instances, while at other times they give no indication of pollutant concentrations. This is due to the fact that these samples represent only the concentration of a stream at the time of sample extraction. No information on concentration between samples can be found using grab samples.

Another disadvantage of grab sampling is that total mass loadings calculated from grab samples are accurate only in a spatially homogenous stream of constant flow. Tarazi et al. (1970) concluded that the use of grab samples is more expensive than flow weighted composites, and that they also create difficulties in data handling because of the relatively large number of samples needed to accurately cover a storm event.

At high sampling frequencies, grab samples are useful in detecting fluctuations in both pollutant composition and pollutant discharge. A grab sample can be useful in obtaining the waste characteristics of a batch dump in a stream that does not flow

continuously, but only if the time of dumping is known. A grab sample is also useful in sampling streams in which the waste characteristics are constant.

Composite Samples

Composite samples are composed of a number of grab samples taken during a compositing period. Composite samples essentially represent an average of the characteristics of the source over the elapsed time of sampling. Composite sampling is normally used for accounting for variations in flow and waste constituents and minimizing the analytical effort.

Composite samples may be prepared manually or automatically to produce information on variability, average composition, pollution loads, or trends in performance. Enough samples should be taken so that, when mixed together before being analyzed, the result will be similar to taking a grab sample from a completely mixed tank that had collected all the flow from a stream (BNA, 1989). The greater the frequency of taking grab samples, the more accurate the composite will be.

The four basic types of composite samples include time interval composites, flow proportional composites, areal composites, and vertical composites. Time interval composites are comprised of a varying number of grab samples collected at equal time intervals during the compositing period. A flow proportional composite is made up of a series of samples collected proportional to either flow rate or total flow in a stream. An areal composite is a sample composed of individual grab samples collected on an areal or cross-sectional basis. A vertical composite is made up of individual grab samples collected from a vertical cross section.

Flow proportioned samples provide the most representative sample of flow over a given time period (Keith, 1988). For most studies either a time interval composite or a flow interval composite is taken because they require less labor than areal and vertical composites. Time interval and flow proportional composite samples that are taken frequently and stored in a small container are known as sequential composites. This method of compositing provides a more representative sample, while retaining grab sample information and reducing sample volume.

Compositing individual grab samples is one of the easier methods used to monitor a stream. However, once the samples are composited into a single container, information on the timing of chemical movement is destroyed. Composite samples may miss sudden changes in concentrations because they are merely a series of grab samples.

Continuous Samples

Continuously extracting a sample from a stream is the third technique of sampling. This method is accomplished by using automatic sampling equipment. The sample flow rate may be held constant or varied in proportion to the flow. The advantage of this method is that it ensures complete coverage of the flow because a portion of flow is being continuously extracted and stored. The disadvantage of this approach is that, for current samplers, the sample volume is too large for practical applications. This method is currently only practical in streams with low flow rates.

Existing Sampling Devices

Grab samples are normally taken by using a wide mouth bottle with an opening of at least 2 inches. The wide mouth bottle is necessary for rapidly obtaining samples. Economical and safe 1 L polyethylene bottles are commercially available. A long handled, cylindrical dipper can be used to obtain a sufficient volume for sampling.

Point samplers are used to collect a grab sample at a specified depth. These samplers are normally composed of a weighted bottle with a cork. When the bottle is lowered to the specified depth, the cork is removed either by a string or a mechanical device, allowing a sample to be captured.

For hard to reach sites, special samplers must be used. Although a bucket and rope can be used to sample streams that are hard to access, a hand operated pump may also be used. A sampling tube is lowered into the stream, then the sample is pumped from the tube. The Sirco Uniscoop Liquid Sampler is a sampler capable of sampling hard to reach spaces. This sampler is lowered into the stream to a desired level, then by manually pulling on the handle, a plug opens that admits liquid into a sample container (BNA, 1989).

Continuous proportional samplers, commonly used to measure runoff from agricultural lands, are used to sample streamflow. The most widely used proportional sampling device is the Coshocton wheel sampler. This device was first developed by W.H. Pomerene in 1947 and later modified by D.H. Parsons (1954). The Coshocton wheel sampler is composed of an H-flume equipped with a sampling wheel that will extract approximately 1% of total streamflow. The Coshocton wheel works well for low flows, but as flow increases sampling becomes erratic. Coshocton wheel

samplers also require a large storage container for even small amounts of flow (Carter and Parsons, 1967).

Coote and Zwerman (1972) developed a divisor to reduce the 1% Coshocton wheel sample to 0.1 to 0.2% . This device divides the flow from the Coshocton outlet into ten equal portions, eight or nine of which are discharged to waste.

Replogle and Johnson (1963) replaced the Coshocton wheel with an electrically driven slotted wheel. Although this sampling device increased the accuracy of the sample taken, the sample volume was still too large for stream sampling.

Geib (1933) was the first to suggest using divisor boxes to collect runoff samples. Geib's multi-slot divisor box consisted of a number of identical rectangular slots, stamped out with a die to ensure sampling accuracy and uniformity. This device was found to be suitable for obtaining a definite sample of the runoff from small erosion plots. A disadvantage of these boxes is that as flow increases the divisor boxes require a larger amount of storage space.

Barnes and Frevert (1954) developed and tested, respectively, a slotted conduit sampler for use on large watersheds (Barnes and Johnson, 1956). This slot sampler was designed to take 0.01% of the flow through a 1-foot notch, or 1/3000 of the flow through a 30-foot notch. To further reduce the sampling ratio, a Coshocton wheel was installed. The problems with this sampler included poor sampling at low flows, and susceptibility to clogging by trash and debris.

Laflen (1975) developed a two-stage multi-weir divisor for measuring and sampling tile effluent. The system consists of two flumes in series, with two sample collection tanks and a stilling basin for recording water levels. Each flume stage discharges through a weir plate that has thirteen identical 22.5 degree "V" notch

weirs. In each stage, the flow from 12 of the weirs was wasted while the flow from the center weir was collected. This system was determined to work well with flow rates in excess of 25 gpm. Maximum flow rates of 1,000 gpm have been measured with this device.

Nixon (1976) developed a submersible bag sampler for use on small feedlot runoff plots. This sampler used one large tube and one small tube extending from a horizontal plate. Samples were collected in a plastic bag from the smaller tube. In field tests, where the sampler was submerged, the sampling tube would become clogged with debris. For unsubmerged flow, the sampling ratio could not be held constant. Dressing et al. (1987) modified this bag sampler by installing a settling box, trash screen, and maintaining high flushing rates that keep a flush valve and float free from interference. A major problem of sampling streams with this sampler would be that total mass/unit loadings would be difficult to determine.

Schwab and Brehm (1974) reported on a surface flow sampler for obtaining 1/1000 of the total volume at varying flow rates. The sampler consists of a series of small tubes or buckets of different lengths mounted on a chain running around two sprockets in a vertical plane. Each bucket picks up a fixed amount of water and dumps it into a collection pan. The number of buckets extracting water is proportional to the flow rate past the sampler. An electric motor activated by a float switch is used to drive the chain and sprockets. The problem with this sampler is that the mechanical parts are susceptible to failure.

Kohnke and Hickok (1943) developed an automatic runoff sampler for small watersheds. A plate providing a vertical series of circular holes was set into the side wall of a H-type water flume to conduct 1% of the flow into a collector manifold.

One-ninth of this water is directed into a tank. Theoretically, the sample contains the constituents of the runoff water in concentrations corresponding to their weighted averages throughout any period of runoff. Problems with this sampler include excessively large sample volumes and clogging by trash and debris.

Heinemann and Brown (1972) developed a fractional sediment sampler that collects large volume representative samples of water and sediment from surface drainage streams. The sampler was designed to operate at the nape of a drop structure having a fall of 30 cm or more. The design was developed to collect the full vertical profile by moving the sampler across the stream width to collect fully integrated representative samples. When the flow through the sampler is too large to handle conveniently, splitter stages can be added to subdivide the flow from 25 to 50% of the original sample volume. The disadvantage of this sampler is that it takes two people to operate it. It is also difficult to use on streams because of the required drop structure.

Russell (1945) developed a runoff sampler based on the principle of the tipping bucket. It has the advantages of being mechanically simple, unaffected by debris, and readily cleans itself of soil deposited when the velocity is lowered. An automatic tipping bucket sampler can be built that will allow the sampling of flows in the range of 0.1 to 20 gpm (BNA, 1989).

Bottcher and Miller (1991) designed a self-propelled flow integrating water sampler for use on small runoff plots. The sampler collects a flow proportional composite sample using a helical tube attached to a paddle wheel rotating through the control flume of the sampler. The helical tube collects a sample volume proportional

to the water depth and delivers it to a composite bottle with each rotation. In field tests it performed well over a wide range of submerged conditions.

Proportional samplers work well when calculating mass loadings from runoff events. The problem with all proportional samplers is that they can not give any information on the timing of pollutant discharges. Most of these samplers sample continuously, which ensures adequate coverage of the flow. However, because all the sample is combined into a single container, there is no way of distinguishing between different periods of flow.

Automatic Samplers

Justification

The problem with manual sampling is that most storm runoff events or pollutant discharges occur when personnel are not available for sampling. It also becomes rather expensive to sample continuously. To overcome these problems, automatic samplers have been developed to sample at timed or flow proportional intervals.

Single-stage samplers are among the simplest automatic devices available. These samplers consist of a sample container, an air exhaust, and a sample intake tube. Each tube is bent to a proper shape and inserted into the sample bottle's stopper. These samplers have been extensively used and tested on flashy or ephemeral streams where it's difficult to reach a station to manually collect samples. A disadvantage of these samplers is that they sample only the rising limb of a hydrograph; the recession limb is ignored. Another limitation is that the samples are

not proportional to flow. Examples of single-stage samplers include the U-59 and the U-73 sediment samplers used by the United States Geological Survey (USGS).

Knisel et al. (1971) combined single-stage samplers, attached to H-flumes, with a mechanically driven automated recession sampler. The single-stage samplers sampled the rising limb of a hydrograph. The recession sampler, activated by a water level recorder, then engages to sample the falling limb. These samplers operate well on single peak storms but they require considerable modification to sample more complicated multi-peak storms.

Automatic Sampler Requirements

Automatic pumping samples are the most commonly used commercially available samplers. These samplers are used to sample remote locations, but there are the following disadvantages:

1. They do not sample isokinetically because the pump speed cannot be adjusted when flow rate changes. Pumping forces attempt to pull particles laterally from their streamlines and accelerates them in the direction of the intake.
2. A possibility of cross contamination exists from sample to sample as a result of residues remaining in a system after the purge cycle.
3. Where streamflow duration often continues for several days, the limited number of sample bottles prohibits the selection of a reasonable time interval between samples.
4. Sample calibrations are affected by fouling from marine growth and sediment.
5. Blockages occur in the sampling lines from debris and marine growth.
6. Samples are subject to biodegradation before analysis.

7. Sampling equipment is susceptible to corrosion.
8. The pumping lift for most samplers is relatively small and may be less than the normal fluctuations in stage at some sites.

To improve sample quality, the EPA (1991) established the following requirements for automatic samplers:

1. Sampling equipment must be properly cleaned to avoid cross contamination that could result from prior use.
2. No plastic or metal parts of the sampler shall come in contact with the water or wastewater stream when parameters to be analyzed could be impacted by these materials.
3. The automatic sampler must be able to provide adequate refrigeration during the sampling period. Ideally, the sample should be maintained near 4°C. This can be accomplished in the field by using ice.
4. The automatic sampler must be able to collect a large enough sample for all parameters to be analyzed.
5. if a peristaltic pump is used, a minimum of 100 mL should be collected each time the sampler is activated in order to make sure sample lines are not contaminated.
6. The automatic sampler should provide a lift of at least 20 feet, and the sampler should be adjustable so that the volume is not a function of the pumping head.
7. Pumping velocity must be adequate to transport solids and not allow them to settle.
8. The intake line leading to the pump should be purged before each sample is taken.
9. The minimum inside diameter of the intake line should be 0.25 inch.
10. An adequate power source should be available to operate the sampler for 48 hours at a 30 minute sampling interval.

The USGS has the following criteria for sediment sampling with automatic samplers (Edwards and Glysson, 1988):

- 1. Stream velocity and sampler intake velocity should be equal to allow for isokinetic sample collection if the intake is aligned with the approaching flow.**
- 2. A suspended sediment sample should be delivered from stream to sample container without a change in sediment concentration and particle size distribution.**
- 3. Cross contamination of a sample caused by sediment carry over in the system between sample collection periods should be prevented.**
- 4. The sampler should be capable of sediment collection when concentrations reach 50,000 mg/L and when particle diameters reach 0.25 mm. This is to ensure that sediments will not settle in intake and sampling lines.**
- 5. Sample container volumes should be at least 350 mL to assure a representative sediment sample is taken.**
- 6. The inside diameter of the intake should be 9.5 or 19 mm, depending upon the size of the sampler being used.**
- 7. The mean velocity within the sampler plumbing should be great enough to ensure turbulent flow.**
- 8. The sampler should be capable of vertical pumping lifts up to 35 feet from intake to sample container.**
- 9. The sampler should be capable of collecting a reasonable number of samples. The number of samples will be dependent upon the purpose of sample collection and flow conditions.**
- 10. Some provision should be made for protection against freezing, evaporation, and dust contamination.**
- 11. The sampler container unit should be constructed to facilitate removal and transport as a unit.**
- 12. The sampling cycle should be initiated in response to a timing device or stage change.**
- 13. The capability of recording the sample collection date and time should exist.**

14. The provision for operation using DC battery power or 110 volt AC power should exist.
15. The weight of the entire sampler or any one of its principle components should not exceed 100 pounds.
16. The maximum dimensions of the entire sampler or any of its components should not exceed 35 inches in width or 79 inches in height.
17. The required floor area for the fully assembled sampler should not exceed 9 square feet.

Archer (1980) stated that automatic pumping samplers should offer the following features:

1. A self priming pump with minimal aeration or degassing of the sample.
2. A back flushing facility to clear the sampling inlet periodically.
3. An adequate flow rate in sampling lines to minimize settlement and marine growth.
4. An adequate filtration system to protect sensors from abrasion or sediment.
5. Flow sensor self-calibration or standardization.
6. Sensor self cleaning.
7. System modularity for easy maintenance and repair.
8. A continuous maintenance and calibration program will be required to ensure reliable operation and to correlate sensor readings against standard chemical procedures.

Scholfield (1980) stated that an automatic sampler should be used to take samples continuously in proportion to flow in order to ensure complete coverage of the

flow. Because this type of sampling requires large collection bottles and also presents a challenging maintenance problem, continuous sampling is seldom used in automatic samplers. When continuous sampling is not used, the sampling frequency should be as high as possible to produce a near representative sample. A desirable feature of an automatic sampler is the ability to store multi-aliquot samples in discrete bottles.

Types of Automatic Samplers

An automatic pumping sampler generally consists of five subsystems. The sampler intake system should reliably gather samples from a stream. The sample gathering system is responsible for moving the source to the storage container. The sample transport system transports the sample from the intake to the sample container by a plastic or teflon tube. The sample storage system limits the amount of sample that can be taken. The power and control system supplies the sampler with power and allows the collection of the time interval or composited samples.

The sample gathering procedure can be accomplished by mechanical, forced flow, or suction lift devices. A mechanical gathering system consists of cups, buckets, or scoops. Mechanical systems are used to collect a fixed or flow proportional volume of liquids for sites that require high lifts. However, mechanical systems can obstruct the flow in the stream, and they must be periodically inspected and maintained to prevent failure.

In a forced flow gathering system, pressure is applied to the liquid at the source, forcing the sample into a storage container. Examples of forced flow devices are pneumatic ejectors and submersible pumps. This method can sample at greater

depths due to high discharge pressures. Unfortunately, forced flow systems obstruct streamflow and are vulnerable to blockages.

Suction lift gathering systems are the most widely used because they have the greatest versatility and only minimally affect flow patterns. These systems have high intake and transport velocities in which the sample does not come into contact with the pumping device. A suction lift system consists of a vacuum or a peristaltic pump. Peristaltic pumps are normally used because they are generally lightweight and portable, and may be powered by 12 volt batteries. Problems associated with suction lift devices include lifts that are limited to less than 25 feet due to internal friction losses, and increases in solids concentrations from the release of dissolved gases caused by the application of negative pressure (therefore, suction lift collected samples are not suitable for the analysis of purgeable organics).

Fredrickson (1969) developed a battery powered automatic sampler that offers the advantage of extracting samples proportional to streamflow. This is accomplished by using a streamflow sensing unit, coupled to a water level recorder, to divide the expected range of discharge rates into 20 equal increments. The number of samples taken for each flow rate class is 20 times that of the lowest flow rate class. The number of samples taken for each flow rate class increases linearly from the lowest to highest thereby assuring proportionality of sampling. With this device, the intake velocity is standardized, the mean concentration of pollutants can be calculated, trash clogging at the intake is minimized, and the short pumping times helps maintain the power supplying capacity of the batteries.

Swanson (1973) developed a programmable, automatic sampler that collects a sequence of composite samples of runoff. This sampler can be programmed to collect individual samples for any 14 5-minute periods during a total of 12 hours of runoff. The time of collection for each sample is recorded to relate to the runoff hydrograph and recording rain gauge chart. The sampler consists of an arm and dipper, electrically driven by a gear reduction motor through sprockets and a chain, a tipping bucket that collects the aliquot from several rotations of the dipper and delivers them as a single sample, a turntable holding successive sample containers, a gear reduction motor moving the turntable by a friction drive, and a program timer. This sampler permits both quantitative and qualitative analysis of a runoff event with relation to time.

Claridge (1975) developed an automated system for collecting stream water samples at a rate proportional to flow rate with the use of magnetic flow tubes, electronic integration, and a pump operated sampler. When the contacts in a flowmeter close, indicating that the desired quantity of water has been discharged, a small synchronous motor is switched on. Cams open and close switches, governing the operation of the sampler and also permitting power from the sampler to be used to reset the counting mechanism and operate an event marker on the chart recorder of the flowmeter to record when samples are taken. The sampler takes constant volume samples of 100 mL. Claridge's sampler made it possible for the first time to measure the change in concentration of the same elements during flood periods.

Hanson (1966) field tested a non-portable automatic sampler that consists of intakes, a pump, a splitter which draws off the desired volume of sample, a circular table holding 144 bottles, and a water supply for priming the pump and flushing the

intake before sampling. A clock activates the sequence timer in the control box once an hour. When the timer is activated one of three things happens:

1. At stages below the lower float, no sample is pumped and the sampler checks for higher flow in 1 hour.
2. At stages between the lower and upper floats, samples are collected at 2 to 12 hour frequencies depending on which frequency is selected in the control box.
3. At stages above the upper float, the sampler collects one sample every hour. A maximum of two samples per hour can be collected.

Hanson concluded that his sampler would be an asset in a sampling program where either a large number of suspended sediment samples are required from a single sampling site, or a substantial number of samples are needed from a remote site which requires considerable travel time to reach.

Miller et al. (1969) described a battery operated system that takes 28 samples in 12 hours with the sampling initiated by an increase in streamflow. When the water stage rises to a preselected level, a water level sensor closes, permitting electric current to flow from a battery to a timing drive unit. This sampler, called the Chickasaw sediment sampler, has proved to be effective and reliable for taking sediment samples automatically.

The Federal Inter-Agency Sedimentation Project has developed several pumping type samplers to automatically sample suspended sediment loads in streams. Some of the later developments include a volume recording system and an individual sample bottling system. The US PS-69 is a stage activated, electrically driven, sediment sampler capable of collecting up to 72 samples at volumes to 1000 mL. The US PS-82

pumping type sampler is the most recent automatic sampler available from the USGS. It is a lightweight, portable sampler, driven by 12 volt battery power. This sampler is used to sample streamflows transporting particles with a wide range in sizes (Edwards and Glysson, 1988).

The Manning S-4050 sampler uses an air pump to cause alternate pressure and vacuum in a measurement chamber to purge the sampling hose and draw a sample. Particle suspension is maintained by a swirling action of the sample as it passes through the measuring chamber into the sample container. This sampler produces a line velocity of over 1 m/s.

The ISCO model 1680 sampler features an electrically driven peristaltic pump, which is activated on a predetermined schedule by an internal timer or in response to a stage change. The intake tube is purged before and after each pumping period by automatic reversal of the pump. ISCO's model 3700 storm water samplers, when connected with the appropriate flow measuring devices, can be activated by conditions such as stream level, time intervals, or a combination of these conditions. These samplers can be used to collect both first flush grab samples as well as flow proportional composite samples. The ISCO samplers have been found to have a line velocity of 0.62 m/s (Thomas and Eads, 1983).

Sirco manufactures an automatic sampler that uses a cup to draw the sample. The cup travels through a perforated guide into the stream, then empties the sample into a container. This system is motor controlled and can be regulated by a timer or a flow proportional recorder (BNA, 1989).

Markland Specialty Engineering Ltd. has developed a sampler that uses compressed air to actually blow a sample from a stream. A "Duckbill" acts as a check

valve at the sample inlet preventing air from escaping back through the inlet. This sampler may be portable and is capable of taking flow proportional samples. The cost for this sampler varies between \$500 and \$1000 (BNA, 1989).

Summary

The stream sampling techniques that are currently used have many problems associated with them. Because grab samples are instantaneously collected, they are merely "snapshots" in time and may miss sudden spikes in concentration. Abnormally low or high concentrations in grab samples may bias sampling results, and for this reason they do not provide a representative composite for streams with non-uniform pollutant discharges. Mass movement calculations require assumptions to be made concerning stream concentrations during the flow period between grab samples. Another problem with grab sampling is that laboratory analysis may be extensive and becomes rather expensive for long term monitoring.

Composite samples are made by combining a series of grab samples over a flow interval. Because the concentrations of each grab sample are unknown, composite sampling provides no information on the timing of pollutant discharges. Thus, sudden spikes in concentration are missed.

Continuous sampling offers the most complete coverage of flow because a portion of flow is continuously being sampled. The problem with current continuous samplers is that the sample volumes are too large to be handled easily.

No information was found in the literature about a sampling technique that combines the advantages of grab, composite, and continuous samplers. This type of

technique would continuously sample a flow proportioned portion of flow, split the sample, and then composite over a relatively short period into a grab sample sized container. This sampling technique could possibly be used to sample for parameters such as pH because the sampling period will be shorter than a normal composite sample. This technique would allow the calculation of mass/unit loadings, and will also allow the determination in the concentrations of pollutants with time. This technique would make it possible to take an approximate real-time continuous sample.

DESIGN OF PROTOTYPE SAMPLER

Theory of Operation

A sampling unit was designed to continuously extract a 1/500 portion of a stream using a two-stage pump system. The first stage consists of a transfer pump that continuously extracts a portion of the flow, passes it through a mixing chamber, then discharges it downstream of the sampling inlet. The mixing chamber ensures that the sample is well mixed and representative of the stream being sampled. The second pump stage consists of two metering pumps used to extract flow proportional samples from the mixing chamber. Two different sized peristaltic pumps are used in this stage of pumping to allow sampling of a broader flow range.

Flow from the metering pumps is controlled using two three-way solenoid valves. From the metering valves, flow passes through flexible tubing into the sample distribution system. The sample distribution consists of 24 1 L discrete sample bottles

and a delivery system. The sampling unit was automated using a single board computer (SBC) with software that allows the continuous extraction of an automatic, flow proportional, discrete sample. Figure 12 illustrates the major components of the sampling unit.

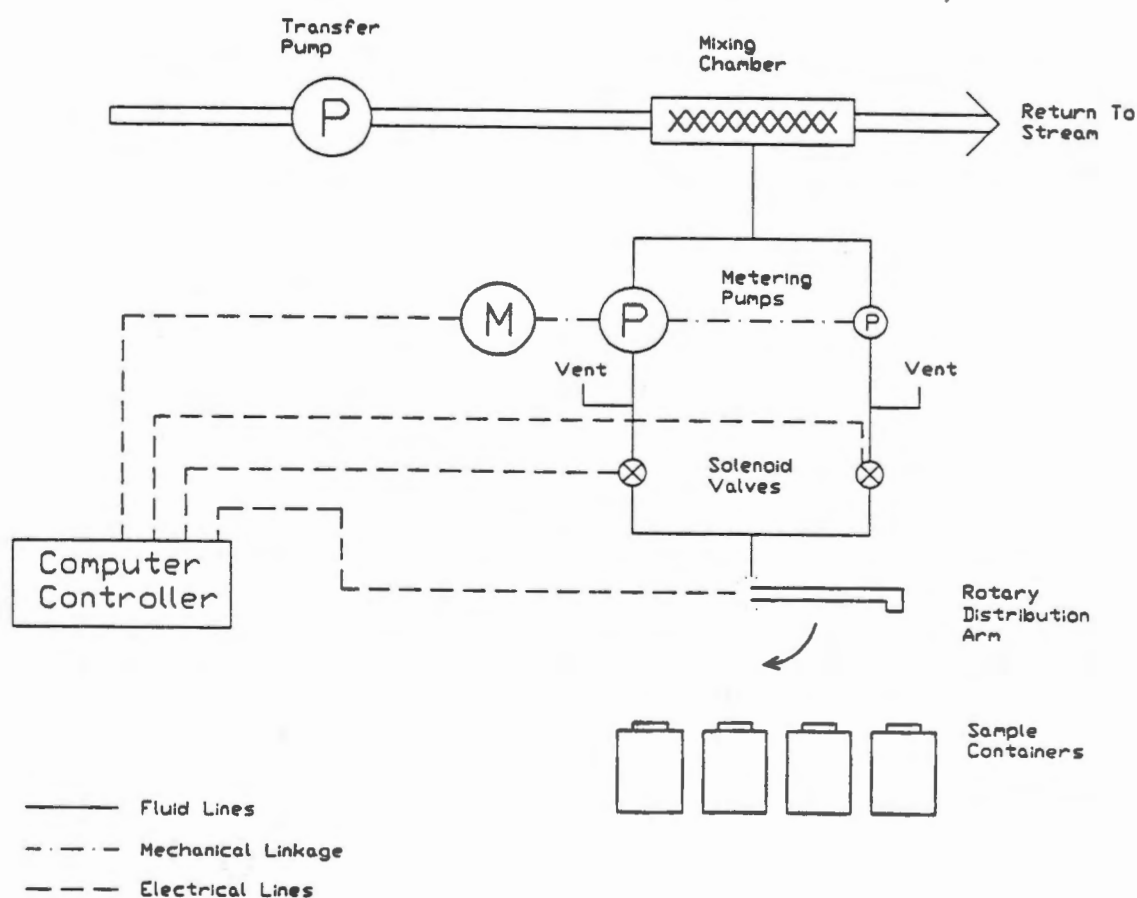


Figure 12. Major components of the sampling unit

Mechanical System

Overview of Mechanical System

The prototype sampling unit uses a small transfer pump to continuously extract a portion of streamflow. The sample is passed into a mixing chamber from which peristaltic metering pumps extract a 1/500 portion of flow. Solenoid valves, along with the peristaltic pumps, allow the sampler to have sensitive flow control over a broad range of flow rates. A distribution system is used to allow discrete sample storage. Instrumentation was mounted so that a programmable control unit can be used to fully automate the sampler.

Transfer Pump

A transfer pump is used to continuously withdraw a portion of a stream and to carry this flow through a mixing chamber. The pump chosen for laboratory purposes was a self priming, 115 VAC, series demand pump (Flojet). This transfer pump has a continuous discharge of 8 L/min.

Mixing Chamber

To ensure that a well mixed representative sample is taken, the flow from the primary pump is passed through a mixing chamber. The mixing chamber is used as a small reservoir from which the metering pumps extracts samples.

The chamber's shell is a 12.7 cm long section of 1.27 cm diameter schedule 40 clear PVC. To provide mixing as flow moves through the chamber, a 1.27 cm wide strip of sheet metal was cut and bent into a spiral shape, 12.7 cm long.

Metering Pumps

The purpose of the metering pump system is to draw a continuous sample from the mixing chamber at a rate proportional to streamflow rate. To meet the design criteria, the metering pumps extract a 1/500 portion of a generated stream that had a maximum flow rate of 1135 L/min.

To provide sampling rates over a wide dynamic flow range, peristaltic metering pumps are used (Cole Parmer, Model 7016 and Model 7018 Masterflex L/S). These peristaltic pump heads have a three-roller design which minimizes pulsations in flow. Each revolution delivers a precisely determined volume, which is specific to the pump head and tubing combination.

The smaller of the two pump heads (Model 7016) was used with 3.1 mm diameter flexible tubing to produce approximately 0.8 mL of fluid per revolution. The maximum flow rate from this head at 600 rpm was 0.48 L/min.

The larger pump head (Model 7018) was used with 7.9 mm diameter tubing to produce 3.8 mL per revolution. The maximum flow rate from this pump head at 600 rpm was 2.28 L/min.

To operate these pump heads from 60 to 600 rpm, a 24 VDC permanent magnet motor was purchased (Dayton Model 4Z145). This motor produces 0.078 Newton-meters of torque and has a maximum speed of 1800 rpm at 12 VDC and 3600 at 24 VDC. To reduce speed and increase torque, a 3.75:1 reduction was installed between the motor and pump shaft. A motor sprocket with 20 teeth is used to drive a 75-tooth pulley located on the secondary pump's shaft.

The two peristaltic metering pumps draw samples from the mixing chamber through a "Y" tube fitting. The outlet line of each pump leads to a solenoid valve used to control the direction of flow from each pump head.

The small pump head is used to fill sample bottles at sampling rates not exceeding 0.42 L/min. In this instance, the solenoid valve for the small pump head is opened, allowing flow to pass into the sample bottles. The solenoid valve for the larger valve is closed, causing flow to be discharged downstream of the sample inlet.

At sampling rates between 0.42 and 1.9 L/min, flow from the large pump is allowed to pass through its valve into the sample bottles. Sample flow from the small pump head is discharged downstream in this range of sampling rates.

At sampling rates greater than 1.9 L/min, both valves are opened to allow both pumps to combine flow into the sample bottles. During each sampling range, the flow rate is controlled by varying the speed of the pump motor.

Distribution System

The sampler distribution system takes the combined flow coming from the solenoid valves to fill the discrete sample bottles. The distribution system is designed to switch bottles quickly and without cross contamination within bottles. It consists of a plate with 24 bottle funnels, a distribution arm and indexing motor, and flexible tubing leading to the sample bottles. Figure 13 illustrates the distribution system.

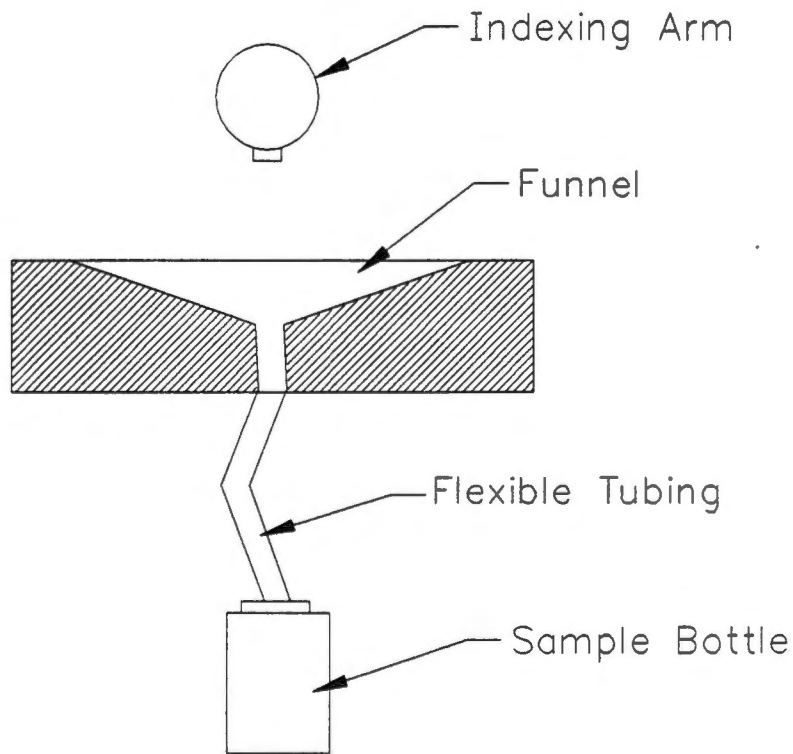


Figure 13. Components of sampler's distribution system.

The sampler distribution system is designed to fit in a prototype stage wooden frame. A 1.27 cm thick PVC plate, 40.6 cm by 40.6 cm, is the support for the distribution system. From the center of this plate, 24 holes were drilled and tapped for 1.9 cm pipe threaded nipples. These holes were at a radius of 16.5 cm from the center at 15 degree increments. On the upper side of the plate, a 3.8 cm diameter drill bit is used to countersink a funnel shape around the holes. The funnel shaped holes

and threaded nipples were used along with flexible tubing to drain sample volumes into the appropriate sample bottle.

The distribution arm and stepping motor that are used to change from one bottle to another were taken from an existing commercially available sampler (Manning Model S-4050). The distribution arm has a radius of 16.5 cm. A 12 volt indexing motor with 12 steps per revolution drives the distribution arm. A 2:1 gear reduction allows the distribution arm to fill 24 bottles per revolution.

System Electronics

Design Criteria

The sampling system was designed with flexibility and automation in mind using a SBC. The motor that drives the peristaltic pumps is controlled by the SBC, and a feedback signal of the actual motor speed is provided. The number of revolutions of the pump's shaft are measured and used along with the flow information from the metering pumps to calculate the sample volume in a bottle. After a bottle is filled to a predetermined volume, the sampling distribution system automatically indexes to a new bottle. Figure 14 is a schematic of the electronic system.

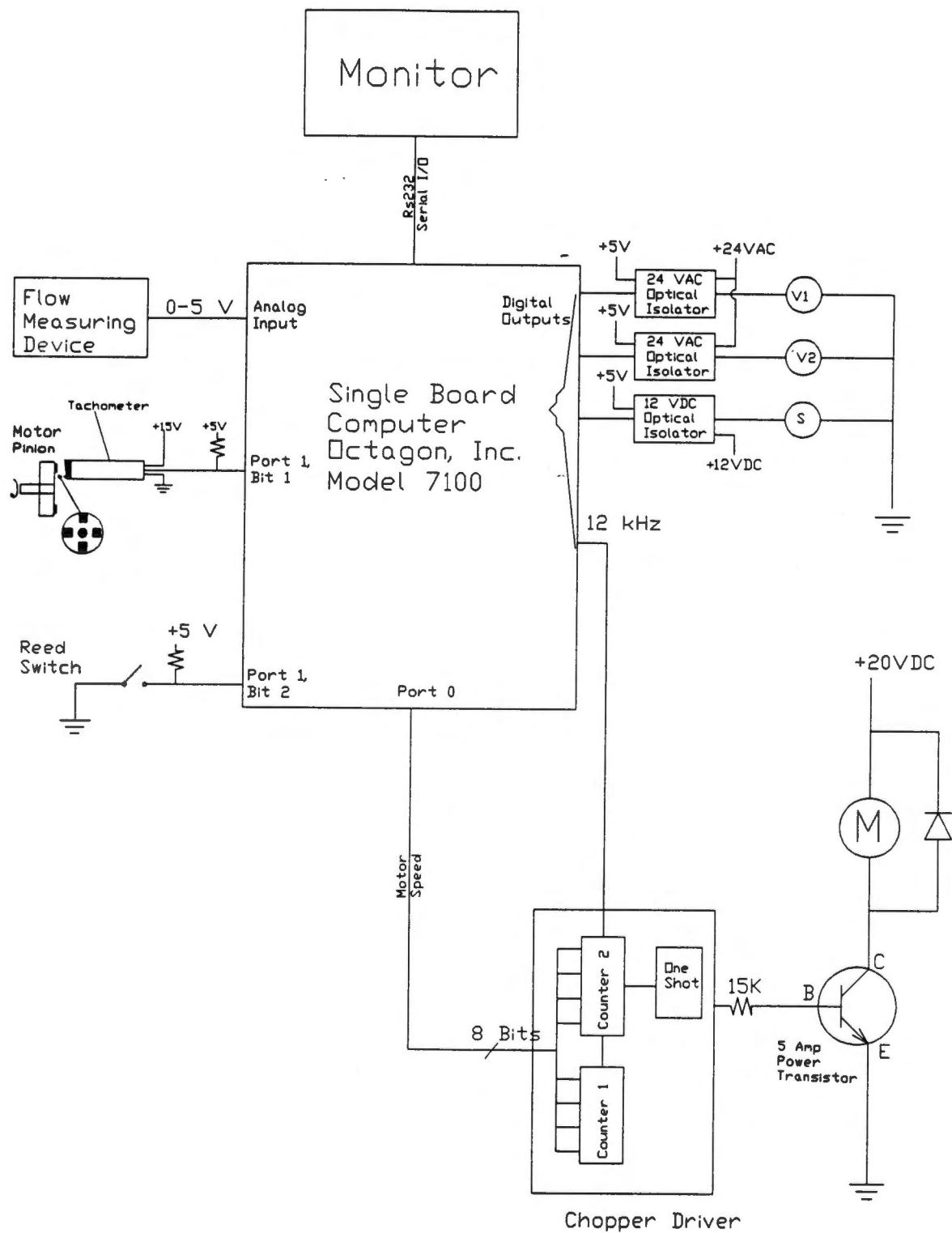


Figure 14. Components of sampler's electrical system

Single Board Computer

The SBC is used as the controller for the sampling unit (Octagon Systems Corporation, Model 7100 Systems Card). This controller requires +5 volts at 100 milliamps and +/- 12 volts at 20 milliamps to operate. The SBC has eight single-ended analog inputs with an input range of 0-5 volts with 10 bits of resolution, and 40 digital input/output lines. The SBC also has an on-board programming language (STD BASIC II)®.

Flow Rate Measurement

To extract a continuous flow proportional sample, the sampler must measure stream flow rates continuously. For this project, the stream was produced by a computer-controlled device known as a hydrograph generator (See Part 2). This device reads a desired flow rate from a data file and generates that flow rate by comparing the pressure in the system to the desired pressure at which the desired flow rate occurs. The pressure signal from the hydrograph generator is read from a pressure transducer using an analog to digital converter and an IBM PC.

The IBM PC used in controlling the hydrograph generator is equipped with a digital-to-analog (D/A) conversion card. This D/A card sends to the SBC a 0-5 volt signal that is proportional to the pressure in the hydrograph generator. This 0-5 volt signal is read by an analog input channel and converted to a pressure reading between 0 and 34.5 kPa. Using the pressure to flow rate calibration equation for the hydrograph generator, the pressure reading is converted to the actual flow rate in the system. Flow rate is used to calculate the sample flow rate and the desired pumping rate for the two metering pumps.

Motor Control

The sampling rate is used to determine the speed of the metering pump's motor. To control the motor's speed, a chopper drive was designed to control the duty cycle of power to the DC motor (Figure 15).

The pulse width from a one-shot is controlled by a time constant determined by selection of external resistance and capacitance values. A 15,000 ohm resistor and 0.1 uF capacitor were used to produce a pulse width of 1 mS. The time between these pulses is a function of the digital number loaded into the counters and the frequency of the clock input. By triggering the "one-shot" at a variable rate, the motor speed can be controlled.

Pump Speed

The tachometer was mounted 4 mm from its sensing objects, four identical pieces of sheet metal that were glued at equally spaced intervals to the face of the motor pulley.

Distribution System

Solenoid valves control the direction of flow from the sampling pumps. These valves are controlled using two solid state relays (Opto 22, Model PB4) and two digital output lines from the SBC. A 24 volt AC power supply is used to provide the power needed to energize the solenoid valves.

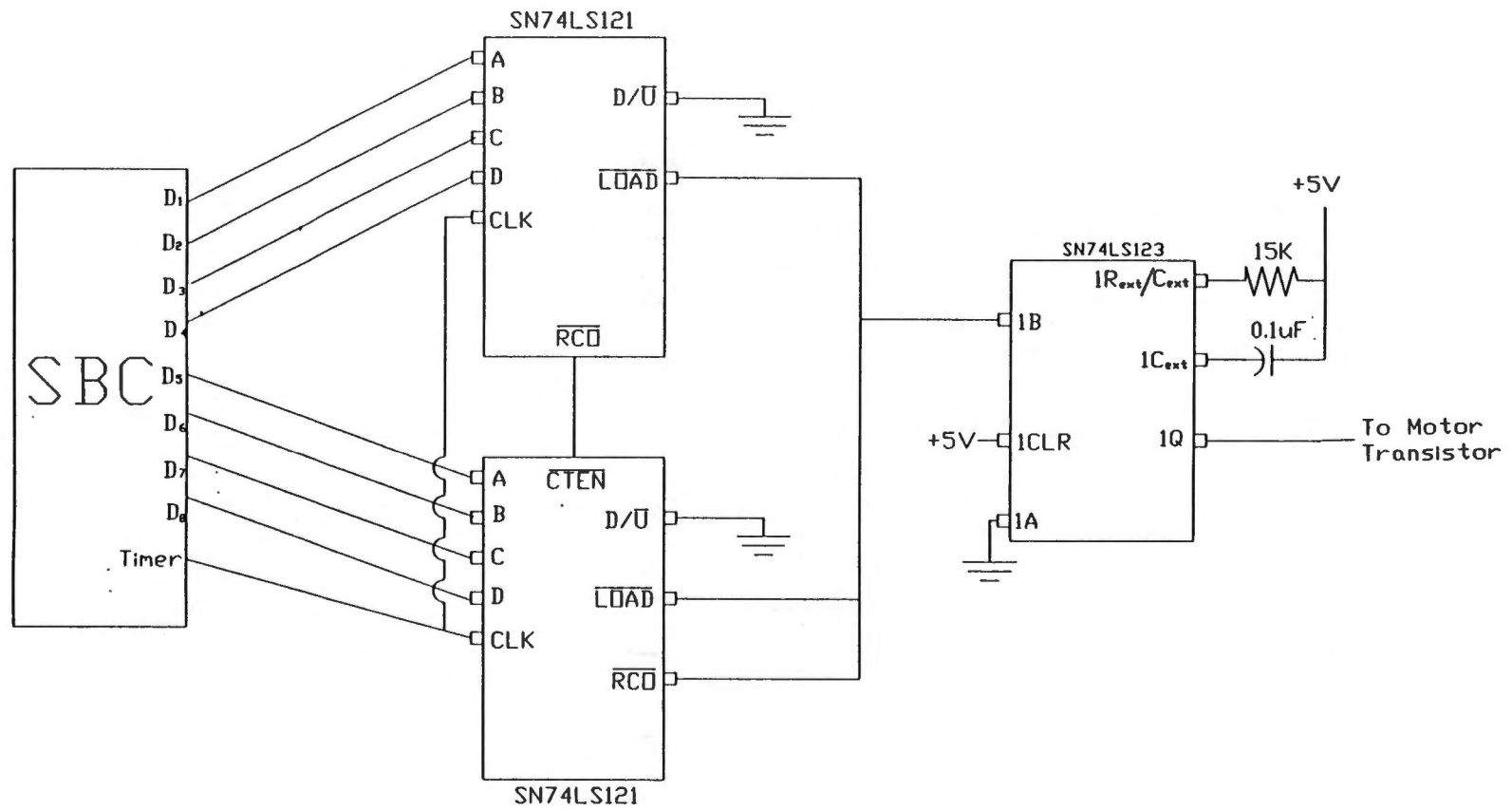


Figure 15. Motor Control Circuit

A DC output module is used to switch the voltage to the 12 V indexing motor of the distribution system. For the indexing motor to increment by one step only, power was supplied for less than a second.

A reed switch is used to measure the number of revolutions of the pump's shaft, which is used to determine the sample volume in a bottle. A magnet located on the pulley attached to the pump's shaft is used to energize the switch each time a revolution is made. The output signal from the reed switch is read by the SBC from a digital input channel.

Control Program

The program used to control the sampler was written using STD BASIC II and is listed in Appendix B. Listed below is a condensed version of the control algorithm:

1. Initialize the serial console port, configure the I/O ports as either inputs or outputs, and set one of the ports for the frequency input for use by the tachometer.
2. Main body of the program loops. Determine the flow rate from the hydrograph generator and compute the desired speed of the metering pumps. Determine which valves are to be opened to achieve the desired flow rate. Start the motor by sending an 8-bit binary value to the input of the chopper driver. The actual speed of the motor is then read from the tachometer. Adjust the motor speed by adding to or subtracting from the number of bits sent to the chopper driver which is a function of the difference between the desired and actual speeds. Compute the sample bottle volume. If the volume of sample in a bottle is equal to 950 mL, signal the indexing motor to change bottles. The solenoid valves are closed for a short period of time during a bottle change so that no cross contamination between samples will occur.
3. The control program continuously cycles until all of the sample bottles are filled or until the program is terminated.

EVALUATION TEST PROCEDURES

Overview

Testing of the new sampling system required side-by-side comparisons with existing technology in realistic situations. An ISCO¹ Model 3700 water sampler was selected to be the representative example of state-of-the-art technology. The two sampling units were compared on how accurately extracted samples from each unit represented the dynamic concentration and flow changes found in natural settings. Four testing procedures were conducted to compare the samplers. All testing procedures injected a mass of bromide into a constructed streamflow channel. From this stream, samples were extracted by both samplers. The samples were then analyzed for bromide concentrations using an ion specific probe.

Equipment and Materials

Potassium Bromide

Potassium bromide (KBr) was chosen as the tracer for this study because of it's highly soluble and easy to measure. Potassium bromide is a white granular material (colorless crystal or powder) that will readily dissolve in water.

To determine the correct amount of KBr to yield a specific bromide ion concentration, the relationship between individual atomic weights of potassium and

¹Company and trade names are given for the benefit of the reader and do not imply endorsement of the product by the author or The University of Tennessee.

bromide were considered. For every mole (119 mg/L) of KBr, the bromide constitutes 67.15%, which equates to 79.909 mg of bromide. By knowing the desired concentration and the volume, the mass of bromide needed to produce the desired concentration can be calculated.

Mallinckrodt analytical reagent grade potassium bromide crystals were used to formulate tracer solutions and calibration standards. Bromide ion concentrations for calibration standards were expressed as mg/L or ppm. Five 100 mL concentrations were prepared (10,000, 1,000, 100, 50, and 10 ppm). During formulation of calibration standards, potassium bromide reagent weights were determined with an analytical balance (Sartorius model B120S) to the nearest 0.0001 g. Standards were made daily or as needed to eliminate degradation problems. The standards were stored at room temperature out of direct light.

Selective Ion Probe

An Orion model 290A portable selective ion meter was used to measure sample bromide concentrations. This meter was equipped with an ion specific bromide electrode (Orion model 94-35) and a corresponding double junction reference electrode (Orion model 90-92) to allow for bromide detection. These electrodes allowed direct concentration measurements ranging from 0 to 19,900 ppm. The relative accuracy of the meter was $\pm 0.5\%$ of the reading.

An internal calibration, with up to five points, could be performed directly with the meter. Before calibrating the meter, the 290A internal setup routine was initiated to verify concentrations would display three significant digits.

Following completion of the meter setup procedure, all probes were inspected for essential periodic maintenance. According to Davis (1992), a soiled bromide probe caused drift, loss of low-level response, and poor reproducibility. Polishing strips (Orion, #94829) were used to clean the membrane and restore performance. An inner filling (Orion, #900003) and an outer filling solution (Orion, # 900003, 10% KNO_3) were required by the double junction reference electrode.

Calibration of the 290A was accomplished by using the laboratory standards discussed earlier. After agitating the standards by manually shaking the bottles, approximately 50 mL of each concentration were dispensed into 100 mL glass beakers. Meter calibration protocol demanded that the lowest concentration be calibrated first, then continued in ascending order until all five standards had been recorded. Probes were positioned approximately 25.4 mm below the liquid surface. After establishment of a measured concentration value, the meter's display was adjusted to display the actual calculated sample concentration. Probe sensitivity (slope) was determined, and maintained internally by the meter following the final calibration standard measurement.

Simulated Stream

The two samplers were evaluated using a computer-controlled flow device known as a hydrograph generator (See Part 2). The hydrograph generator was computer controlled to produce static flow rates or flow rates that followed a predefined hydrograph shape. This generator can produce controllable flow rates between 0 to 1325 L/min. Hydrographs were produced from data files based on

known hydrograph models. The hydrographs used in this project followed the pattern of a Soil Conservation Survey dimensionless unit hydrograph.

Flow from the hydrograph generator was discharged into a constructed channel bed within which the two samplers intakes were placed. This channel was constructed so that the sides of the channel were on a 45 degree slope. The channel was 2.44 m long and had side walls 45.72 cm wide. The channel was set on a slope of 2%. A flow rate of 1100 L/min produced a depth of approximately 18 cm in the channel.

The channel was constructed entirely of wood. To seal the wood and prevent leaking, the channel was coated with an epoxy sealer. Sand was sprinkled in the wet epoxy and allowed to dry. The sand was used to provide roughness along the sides of the channel. After the sand and epoxy had dried, pebbles were glued along the sides of the channel to provide better mixing and to simulate flow in actual streams.

The bromide solution was injected into a box at the discharge outlet of the hydrograph generator just upstream of the constructed channel to ensure that adequate mixing took place. The assumption was made that the turbulent flow would mix the bromide solution. The intakes for both samplers were placed nearly 2 m downstream of the dissipation box. Because the flow in the channel was turbulent and the bromide solution was being mixed inside the box, the flow was assumed to be well mixed before entering the sampler intakes.

Commercial Sampler

For each of the testing procedures, an ISCO Model 3700 sampler was used as an example of a commercially available DSI sampler. The sampler was programmed

to collect samples at 1 minute time intervals. This interval was chosen to ensure that the commercial unit would provide the greatest possible amount of information on sample timing and on constituent mass movement.

Phases of Testing

Phase I. Baseline Variation Tests

The first sampling procedure was used to establish the sample tracer baseline variability. Samples were taken from a stream that was continuously injected with a known concentration of bromide. The commercial sampler was programmed to take samples at its fastest rate, one bottle per minute. This was done to make sure that the sampler would provide as much information on sample timing as possible.

The pump used to continuously inject the bromide solution was composed of a peristaltic pump head mounted in a Masterflex pump drive (Cole-Parmer). The speed of the pump drive was set to produce a continuous flow rate of 0.4 L/min. Four different streamflow rates were used in this procedure. For each flow rate, the amount of potassium bromide injected was calculated to produce a continuous stream concentration of 30 ppm. Table 3 summarizes the mixing of the bromide solution and the actual concentrations measured in the stream by the ion specific probe.

Table 3. Summary of Testing Parameters for Phase I Tests

Stream Flow Rate (L/min)	Mass of KBr Added (g)	Volume of H ₂ O Added (L)	Measured Br- Mixture (ppm)	Measured Stream Conc. (ppm)
94	158.5	15	7,589	32.0
189	317.1	15	15,440	32.6
454	761.1	15	41,280	36.3
946	528.5	5	72,500	30.6

NOTES: L/min = liters per minute; g = grams; L = liters; ppm = parts per million

Phase II. Instantaneous Pulse Loading Tests

The second testing procedure involved conducting dynamic single impulse tests to examine the response of each sampling system in dynamic situations. A single concentrated mass of bromide was injected as instantaneously as possible into a stream with a static flow rate of 454.2 L/min. The timing of the injection was varied randomly from the beginning of the cycle to somewhere in the middle of the cycle. The sampling interval of the commercial sampler was set at the fastest sampling rate, one bottle per minute.

Three pulses were injected during each sampling interval. Each pulse was composed of 500 mL of a bromide solution. Bromide solutions were stored in 1000 mL plastic beakers until they were near-instantaneously dumped into the stream.

Three numbers between 0 and 900 were selected from a random number table for injection of the bromide. The length of the sampling cycle was 900 seconds. Each

pulse consisted of 500 mL of bromide solution that had an approximate concentration of 200,000 ppm. Table 4 summarizes the conditions of the four tests.

Table 4. Summary of Conditions for Phase II Tests

Test Number	Inj. Timing (sec)	Mass KBr Added (g)	Water Added (L)	Pulse Volume (mL)	Measured Pulse Conc. (ppm)
1	130 368 480	596	2	500	197,000
2	130 368 480	596	2	500	197,000
3	334 488 639	597	2	500	197,000
4	320 663 865	558	2	500	180,000

NOTES: sec = seconds; g = grams; L = liters; mL = milliliters; ppm = parts per million

Phase III. Continuous Loading, Random Timing Tests

The third test procedure involved conducting dynamically varying concentration tests to examine the response of both samplers to a system with different loading characteristics. A single concentrated pulse of bromide solution of a certain length was applied to a stream with a static flow rate of 454.2 L/min. Injection pulse length, pulse concentration, and timing of the pulse injection were determined randomly by consulting a random number table. The injection rate was 0.4 L/min. The sampling rate of the commercial sampler was one bottle per minute. The length of the sampling

cycle for these tests was 1200 seconds (20 minutes). Table 5 summarizes the conditions for this phase of testing.

Table 5. Summary of Conditions in Phase III Tests

Test #	Pulse Timing (sec)	Pulse Length (sec)	Desired Pulse Conc. (ppm)	Mass KBr Added (g)	Vol. Water Added (L)	Meas. Stream Conc. (ppm)
1	280	110	129,000	288.2	1.5	128,000
2	398	213	178,000	530.0	2.0	180,000
3	728	425	103,000	536.4	3.5	117,000
4	658	135	91,200	203.7	1.5	92,500
5	144	819	85,200	824.8	6.5	88,000

NOTES: sec = seconds; ppm = parts per million; g = grams; L = liters

Phase IV. Varying Flow, Varying Concentration Tests

The fourth testing procedure was used to determine the accuracy of each sampler in sampling streams with dynamic flow rates and varying concentration levels. A continuously varied flow rate that followed a general hydrograph shape was passed through the stream channel. A continuously varied concentration injection that followed a different shape than the hydrograph was applied to the stream. The timing of injection was varied for four different tests.

To obtain a continuously varied concentration injection rate, a Nalgene carboy with a capacity of 25 L was modified by placing three 3-mm diameter tube barbs into it. One barb was glued with epoxy into the bottom of the carboy. A second barb was

glued into the carboy approximately midway up the height of the carboy. The third barb was placed about 5 cm below the top of the carboy.

The flow from these barbs was combined to compose the continuous varied concentration flow rate. At the beginning of the injection, the flow rate was at the maximum. The flow decreased slowly until the height of bromide solution reached the top barb, then the flow dropped dramatically because only two of the outlet ports were producing flow. The flow rate then decreased slowly until the height of the bromide solution was such that the second outlet stopped contributing to the flow. From this level on, the bottom barb produced a slowly decreasing flow until all the solution was passed from the container.

To develop a curve of flow rate versus time for the flow from the container, a digital scale was used to read the weight at short time increments. By knowing the change in weight over a short change in time, many data points of flow rate versus time were calculated. These flow rates were plotted against time to produce an injection curve for the container. These tests conducted on the digital scale were repeated several times to prove that the flow from the carboy was repeatable.

The hydrograph used for this testing procedure had a minimum flow rate of under 50 L/min and had a maximum flow rate of over 750 L/min. The length of the hydrograph was the same as the length of the sampling cycle, which is 1500 seconds. As with the three previous tests, the commercial sampler was set at its fastest rate of one bottle per minute. Table 6 summarizes the conditions for this round of tests.

Table 6. Summary of Conditions in Phase IV Tests

Test #	Inject. Timing (sec)	Mass KBr Added (g)	Volume Water (L)	Desired Bromide Conc. (ppm)	Measured Bromide Conc. (ppm)
1	150	1026	24	28,967	32,775
2	300	895	24	24,037	23,633
3	450	1078	24	30,170	29,400
4	600	1272	24	35,588	33,500

NOTES: sec = seconds; g = grams; L = liters; ppm = parts per million

RESULTS AND DISCUSSION

Phase I. Baseline Variation Tests

The calibration procedure conducted in Phase I was used to determine the bottle-to-bottle variation for each sampler. This bottle-to-bottle variation was used as the baseline experimental error of the testing system. The baseline experimental error was subtracted from the total error calculations for the purpose of comparing the effectiveness of the two samplers. No conclusions concerning the differences between the two samplers were made unless the total error in the testing system was accounted.

As mentioned in the previous chapter, Phase I tests were conducted using a continuous injection of bromide into streams with four different flow rates. The four

static flow rates used in Phase I tests were 95, 189, 454 and 946 L/min. The average measurement errors for stream concentrations of bromide are listed in the Table 7.

The results of this test show that the bromide concentration being injected into the stream was mixing thoroughly into the stream channel, as evidenced by the fact that the error readings for both samplers are nearly the same for all four tests.

The results from Phase I tests indicated that both samplers are taking representative samples from the test stream under static flow conditions. This series of tests also showed that, for analysis of future tests, a difference of 4.4% variation in bromide concentration measurements between the two samplers would not be significant due to the bottle-to-bottle variation of the testing system.

Table 7. Summary of Phase I - Baseline Variability Tests

	Sampling Method							
	Commercial (DSI)				Prototype (CFI)			
Flow Rate (L/min)	# Samp	Max Err %	Avg. Abs. Error %	Std Dev	# Samp	Max Err %	Avg. Abs. Error %	Std Dev
95	24	8.3	3.7	2.1	7	4.9	1.6	1.7
189	24	10.2	6.6	2.3	13	11.7	4.9	2.7
454	17	10.6	4.7	2.0	15	7.0	4.7	1.4
946	9	8.2	2.7	2.0	15	5.4	2.4	1.3
Mean	18	9.3	4.4	2.1	12	7.2	3.4	1.8

NOTES: L/min = liters per minute

Phase II. Instantaneous Pulse Loading Tests

The second test involved instantaneously injecting single pulses of bromide with very high concentrations into streams with a static flow rate of 454.2 L/min. This test was replicated four times using three randomly selected times for instantaneous injection of the pulses. The error associated with each sampler during these tests is shown in Table 8.

Table 8. Results of Instantaneous Pulse Loading Tests

Test #	Bromide Inject. (g)	Sampling Method			
		Commercial (DSI)		Prototype (CFI)	
		Bromide Detected (g)	Error (%)	Bromide Detected (g)	Error (%)
1	220.1	490.5	+ 122	166.1	-24.5
2	220.1	545.0	+ 147	151.4	-31.2
3	225.0	63.5	-72	170.5	-24.2
4	206.2	499.6	+ 142	145.5	-29.5
Mean Abs. Error			120		27.4
Std Dev			90.9		3.1

NOTES: g = grams

Results of these tests show that the continuous sampler does a better job in obtaining a representative portion of the test stream over the entire sampling period. Table 9 summarizes the effectiveness of each sampler in defining the timing of the pulse.

Table 9. Accuracy of Samplers in Sampling Instantaneous Pulses

Test #	Inject Timing	Commercial (DSI)		Prototype (CFI)	
		Pulses Sample	Bottle Time	Pulses Sample	Bottle Time
1	2:10 6:08 8:00	1	7:30-8:30	1 1 1	2:08-3:10 5:20-6:15 7:30-8:33
2	2:10 6:08 8:00	1	8:30-9:30	1 2 1	2:05-3:06 5:11-6:18 6:18-7:26 7:26-8:33
3	5:34 8:05 10:39	1	7:30-8:30	1 1 1	5:26-6:33 7:40-8:26 9:48-10:48
4	5:20 11:03 14:25	1	10:30 - 11:30	1 1 1	5:24-6:31 10:59-12:05 14:19-15:26

NOTES: DSI = Discrete, set time intervals, individual
 CSI = Continuous, set time intervals, individual

The prototype sampler sampled every pulse for all four runs of this test. The commercial sampler caught only one pulse per test and the measured concentration was so high that the calculation of total bromide injected was erroneously high for the sampling period.

The prototype sampler's calculation of total bromide injected for each period was low. The reason for this low estimation was due to the prototype sampler indexing from one bottle to the next. During this indexing period, some of the pulse's mass was missed due to the fact that the sampler did not sample for the 2 to 4 second period the solenoid valves were closed. Thus, when a pulse occurred during a bottle

change, the sampler detected the pulse, but the concentration measured was affected because some bromide mass was passed without being collected and stored.

In Test 2 of Phase II, the second pulse occurred at 6 minutes and 8 seconds into the sampling cycle. The prototype sampler caught this pulse in two bottles (#6 and #7). Bottle #6 had a measured bromide concentration of 41.9 mg and bottle #7 had a concentration of 23.0 mg. The sum of these two gave a mass concentration of 64.9 mg. The average concentration of the two other identical pulses in this sampling cycle was 127 mg. Thus, by the instantaneous pulse occurring at the time of bottle change, a large percentage of the pulse's mass was not sampled.

Phase II tests showed the advantages of a continuous real time sampler over discrete grab sampling. Because a continuous portion of the test stream was being sampled, sudden spikes in concentration were detected accurately, except in the case discussed above. The discrete grab sampling technique either missed the spikes in concentrations or caught the spikes in concentrations that did not represent the stream during the entire sampling cycle. Had a composite grab sample been taken by the commercial sampler, a better job of total bromide movement could have been calculated, but no information on the timing of the pulses would have been available.

Phase III. Continuous Loading, Random Timing Tests

Phase III tests involved continuously injecting a concentrated bromide pulse for a randomly selected length of time. The time at which this continuous pulse of bromide began was also randomly selected. The results of these tests are summarized in Table 10.

Table 10. Results of Phase III - Continuous Loading, Varied Timing Tests

Test Stream					Commercial			Prototype		
Test #	Begin Pulse (minutes into cycle)	Length of Pulse (minutes)	Stream Conc. (ppm)	Total Br Injected (g)	Sample Bottles	Total Br (g)	Error %	Sample Bottles	Total Br (g)	Error %
1	4:40	1:50	75	63	2	62	-0.04			360-4.0
2	6:38	3:33								
3	12:08	7:05	64			3	-0.3	8	20	+1.0
4	10:58	2:15	58	60	3	74	+24.0	3	56	-5.4
5	5:24	13:39	62	383	14	379	-1.1	14	380	-0.7
Mean Absolute Error							7.9			2.6
Standard Deviation							9.9			2.8

NOTES: ppm = parts per million; g = grams.

The results of these tests show the reliability and accuracy of the prototype sampler. The prototype sampler was more accurate because the DSI sampler was not as consistent in total mass calculations and did not give as much information on the timing of the pulses as the prototype sampler. The error associated with the prototype sampler was less than the baseline variability of the testing system found in the first phase of testing, while the error associated with the DSI sampler was greater than the baseline variability of the testing system.

The DSI sampling method gave high total mass movement errors in Tests #2 and #5, while the errors in the other tests were very small. When a pulse ended just after the DSI sampler took a sample, the total mass calculation for the bottle was in

error. This error resulted because the DSI method assumed the stream had the measured concentration for the entire time period that the bottle represented. This was not a problem in the continuous, flow proportional sampler.

Phase IV. Varying Flow, Varying Concentration Tests

Phase IV involved the use of a varying flow injection system to provide a varying, but known, concentration of bromide to the test stream. The varying injection of bromide was supplied to a stream with different flow rates over the duration of the tests. A graph of streamflow and tracer flow versus time is shown in Figure 16. The time into the sampling cycle at which the bromide injection started was varied from 10 to 40% of the total hydrograph length.

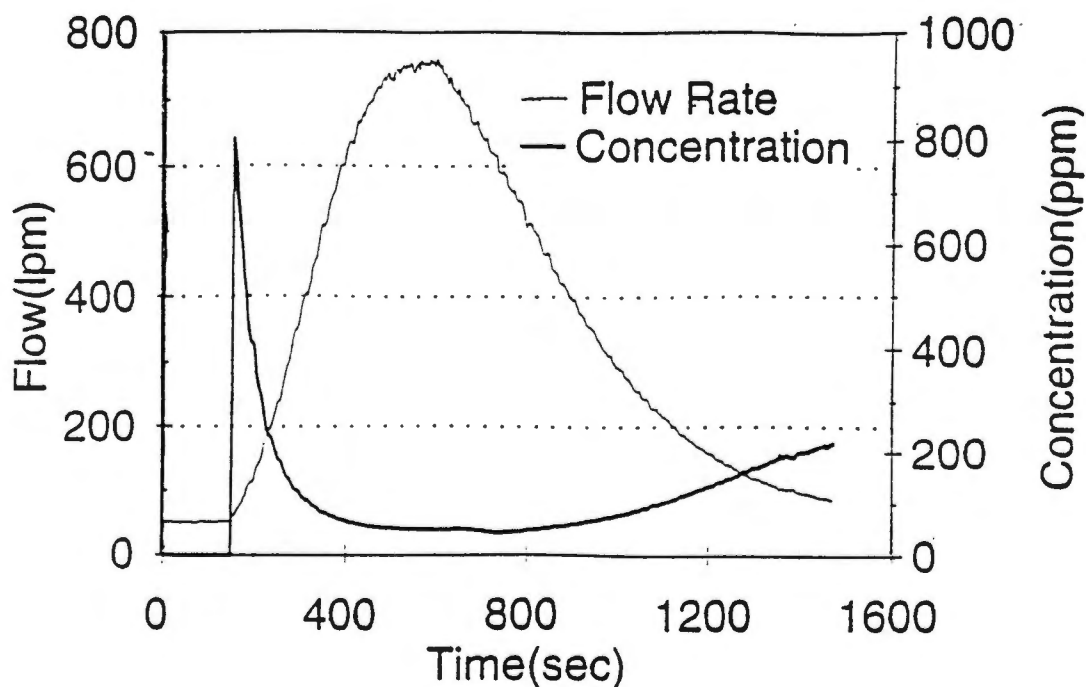


Figure 16. Plot of streamflow and injection rate versus time

The total mass movement of bromide for a sample bottle was calculated by taking the measured concentration for the bottle and multiplying it by the volume of water passed in the stream during a sample bottle's time interval. The total mass movement of bromide in the test stream was calculated by using a curve constructed from stream concentration measurements taken throughout the sampling cycle. Figure 16 shows how concentration and flow varied with time in the first test of Phase IV. This concentration curve was used along with streamflow rate to determine the mass of bromide injected.

The curve shown in Figure 16 was used to calculate the total mass of bromide added during each period that was characterized by an individual sample bottle. The total mass of bromide detected by each sampler was then computed. Table 11 shows the error associated with each sampler in the calculation of total mass movement.

Table 11. Results of Phase IV - Varied Flow, Varied Concentration Tests

Test Number	Total Br Injected (g)	Commercial (DSI)		Prototype (CFI)	
		Total Br Detected (g)	Error %	Total Br Detected (g)	Error %
1	649.2	644.5	-0.7	628.8	-3.2
2	436.5	428.4	-1.9	435.5	+0.3
3	424.9	377.8	-11.1	414.9	-2.3
4	434.8	411.6	-5.4	394.9	-9.2
Mean Absolute Average			4.8		3.7
Standard Deviation			4.0		3.5

NOTES: g = grams

As can be seen from Table 11, this phase of testing did not show the advantages of the prototype sampler from the DSI sampler as anticipated. If the bromide concentration rate had been varied more quickly, more of a difference may have been observed. Although the prototype sampler did not represent changes in concentration more accurately than the DSI sampler, no difference in the two samplers could be concluded on the basis of total mass movement calculations because both sampler's error were within the baseline variability found in the first phase of testing.

Had the injection system varied more rapidly relative to the sampling rate, the prototype sampler would, in theory, provide a more accurate representation of the change in concentration with time.

CONCLUSIONS

From the four separate phases of testing, the continuous, flow proportional real time sampler showed advantages over the time interval discrete grab sampling technique found in most commercially available sampling equipment. The prototype sampler provided information on both the total mass movement and the timing of the movement. Testing which involved the instantaneous injection of concentrated bromide pulses best showed the advantages of continuous proportional sampling over discrete, time interval grab samples. The prototype sampler accurately sampled these pulses and did a good job in providing an estimation of the total mass of bromide passed by the sampler in the pulses.

During instantaneous injection testing, the commercial DSI sampling unit proved why grab samples stored in discrete bottles are merely snapshots in time. The DSI sampler caught only one out of every three pulses injected during this type of testing. The pulses that the device did sample gave very misleading information on the mass of bromide contained in the pulses. Because the pulses were very concentrated, the calculations on total mass movement were overestimated using the discrete grab sampling method.

As for the results of tests using continuous pulse injections of random lengths, the continuous discrete sampler did as good or better than the DSI sampler in taking representative samples that provided information on both the timing of bromide movement and total mass movement. The prototype took more consistently representative samples than the commercial DSI sampler. The errors from the total mass calculations from the prototype sampler never exceeded 10%. Total bromide mass calculations with the DSI sampler ranged from nearly perfect to a 10 to 25% error.

The prototype sampler also provided a better representation of the timing of the pulses in these tests. Because the DSI sampler took samples in short intervals, in comparison to the length of the sampling cycle, the sampler did give information on the timing of the pulses to a certain degree. Had the sampling cycle been longer and the DSI sampling unit's sampling interval longer, less information on pulse timing would have resulted. The prototype accurately gave information on when the pulses started and when they ended.

Phase IV tests did not show the advantages of continuous discrete sampling over discrete grab sampling in streams with a varying concentration of bromide over

a hydrograph shaped flow. Unfortunately, the bromide injection method used in this test did not have enough concentration variation to show how a continuous discrete sampler would better detect changes in concentration.

Results of this study have shown the advantages of a sampling scheme that continuously extracts flow proportional samples from a stream and stores the samples in discrete containers. This sampling strategy provides information on both the total constituent mass movement and on the timing of the movement. The problem with the prototype sampler missing a pollutant mass during bottle change would be insignificant in sampling cycle lengths found in actual sampling situations.

Some disadvantages of a continuous, flow proportional, discrete sampler were also discovered during this study. The major disadvantage is that this sampler would have problems during sediment sampling. Because a continuous sample is being stored, sample flow rates must be small so that adequate bottle space will exist for an entire flow period. To achieve low sampling rates, sample line velocities greater than 0.75 m/s (required to prevent sedimentation) must be sacrificed. A better and more precise method of continuously extracting a small sample, proportional to flow rate, could solve this problem.

Continuous, flow proportional real time sampling was proven to provide more information on actual stream conditions than the time interval discrete grab sampling technique employed in many of today's commercially available automatic samplers. The shortest sampling interval (1 minute) possible in a commercially available DSI sampling unit were used in the lab tests, but the continuous sampler still provided better information on timing.

Continuous, discrete, flow proportional sampling would be an excellent method of sampling runoff from small watersheds such as a parking lot. In most parking lot runoff sampling, sediment is usually not sampled. Oils, phenols, and petroleum products are the primary constituents sampled for analysis. Continuous, discrete, flow proportional sampling would ensure that the peaks and valleys in concentrations would not be missed. Total contaminant movement would also be accurately estimated.

Future work should be conducted in this area of sampling technology to provide scientists with the best possible data on contaminant movement. The end result of this project should produce a product which is commercially viable.

PART 4: SUMMARY OF PARTS 2 AND 3

The following two objectives were accomplished during this study:

- 1) A computer-controlled hydrograph generator was designed and automated to produce controllable flow rates between 0 and 1135 L/min. This device used a calibration procedure that related flow rate out of the system to pressure measured at a point in the system. A control program was written for the device that allowed the generation of a stream with a predefined hydrograph shape. The device produced actual flow rates within a 5% of the predefined flow rates.
- 2) A prototype sampling unit that extracts a continuous, flow proportional sample from a stream and then stores the sample in a discrete container was designed and automated. This prototype sampling unit was then evaluated against a commercially available DSI sampler (ISCO Model 3700), programmed to sample at timed intervals, to determine which sampler produced better information on constituent mass movement and on timing of constituent movement. Both samplers were evaluated using a simulated stream that was injected with a bromide tracer. The samples were analyzed for bromide concentrations using an ion specific probe.

The two samplers were evaluated using streams under static and dynamic flow conditions. The bromide injection rates were also varied in the tests. The continuous sampler proved to be more effective than the DSI sampler in providing information on the timing of bromide movement. This was especially true when concentrated pulses of bromide were instantaneously injected into the test streams. The prototype sampler also proved to be as accurate or more than the DSI sampler in calculating the total mass of bromide passed during a sampling cycle.

This study proved that a continuous, flow proportional real-time streamflow sampling unit would provide more accurate water quality information than most sampling techniques because it ensures full flow coverage and also gives information on sample timing due to its discrete sample collection.

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APPENDICES

Appendix A

Control Program for Hydrograph Generator

```

10 REM *****
20 REM *          CONTROL PROGRAM FOR HYDROGRAPH GENERATOR          *
30 REM *                                                                 *
40 REM *          BY: KENNETH J. HURLEY                               *
45 REM *          MODIFIED BY: JBW ON 10-20-1993                     *
50 REM *****
51 REM DEFINITION OF VARIABLES
52 REM TIME = PRESENT TIME INTO PROGRAM
53 REM STIME = TIME READ FROM HYDROGRAPH DATA FILE
54 REM PRESS = ACTUAL PRESSURE READ FROM TRANSDUCER
55 REM SPRESS = CALCULATED SET POINT PRESSURE
56 REM SFLOW = SET FLOW READ FROM HYDROGRAPH DATA FILE
57 REM EPRESS = DIFFERENCE BETWEEN ACTUAL AND SET PRESSURES
58 REM ETIME = DIFFERENCE BETWEEN SET TIME AND ACTUAL TIME
59 REM A = BITS TO CONTROL THE SPEED OF THE MOTOR
60 CLS
70 Y=1          ' EOF POINTER
80 SAMPLES%=150 ' # SAMPLES TO TAKE AND AVG. FOR EACH
PRESS. READ
100 DIM D(2,1000)          ' DIMENSION DATA ARRAY
104 REM
*****
105 REM ***** LOAD A/D CARD *****
106 REM *****
110 DIM D%(12)
120 SEG1 = &H6000
125 DEF SEG = SEG1
130 BLOAD "C:CIO8.BIN",0
131 REM ***** LOAD D/A CARD *****
132 SEG2 = SEG1 + 6144/16
133 DEF SEG = SEG2
134 BLOAD "c:ciodda.bin",0
138 REM ***** INITIALIZE A/D CARD *****
139 DEF SEG = SEG1
140 MD%=0 : D%(0)=&H300 : D%(1)=0 : D%(2)=24 : F%=0
141 CALL CIO8(MD%,D%(0),F%)
150 DEF SEG = SEG1
151 MD%=1 : D%(0)=0 : D%(1)=0
152 CALL CIO8(MD%,D%(0),F%)
153 OUT &H303,5          'SET THE GAIN ON THE AMPLIFIER
160 DEF SEG = SEG1
161 MD%=14          'SETS CONTROL VALVE TO OFF
162 D%(0)=15
163 CALL CIO8(MD%,D%(0),F%)
169 REM *****
170 REM ***** INITIALIZE D/A CARD *****
171 DEF SEG = SEG2
172 MD%=0: D%(0)=&H310 : F%=0
175 CALL CIODDA(MD%,D%(0),F%)
180 REM SCALE CHANNEL 1 OF D/A TO 0-10 VOLTS
181 DEF SEG = SEG2
182 MD%=1: D%(0)=4095 : D%(1)=1

```

```

183 CALL CIODDA(MD%,D%(0),F%)
199 REM *****
200 REM ***** OPEN FILE AND READ DATA INTO ARRAY *****
205 REM *****
210 LOCATE 10,3:INPUT "ENTER FILENAME OF HYDROGRAPH DATA
FILE";FIL$
220 OPEN FIL$+".prn" FOR INPUT AS #1
230 OPEN FIL$+".dat" FOR OUTPUT AS #2
240 FOR X=1 TO 2
245 INPUT#1, D(X,Y)
246 IF EOF(1) THEN CLOSE #1: GOTO 300
250 NEXT X
260 Y=Y+1 'INCREMENT ARRAY POINTER
265 EODF=Y
270 GOTO 240
290 REM *****
300 REM ***** MAIN BODY OF PROGRAM *****
305 REM *****
496 GOSUB 10000
498 TIME$="00:00:00" ' SET STARTING TIME TO ZERO
500 FOR P=1 TO EODF ' P DATA FILE POINTER
510 STIME= D(1,P)
520 SFLOW = D(2,P)
530 GOSUB 4000 'CALCULATE SET PRESSURE
540 GOSUB 7000 'CONVERT CURRENT TIME INTO
SECONDS
550 IF TIME < STIME THEN 555 ELSE 630
555 IF P=EODF THEN GOSUB 1000 ELSE 560
560 GOSUB 6000 'READ PRESSURE FROM TRANSDUCER
570 GOSUB 5000 'CALCULATE ERROR AND A
575 GOSUB 8000 'update display
600 X$=INKEY$
601 IF X$="q" OR X$="Q" THEN GOSUB 1000
620 GOTO 540
630 NEXT P
1000 REM ***** SUBROUTINE TO STOP NEEDLE *****
1050 DEF SEG = SEG1
1070 MD%=14
1080 D%(0)=15
1090 CALL CIO8(MD%,D%(0),F%)
1100 CLOSE#2:END
4000 REM ***** SUBROUTINE TO CALCULATE SET PRESSURE *
4010 LNFLOW = LOG(SFLOW)
4020 TOP = 1.38266 + (-.10489057# * LNFLOW)
4030 BOT = 1 + (-.14154267# * LNFLOW)
4040 SPRESS = TOP/BOT
4050 RETURN
5000 REM **** SUBROUTINE TO CALCULATE ERROR, DIRECTION, AND
GAIN (A)**
5010 DIFF = SPRESS - PRESS 'CALCULATE ERROR
5020 K=5000
5050 A = ABS(DIFF * K) + 3000 'CALCULATE GAIN

```

```

5062 IF A > 3700 THEN A=3700      ' SET MAX SPEED
5090 MAXERR = (SPRESS * .04) + .05
5100 IF ABS(DIFF) < .05 THEN GOTO 5500
5150 REM CHANGE DIRECTION OF VALVE
5200 IF SGN(DIFF) = +1 THEN D%(0)=14 ELSE D%(0)=12
5300 MD%=14
5400 CALL CIO8(MD%,D%(0),F%)
5410 IF SGN(DIFF)=+1 THEN DIRECT$="DOWN" ELSE DIRECT$="UP"
5500 REM set control speed
5851 DEF SEG = SEG2              'SET GAIN ON SERVO CONTROL
5852 MD%=1: D%(0)=A : D%(1)=2
5853 CALL CIODDA(MD%,D%(0),F%)
5900 RETURN
6000 REM ***** SUBROUTINE TO READ PRESSURE TRANSDUCER
6010 COUNT%=0 : SUM!=0
6030 WHILE COUNT% < SAMPLES%
6032 DEF SEG = SEG1
6034 MD%=4
6040 CALL CIO8(MD%,D%(0),F%)
6050 D%(0)= D%(0) + 2048
6060 SUM! = SUM! + D%(0)
6070 COUNT% = COUNT% + 1
6080 WEND
6090 AVERAGE = SUM!/COUNT%
6100 PRESS = AVERAGE * .004067
6105 VOLT = AVERAGE * .0244
6110 RETURN
7000 REM * SUBROUTINE TO READ TIME IN SECONDS ***
7010 T$=TIME$
7020 SECONDS = VAL(RIGHT$(TIME$,2))
7030 HOURS = VAL(LEFT$(TIME$,2))
7040 MINUTES = VAL(MID$(TIME$,4,2))
7050 TIME = SECONDS + MINUTES*60 + HOURS*3600
7055 ETIME = STIME - TIME
7060 RETURN
8000 REM ****UPDATE DISPLAY SUBROUTINE*****
8010 LOCATE 16,22 : PRINT USING"####";A
8020 LOCATE 19,23: PRINT USING"#.###";A*(5/4096)
8030 REM LOCATE 10,58: PRINT USING"##.###";EVOLT
8040 LOCATE 9,59: PRINT USING"##.###";DIFF
8050 LOCATE 11,58: PRINT USING"###";ETIME
8060 LOCATE 16,52: PRINT DIRECT$
8070 REM LOCATE 8,20: PRINT USING"###.###";FLOW
8080 LOCATE 9,22: PRINT USING"#.###";PRESS
8090 LOCATE 11,22: PRINT USING"####";TIME
8100 LOCATE 10,22: PRINT USING"#.###";VOLT
8110 LOCATE 8,39: PRINT USING"###.###";SFLOW
8120 LOCATE 9,41: PRINT USING"#.###";SPRESS
8138 LOCATE 11,40: PRINT USING"####";STIME
8150 PRINT #2,TIME,PRESS,SPRESS
8200 RETURN
10000 REM *****SUBROUTINE TO OUTLINE SCREEN *****

```

```

10010 CLS: KEY OFF
10020 LOCATE 3,19: PRINT"HYDROGRAPH GENERATOR CONTROL
      PROGRAM"
10030 LOCATE 3,10: PRINT"DATA FILE - ";FIL$
10040 LOCATE 5,15:PRINT"      INPUT      COMMAND
      ERROR"
10050 LOCATE 6,15:PRINT"      SIGNAL      SIGNAL
      SIGNAL"
10060 LOCATE 8,3:PRINT"FLOW(gpm) "
10070 LOCATE 9,3:PRINT"PRESSURE(psi) "
10080 LOCATE 10,3:PRINT"VOLTAGE"
10085 LOCATE 11,3:PRINT"TIME(sec) "
10090 X=1:Y=1:WID=78:LENGTH=2:GOSUB 20000
10095 X=1:Y=13:WID=78:LENGTH=1:GOSUB 20000
10096 X=1:Y=1:WID=78:LENGTH=22:GOSUB 20000
10100 LOCATE 14,32:PRINT"SERVO CONTROL"
10110 LOCATE 16,10:PRINT"GAIN "
10120 LOCATE 19,10:PRINT"VOLTAGE "
10130 LOCATE 16,40:PRINT"DIRECTION (      )"
10140 LOCATE 24,30:PRINT"PRESS 'Q' TO QUIT";
10150 RETURN
20000 REM **SUBROUTINE TO DRAW A BOX*****
20040 LOCATE Y-J,X-J:PRINT CHR$(201)+STRING$(WID+J*2,205)+
      CHR$(187);
20050 FOR I=1 TO LENGTH +J*2
20060 LOCATE Y-J+I,X-J: PRINT CHR$(186);:LOCATE
      Y-J+I,X+WID+J+1:PRINT CHR$(186);
20070 NEXT I
20080 LOCATE Y+J+LENGTH,X-J: PRINT
      CHR$(200)+STRING$(WID+J*2,205)+CHR$(188);
20090 RETURN

```

PROGRAM FOR STATIC FLOW RATES

```

10 REM *****
20 REM *      CONTROL PROGRAM FOR HYDROGRAPH GENERATOR
30 REM *
40 REM *      BY: KENNETH J. HURLEY
45 REM *      MODIFIED BY: JBW ON 10-20-1993
50 REM *****
51 REM DEFINITION OF VARIABLES
52 REM TIME = PRESENT TIME INTO PROGRAM
53 REM STIME = TIME READ FROM HYDROGRAPH DATA FILE
54 REM PRESS = ACTUAL PRESSURE READ FROM TRANSDUCER
55 REM SPRESS = CALCULATED SET POINT PRESSURE
56 REM SFLOW = SET FLOW READ FROM HYDROGRAPH DATA FILE
57 REM EPRESS = DIFFERENCE BETWEEN ACTUAL AND SET PRESSURES
58 REM ETIME = DIFFERENCE BETWEEN SET TIME AND ACTUAL TIME

```

```

59 REM A = BITS TO CONTROL THE SPEED OF THE MOTOR
60 CLS
70 Y=1 ' EOF POINTER
80 SAMPLES%=150 ' # SAMPLES TO TAKE AND AVG. FOR EACH PRESS.
  READ
100 DIM D(2,1000) ' DIMENSION DATA ARRAY
105 REM ***** LOAD A/D CARD *****
110 DIM D%(12)
125 DEF SEG = &H6000
130 BLOAD "C:CIO8.BIN",0
131 REM ***** LOAD D/A CARD *****
138 REM ***** INITIALIZE A/D CARD *****
140 MD%=0 : D%(0)=&H300 : D%(1)=0 : D%(2)=24 : F%=0
141 CALL CIO8(MD%,D%(0),F%)
151 MD%=1 : D%(0)=0 : D%(1)=0
152 CALL CIO8(MD%,D%(0),F%)
153 OUT &H303,5 'SET THE GAIN ON THE AMPLIFIER
161 MD%=14 'SETS CONTROL VALVE TO OFF
162 D%(0)=15
163 CALL CIO8(MD%,D%(0),F%)
170 REM ***** INITIALIZE D/A CARD *****
180 REM SCALE CHANNEL 1 OF D/A TO 0-10 VOLTS
182 MSB%=INT(4095/16): LSB%=(4095-MSB%*16)*16
183 OUT &H310,LSB% : OUT &H311,MSB%
210 LOCATE 10,3:INPUT "ENTER DESIRED FLOW RATE";SFLOW
230 OPEN "CAL.DAT" FOR OUTPUT AS #1
290 REM *****
300 REM ***** MAIN BODY OF PROGRAM *****
495 REM *****
496 GOSUB 10000
530 GOSUB 4000 'CALCULATE SET PRESSURE
560 GOSUB 6000 'READ PRESSURE FROM TRANSDUCER
570 GOSUB 5000 'CALCULATE ERROR AND A
575 GOSUB 8000 'update display
600 X$=INKEY$
601 IF X$="q" OR X$="Q" THEN GOSUB 1000
602 IF X$="N" OR X$="n" THEN GOSUB 2000
620 GOTO 530
1000 REM ***** SUBROUTINE TO STOP NEEDLE *****
1070 MD%=14
1080 D%(0)=15
1090 CALL CIO8(MD%,D%(0),F%)
1100 CLOSE#2:END
2000 CLS
2050 REM ***** ENTER DESIRED FLOW RATE *****
2100 INPUT "ENTER DESIRED FLOW RATE";SFLOW
2150 GOSUB 10000
2200 RETURN
4000 REM ***** SUBROUTINE TO CALCULATE SET PRESSURE ***
4010 LNFLOW = LOG(SFLOW)
4020 TOP = 1.546506 + (-.118159# * LNFLOW)
4030 BOT = 1 + (-.139063# * LNFLOW)

```

```

4040 SPRESS = TOP/BOT
4050 RETURN
5000 REM **** SUBROUTINE TO CALCULATE ERROR, DIRECTION, AND
      GAIN (A)**
5010 DIFF = SPRESS - PRESS      'CALCULATE ERROR
5020 K=5000
5050 A = ABS(DIFF * K) + 3000    'CALCULATE GAIN
5060 IF A<3100 THEN A=0
5062 IF A > 3850 THEN A=3850    ' SET MAX SPEED
5090 MAXERR = (SPRESS * .04) + .05
5100 IF ABS(DIFF) < .03 THEN GOTO 5500
5150 REM CHANGE DIRECTION OF VALVE
5200 IF SGN(DIFF) = +1 THEN D%(0)=14 ELSE D%(0)=12
5300 MD%=14
5400 CALL CIO8(MD%,D%(0),F%)
5410 IF SGN(DIFF)=+1 THEN DIRECT$="DOWN" ELSE DIRECT$=" UP  "
5500 REM set control speed
5852 MSB1%=INT(A/16): LSB1%=(A - MSB1%*16)*16
5853 OUT &H312,LSB1% : OUT &H313,MSB1%
5900 RETURN
6000 REM ***** SUBROUTINE TO READ PRESSURE TRANSDUCER **
6010 COUNT%=0 : SUM!=0
6030 WHILE COUNT% < SAMPLES%
6034 MD%=4
6040 CALL CIO8(MD%,D%(0),F%)
6050 D%(0)= D%(0) + 2048
6060 SUM! = SUM! + D%(0)
6070 COUNT% = COUNT% + 1
6080 WEND
6090 AVERAGE = SUM!/COUNT%
6100 PRESS = AVERAGE * .004067
6105 VOLT = AVERAGE * .0244
6110 RETURN
8000 REM ****UPDATE DISPLAY SUBROUTINE*****
8010 LOCATE 16,22 : PRINT USING"####";A
8020 LOCATE 19,23: PRINT USING"###.";A*(5/4096)
8030 REM LOCATE 10,58: PRINT USING"###.";EVOLT
8040 LOCATE 9,59: PRINT USING"###.";DIFF
8050 LOCATE 11,58: PRINT USING"###.";ETIME
8060 LOCATE 16,52: PRINT DIRECT$
8070 REM LOCATE 8,20: PRINT USING"###.";FLOW
8080 LOCATE 9,22: PRINT USING"###.";PRESS
8090 LOCATE 11,22: PRINT USING"###.";TIME
8100 LOCATE 10,22: PRINT USING"###.";VOLT
8110 LOCATE 8,39: PRINT USING"###.";SFLOW
8120 LOCATE 9,41: PRINT USING"###.";SPRESS
8138 LOCATE 11,40: PRINT USING"###.";STIME
8150 PRINT #1,TIME,PRESS,SPRESS
8200 RETURN
10000 REM *****SUBROUTINE TO OUTLINE OUTPUT
      INTERFACE*
10010 CLS: KEY OFF

```

```

10020 LOCATE 3,19: PRINT"HYDROGRAPH GENERATOR CONTROL PROGRAM"
10030 LOCATE 3,10: PRINT"DATA FILE - ";FIL$
10040 LOCATE 5,15:PRINT"      INPUT      COMMAND
      ERROR"
10050 LOCATE 6,15:PRINT"      SIGNAL      SIGNAL
      SIGNAL"
10060 LOCATE 8,3:PRINT"FLOW(gpm) "
10070 LOCATE 9,3:PRINT"PRESSURE(psi) "
10080 LOCATE 10,3:PRINT"VOLTAGE"
10085 LOCATE 11,3:PRINT"TIME(sec) "
10090 X=1:Y=1:WID=78:LENGTH=2:GOSUB 20000
10095 X=1:Y=13:WID=78:LENGTH=1:GOSUB 20000
10096 X=1:Y=1:WID=78:LENGTH=22:GOSUB 20000
10100 LOCATE 14,32:PRINT"SERVO CONTROL"
10110 LOCATE 16,10:PRINT"GAIN "
10120 LOCATE 19,10:PRINT"VOLTAGE "
10130 LOCATE 16,40:PRINT"DIRECTION (      )"
10140 LOCATE 24,30:PRINT"PRESS 'Q' TO QUIT";
10145 LOCATE 23,30:PRINT "PRESS 'N' TO CHANGE FLOW"
10150 RETURN
20000 REM **SUBROUTINE TO DRAW A BOX*****
20040 LOCATE Y-J,X-J:PRINT CHR$(201)+STRING$(WID+J*2,205)+
      CHR$(187);
20050 FOR I=1 TO LENGTH +J*2
20060 LOCATE Y-J+I,X-J: PRINT CHR$(186);:LOCATE
      Y-J+I,X+WID+J+1:PRINT CHR$(186);
20070 NEXT I
20080 LOCATE Y+J+LENGTH,X-J: PRINT
      CHR$(200)+STRING$(WID+J*2,205)+CHR$(188);
20090 RETURN

```

Appendix B

Control Program for Prototype Sampler

CONTROL PROGRAM FOR PROTOTYPE SAMPLER

```

001 REM ***** DEFINE CALIBRATION CONSTANTS*****
002 BOT=0
003 A1= 1.59232
004 B1= 0.132496
005 C1= 0.142543
008 REM ***** CONFIGURE SBC CHANNELS *****
009 CONFIG 1,0,0
010 CONFIG 6,1
012 REM ***** OUTPUT 12 kHz TO CHOPPER DRIVER *****
015 D= 11
020 A= INP(144)
025 A= A AND 221
030 OUT 144,A
035 OUT 150, D MOD 256
040 OUT 151, D/256
045 OUT 148,1
050 OUT 199,0
055 A= INP(144)
060 A= (A AND 247) OR 6
065 OUT 144,A
099 REM **** SET SBC CHANNELS AND STATES(HIGH OR LOW) *****
100 CONFIG 4, 248
105 CONFIG 5,0,0,1,0,0
109 REM ***** CONFIGURE FREQUENCY COUNTERS *****
110 CONFIG FREQ 249,30000
115 CONFIG COUNT 0,249,2
116 START COUNT(0)
119 REM *** SEND BIT VALUE TO CHOPPER DRIVER TO ACTUATE MOTOR
120 G= 18
125 OUT 248,G
129 REM ***** READ AND CALCULATE STREAMFLOW RATE *****
130 GOSUB 300
135 REM ***** CALCULATE DESIRED PUMP RPM *****
140 GOSUB 400
145 OUT 248,G
149 REM ***** READ ACTUAL SPEED FROM TACHOMETER *****
150 GOSUB 500
154 REM ***** ADJUST SPEED TO EQUAL DESIRED SPEED *****
155 GOSUB 700
159 REM ***** CONTROL SOLENOID VALVES *****
160 GOSUB 900
164 REM ***** DETERMINE VOLUME IN SAMPLE BOTTLE *****
165 GOSUB 600
170 DELAY 3
175 CLS
180 GOTO 130
300 REM * SUBROUTINE TO READ FLOW RATE AND CALCULATE SAMPLE
    RATE
301 W=0
305 FOR F= 1 TO 40

```

```

310 W= W + AIN(2)  ' A/D CONVERSIONS'
315 NEXT F
320 BTS = W/40
324 REM ***** READ VOLTAGE FROM HYDROGRAPH GENERATOR *****
325 VLT = BTS * 4.8875E-3
329 REM ***** CONVERT VOLTAGE TO PRESSURE *****
330 PSI = BTS * 5.4250E-3
334 REM ***** CONVERT PRESSURE TO FLOW RATE *****
335 LNQ = (A1 - PSI)/(B1 - C1*PSI)
340 FLO = EXP(LNQ)
345 PRINT "FLOW RATE(gpm) = ";FLO
350 FLO = FLO * 3.785
354 REM ***** CALCULATE SAMPLE FLOW RATE *****
355 PRINT "FLOW RATE(L/min) = ";FLO
360 QS = FLO/500
365 PRINT "SAMPLE RATE = ";QS
370 PRINT "VOLT = ";VLT
390 RETURN
400 REM ***** DETERMINE STATUS OF METERING PUMPS *****
401 REM KL = SMALL METERING PUMP
402 REM KB = LARGE METERING PUMP
403 REM KL = 1 THEN SMALL PUMP ACTIVE, KL=0 THEN DISABLED
405 IF QS>0 AND QS<=0.42 THEN KL=1:KB=0
410 IF QS>0.42 AND QS<=1.9 THEN KL=0:KB=1
420 IF QS>1.9 THEN KL=1:KB=1
422 IF QS<=0.08 THEN QS=0.08
423 REM ***** CALCULATE DESIRED MOTOR SPEED *****
425 RPM = QS/((3.55E-03*KB) + (8.50E-04*KL))
430 PRINT "DESIRED RPM = ";RPM
490 RETURN
500 REM ***** SUBROUTINE TO READ TACHOMETER *****
505 S= 0
510 FOR U= 1 TO 40
520 NEXT U
525 S= INT(S/40)
530 S= S*4
540 PRINT "ACTUAL RPM = ";S
590 RETURN
600 REM ** SUBROUTINE TO READ REVOLUTIONS FROM REED SWITCH*
605 N= COUNT(0)
606 REV=N
607 DRV= REV - LCT
609 REM ** CALCULATE CHANGE IN SAMPLE VOLUME ***
610 DV= (0.85*KL*DRV) + (3.55*KB*DRV)
614 REM ***** CALCULATE TOTAL SAMPLE BOTTLE VOLUME *****
615 VOL= VOL + DV
619 REM ***** DETERMINE IF SAMPLE BOTTLE IS FULL *****
620 IF VOL>=950 THEN GOSUB 800
629 PRINT "NUMBER OF REVOLUTIONS = ";REV
630 PRINT "CURRENT BOTTLE VOLUME = ";VOL
635 LCT= REV
640 RETURN

```

```

700 REM ***** SUBROUTINE TO ADJUST SPEED OF MOTOR *****
710 IF S< RPM-5 THEN G=G+1
711 IF S< RPM-50 THEN G=G+2
712 IF S< RPM-200 THEN G=G+3
720 IF S> RPM+5 THEN G=G-1
721 IF S> RPM+50 THEN G=G-2
722 IF S> RPM+200 THEN G=G-3
725 PRINT "NUMBER OF BITS TO MOTOR = ";G
729 REM **** SEND BIT VALUE TO CHOPPER DRIVER *****
730 OUT 248,G
790 RETURN
800 REM **** SUBROUTINE TO CHANGE BOTTLES *****
810 Z= 200
815 OUT 250,251
820 FOR E= 1 TO Z
825 NEXT E
829 REM **** SEND VOLTAGE TO INDEXING MOTOR *****
830 OUT 250,255
832 BOT= BOT + 1
835 CLEAR COUNT(0)
840 VOL= 0
845 REV= 0
850 PRINT "BOTTLE NUMBER = ";BOT
890 RETURN
900 REM **** SUBROUTINE TO CONTROL STATE OF SOLENOID VALVES **
910 IF KL=1 AND KB=0 THEN D=253
920 IF KL=0 AND KB=1 THEN D=254
930 IF KL=1 AND KB=1 THEN D=252
940 OUT 250,D
950 PRINT 'VALVE POSITION IS =";D
990 RETURN

```

Appendix C

Data Tables

Phase I. Baseline Variability Study

Test 1

Flow Rate = 95 L/min

Average Stream Concentration = 55.8 ppm Br-

Prototype Sampler

Isco Sampler

Bottle Number	Measured Br- Conc.	Absolute Error(%)	Bottle Number	Measured Br- Conc.	Absolute Error
1	53.1	4.9	1	53.8	3.7
2	55.7	0.3	2	55.2	1.2
3	55.7	0.3	3	53.8	3.7
4	56.9	1.9	4	56.4	1.0
5	56.8	1.7	5	57.1	2.2
6	57.4	2.8	6	57.6	3.1
7	55.7	0.3	7	60.5	8.3
			8	57.1	2.2
			9	59.4	6.4
			10	57.6	3.1
			11	57.4	2.8
			12	58.6	4.9
			13	57.6	3.1
			14	59.7	6.9
			15	58.1	4.0
			16	59.7	6.9
			17	59.4	6.4
			18	56.9	1.9
			19	59.4	6.4
			20	58.1	4.0
			21	56.7	1.5
			22	56.4	1.0
			23	58.6	4.9
			24	56.2	0.6
Maximum		4.9			8.3
Average		1.6			3.7
Standard Deviation		1.7			2.1

Test 2

Flow Rate = 189 L/min

Average Stream Concentration = 45.7 ppm Br-

Prototype Sampler

Isco Sampler

Bottle Number	Measured Br- Conc.	Absolute Error(%)	Bottle Number	Measured Br- Conc.	Absolute Error
1	43.5	4.9	1	43.5	4.9
2	44.6	2.5	2	46.0	0.6
3	44.7	2.3	3	47.3	3.4
4	46.8	2.3	4	47.7	4.3
5	46.5	1.7	5	48.5	6.0
6	47.3	3.4	6	48.1	5.2
7	47.1	3.0	7	49.1	7.3
8	48.7	6.5	8	47.7	4.3
9	48.8	6.7	9	48.1	5.2
10	48.6	6.3	10	48.9	6.9
11	48.6	6.3	11	48.7	6.5
12	48.6	6.3	12	49.6	8.4
13	51.1	11.7	13	48.3	5.6
			14	48.9	6.9
			15	49.4	8.0
			16	50.2	9.8
			17	48.5	6.0
			18	48.7	6.5
			19	50.4	10.2
			20	50.4	10.2
			21	49.4	8.0
			22	49.1	7.3
			23	48.7	6.5
			24	50.4	10.2
Maximum		11.7			10.2
Average		4.9			6.6
Standard Deviation		2.7			2.3

Test 3

Flow Rate = 454 L/min

Average Stream Concentration = 36.6 ppm Br-

Prototype Sampler

Isco Sampler

Bottle Number	Measured Br- Conc.	Absolute Error(%)	Bottle Number	Measured Br- Conc.	Absolute Error
1	37.4	2.1	1	37.0	1.0
2	38.2	4.3	2	38.5	5.1
3	38.1	4.0	3	38.3	4.6
4	38.1	4.0	4	38.6	5.4
5	37.3	1.8	5	37.3	1.8
6	38.5	5.1	6	38.1	4.0
7	38.0	3.7	7	38.0	3.7
8	38.4	4.8	8	38.0	3.7
9	38.9	6.2	9	38.0	3.7
10	39.1	6.7	10	37.9	3.5
11	38.2	4.3	11	38.7	5.7
12	38.6	5.4	12	38.0	3.7
13	38.8	5.9	13	38.5	5.1
14	39.2	7.0	14	38.5	5.1
15	38.5	5.1	15	40.5	10.6
			16	38.8	5.9
			17	39.0	6.5
Maximum		7.0			10.6
Average		4.7			4.7
Standard Deviation		1.4			2.0

Test 4**Flow Rate = 946 L/min****Average Stream Concentration = 35.1 ppm Br-****Prototype Sampler****Isco Sampler**

Bottle Number	Measured Br- Conc.	Absolute Error(%)	Bottle Number	Measured Br- Conc.	Absolute Error
1	35.7	0.7	1	33.0	8.2
2	36.0	0.2	2	35.1	2.3
3	34.9	2.9	3	34.9	2.9
4	35.7	0.7	4	35.2	2.1
5	35.3	1.8	5	34.9	2.9
6	34.4	4.3	6	34.4	4.3
7	35.5	1.2	7	35.7	0.7
8	35.1	2.3	8	36.0	0.2
9	35.2	2.1	9	35.5	1.2
10	34.8	3.2			
11	34.8	3.2			
12	34.8	3.2			
13	34.0	5.4			
14	34.9	2.9			
15	35.1	2.3			
Maximum		5.4			8.2
Average		2.4			2.7
Standard Deviation		1.3			2.0

Phase II. Instantaneous Pulse Loading Tests

Test 1

Constant Flow Rate = 454 L/min
Total Bromide Injected = 220,125 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0-1:06	0.0	0.0
2	1:06-2:08	0.0	0.0
3	2:08-3:10	129	61275
4	3:10-4:13	0.0	0.0
5	4:13-5:20	0.0	0.0
6	5:20-6:15	98	46882
7	6:15-7:30	0.0	0.0
8	7:30-8:33	122	57950
9	8:33-9:40	0.0	0.0
10	9:40-10:46	0.0	0.0
11	10:46-11:53	0.0	0.0
12	11:53-13:00	0.0	0.0
13	13:00-14:08	0.0	0.0
14	14:08-15:15	0.0	0.0

Total Bromide Detected	166,107 g
Absolute Error	24.5%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:30	0	0
2	1:30-2:30	0	0
3	2:30-3:30	0	0
4	3:30-4:30	0	0
5	4:30-5:30	0	0
6	5:30-6:30	0	0
7	6:30-7:30	0	0
8	7:30-8:30	0	0
9	8:30-9:30	1080	490536
10	9:30-10:30	0	0
11	10:30-11:30	0	0
12	11:30-12:30	0	0
13	12:30-13:30	0	0
14	13:30-14:30	0	0

Total Bromide Detected	490,536 g
Absolute Error	122%

Test 2

Constant Flow Rate = 454 L/min
Total Bromide Injected = 220,125 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0-1:01	0.0	0.0
2	1:01-2:05	0.0	0.0
3	2:05-3:06	132	62700
4	3:06-4:09	0.0	0.0
5	4:09-5:11	0.0	0.0
6	5:11-6:18	41.9	19902
7	6:18-7:26	23.0	10925
8	7:26-8:33	122	57950
9	8:33-9:41	0.0	0.0
10	9:41-10:48	0.0	0.0
11	10:48-11:55	0.0	0.0
12	11:55-13:02	0.0	0.0
13	13:02-14:10	0.0	0.0
14	14:08-15:15	0.0	0.0

Total Bromide Detected 151,477 mg
Absolute Error 31.2%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:30	0	0
2	1:30-2:30	0	0
3	2:30-3:30	0	0
4	3:30-4:30	0	0
5	4:30-5:30	0	0
6	5:30-6:30	0	0
7	6:30-7:30	0	0
8	7:30-8:30	0	0
9	8:30-9:30	1200	545040
10	9:30-10:30	0	0
11	10:30-11:30	0	0
12	11:30-12:30	0	0
13	12:30-13:30	0	0
14	13:30-14:30	0	0

Total Bromide Detected 545,040 mg
Absolute Error 147%

Test 3

Constant Flow Rate = 454 L/min
Total Bromide Injected = 225,000 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0-1:06	0.0	0.0
2	1:06-2:14	0.0	0.0
3	2:14-3:20	0.0	0.0
4	3:20-4:24	0.0	0.0
5	4:24-5:26	0.0	0.0
6	5:26-6:33	126	59850
7	6:33-7:40	0.0	0.0
8	7:40-8:26	114	54150
9	8:26-9:48	0.0	0.0
10	9:48-10:48	119	56525
11	10:48-11:53	0.0	0.0
12	11:53-13:00	0.0	0.0
13	13:00-14:08	0.0	0.0
14	14:08-15:15	0.0	0.0

Total Bromide Detected 170,525 mg
Absolute Error 24.2%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:30	0	0
2	1:30-2:30	0	0
3	2:30-3:30	0	0
4	3:30-4:30	0	0
5	4:30-5:30	0	0
6	5:30-6:30	0	0
7	6:30-7:30	0	0
8	7:30-8:30	0	0
9	8:30-9:30	140	63588
10	9:30-10:30	0	0
11	10:30-11:30	0	0
12	11:30-12:30	0	0
13	12:30-13:30	0	0
14	13:30-14:30	0	0

Total Bromide Detected 63,588 mg
Absolute Error 71.7%

Test 4

Constant Flow Rate = 454 L/min
Total Bromide Injected = 206,250 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0-1:06	0.0	0.0
2	1:06-2:09	0.0	0.0
3	2:09-3:15	0.0	0.0
4	3:15-4:18	0.0	0.0
5	4:18-5:24	0.0	0.0
6	5:24-6:31	56.3	26743
7	6:31-7:39	0.0	0.0
8	7:39-8:46	0.0	0.0
9	8:46-9:54	0.0	0.0
10	9:54-10:59	0.0	0.0
11	10:59-12:05	133	63175
12	12:05-13:12	0.0	0.0
13	13:12-14:19	0.0	0.0
14	14:19-15:26	117	55575

Total Bromide Detected 145,493 mg
Absolute Error 29.4%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:30	0	0
2	1:30-2:30	0	0
3	2:30-3:30	0	0
4	3:30-4:30	0	0
5	4:30-5:30	0	0
6	5:30-6:30	0	0
7	6:30-7:30	0	0
8	7:30-8:30	0	0
9	8:30-9:30	0	0
10	9:30-10:30	0	0
11	10:30-11:30	0	0
12	11:30-12:30	1100	499620
13	12:30-13:30	0	0
14	13:30-14:30	0	0

Total Bromide Detected 499,620 mg
Absolute Error 142%

Phase III. Continuous Loading, Varied Timing Tests

Test 1

Constant Flow Rate = 454 L/min
Start of Injection = 4:40 into event
End of Injection = 6:30 into event
Total Bromide Injected = 62,618 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:06	0	0
2	1:06-2:09	0	0
3	2:09-3:15	0	0
4	3:15-4:23	0	0
5	4:23-5:29	42.9	20377
6	5:29-6:34	75.2	35720
7	6:34-7:40	8.4	3990
8	7:40-8:47	0	0
9	8:47-9:54	0	0
10	9:54-11:01	0	0
11	11:01-12:10	0	0
12	12:10-13:16	0	0
13	13:16-14:24	0	0
14	14:24-15:31	0	0

Total Bromide Detected 60087 mg
Absolute Error 4%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-0:30	0	0
2	0:30-1:30	0	0
3	1:30-2:30	0	0
4	2:30-3:30	0	0
5	3:30-4:30	0	0
6	4:30-5:30	67.3	30568
7	5:30-6:30	70.5	32021
8	6:30-7:30	0	0
9	7:30-8:30	0	0
10	8:30-9:30	0	0
11	9:30-10:30	0	0
12	10:30-11:30	0	0
13	11:30-12:30	0	0
14	12:30-13:30	0	0
15	13:30-14:30	0	0
16	14:30-15:30	0	0

Total Bromide Detected 62589 mg
Absolute Error 0.04%

Test 2

Constant Flow Rate = 454 L/min
Start of Injection = 6:38 into event
End of Injection = 10:11 into event
Total Bromide Injected = 166,078 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:06	0	0
2	1:06-2:10	0	0
3	2:10-3:16	0	0
4	3:16-4:19	0	0
5	4:19-5:21	0	0
6	5:21-6:23	0	0
7	6:23-7:25	66.3	31492
8	7:25-8:28	106	50530
9	8:28-9:35	107	50825
10	9:35-10:40	76.4	36290
11	10:40-11:45	0	0
12	11:45-12:48	0	0
13	12:48-13:55	0	0
14	13:55-15:03	0	0

Total Bromide Detected 168,957 mg
Absolute Error 1.7%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-0:30	0	0
2	0:30-1:30	0	0
3	1:30-2:30	0	0
4	2:30-3:30	0	0
5	3:30-4:30	0	0
6	4:30-5:30	0	0
7	5:30-6:30	0	0
8	6:30-7:30	100	45420
9	7:30-8:30	103	47683
10	8:30-9:30	107	48599
11	9:30-10:30	106	48145
12	10:30-11:30	0	0
13	11:30-12:30	0	0
14	12:30-13:30	0	0
15	13:30-14:30	0	0
16	14:30-15:30	0	0

Total Bromide Detected 188947 mg
Absolute Error 13%

Test 3

Constant Flow Rate = 454 L/min

Start of Injection = 12:08 into event

End of Injection = 19:13 into event

Total Bromide Injected = 204,349 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:06	0	0
2	1:06-2:14	0	0
3	2:14-3:17	0	0
4	3:17-4:18	0	0
5	4:18-5:20	0	0
6	5:20-6:22	0	0
7	6:22-7:24	0	0
8	7:24-8:25	0	0
9	8:25-9:26	0	0
10	9:26-10:28	0	0
11	10:28-11:31	0	0
12	11:31-12:33	14	6650
13	12:33-13:35	61.5	29212
14	13:35-14:37	64.2	30495
15	14:37-15:40	64.7	30732
16	15:40-16:41	64.4	30590
17	16:41-17:44	65.7	31208
18	17:44-18:47	65	30875
19	18:47-19:49	35.1	16672
20	19:49-20:00	0	0
Total Bromide Detected			206,435 mg
Absolute Error			1.0%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-0:30	0	0
2	0:30-1:30	0	0
3	1:30-2:30	0	0
4	2:30-3:30	0	0
5	3:30-4:30	0	0
6	4:30-5:30	0	0
7	5:30-6:30	0	0
8	6:30-7:30	0	0
9	7:30-8:30	0	0
10	8:30-9:30	0	0
11	9:30-10:30	0	0
12	10:30-11:30	0	0
13	11:30-12:30	0	0
14	12:30-13:30	62.7	28478
15	13:30-14:30	65.7	29841
16	14:30-15:30	65.7	29841
17	15:30-16:30	63.4	28796
18	16:30-17:30	65.5	29750
19	17:30-18:30	64.2	29160
20	18:30-19:30	61.5	27933
21	19:30-20:00	0	0
Total Bromide Detected			203,799 mg
Absolute Error			0.27%

Test 4

Constant Flow Rate = 454 L/min

Start of Injection = 10:58 into event

End of Injection = 13:13 into event

Total Bromide Injected = 59,682 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:01	0	0
2	1:01-2:02	0	0
3	2:02-3:03	0	0
4	3:03-4:05	0	0
5	4:05-5:07	0	0
6	5:07-6:09	0	0
7	6:09-7:11	0	0
8	7:11-8:13	0	0
9	8:13-9:14	0	0
10	9:14-10:16	0	0
11	10:16-11:18	5.3	2518
12	11:18-12:21	55.7	26457
13	12:21-13:23	57.8	27455
14	13:23-14:28	0	0
15	14:28-15:32	0	0
16	15:32-16:34	0	0
17	16:34-17:37	0	0
18	17:37-18:39	0	0
19	18:39-19:41	0	0
20	19:41-20:00	0	0
Total Bromide Detected			56,430 mg
Absolute Error			5.4%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-0:30	0	0
2	0:30-1:30	0	0
3	1:30-2:30	0	0
4	2:30-3:30	0	0
5	3:30-4:30	0	0
6	4:30-5:30	0	0
7	5:30-6:30	0	0
8	6:30-7:30	0	0
9	7:30-8:30	0	0
10	8:30-9:30	0	0
11	9:30-10:30	0	0
12	10:30-11:30	48.8	22165
13	11:30-12:30	55.5	25208
14	12:30-13:30	58.3	26480
15	13:30-14:30	0	0
16	14:30-15:30	0	0
17	15:30-16:30	0	0
18	16:30-17:30	0	0
19	17:30-18:30	0	0
20	18:30-19:30	0	0
21	19:30-20:00	0	0
Total Bromide Detected			73,852 mg
Absolute Error			23.7%

Test 5

Constant Flow Rate = 454 L/min
Start of Injection = 2:24 into event
End of Injection = 16:03 into event
Total Bromide Injected = 383,149 mg

Prototype Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-1:06	0	0
2	1:06-2:09	0	0
3	2:09-3:11	34.5	16387
4	3:11-4:18	59.2	28120
5	4:18-5:26	62.6	29735
6	5:26-6:28	62.9	29878
7	6:28-7:30	62.6	29735
8	7:30-8:33	63.1	29973
9	8:33-9:34	61.5	29212
10	9:34-10:37	63.1	29973
11	10:37-11:39	62.6	29735
12	11:39-12:41	62.9	29878
13	12:41-13:44	62.9	29878
14	13:44-14:47	62.3	29592
15	14:47-15:49	61.5	29212
16	15:49-16:51	19.2	9120
17	16:51-17:53	0	0
18	17:53-18:56	0	0
19	18:56-20:00	0	0
Total Bromide Detected			380,427 mg
Absolute Error			0.7%

Isco Sampler

Bottle	Time	Measured Br- (ppm)	Mass Br- (mg)
1	0:00-0:30	0	0
2	0:30-1:30	0	0
3	1:30-2:30	0	0
4	2:30-3:30	55.6	25253
5	3:30-4:30	60.5	27479
6	4:30-5:30	63.1	28660
7	5:30-6:30	60.8	27615
8	6:30-7:30	61.8	28070
9	7:30-8:30	62.1	28206
10	8:30-9:30	61.8	28069
11	9:30-10:30	64.2	29160
12	10:30-11:30	61.3	27842
13	11:30-12:30	61.5	27933
14	12:30-13:30	62.3	28297
15	13:30-14:30	63.1	28660
16	14:30-15:30	63.1	28660
17	15:30-16:30	33.2	15079
18	16:30-17:30	0	0
19	17:30-18:30	0	0
20	18:30-19:30	0	0
21	19:30-20:00	0	0
Total Bromide Detected			378,984 mg
Absolute Error			1.1%

Phase IV. Varied Flow, Varied Concentration Tests

Test 1

Prototype Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0-4:29	268.0	378.7	101491.6	80305.0	26.4
2	4:29-5:51	136.0	586.1	79713.7	63347.0	25.8
3	5:51-6:47	79.2	534.9	42360.1	37205.0	13.9
4	6:47-7:32	64.7	511.3	33081.1	29668.0	11.5
5	7:32-8:16	55.4	504.5	27949.3	26727.0	4.6
6	8:16-8:57	50.4	519.5	26182.8	26339.0	-0.6
7	8:57-9:37	46.8	525.4	24588.7	25990.0	-5.4
8	9:37-10:17	44.6	475.8	21220.7	23141.0	-8.3
9	10:17-10:57	43.4	467.2	20276.5	23454.0	-13.5
10	10:57-11:41	44.3	516.0	22858.8	25013.0	-8.6
11	11:41-12:27	41.4	472.9	19578.1	20311.0	-3.6
12	12:27-13:17	34.5	455.7	15721.7	20641.0	-23.8
13	13:17-14:13	37.8	455.2	17206.6	23085.0	-25.5
14	14:13-15:20	43.1	460.9	19864.8	27080.0	-26.6
15	15:20-16:42	52.2	448.6	23416.9	31902.0	-26.6
16	16:42-18:36	67.3	476.9	32095.4	44045.0	-27.1
17	18:36-21:35	107.0	470.7	50364.9	64058.0	-21.4
18	21:35-24:30	171.0	297.6	50889.6	56833.0	-10.5

Isco Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-1:30	0.0	76.8	0.0	0.0	0.0
2	1:30-2:30	0.0	51.0	0.0	0.0	0.0
3	2:30-3:30	813.0	92.1	74877.3	42646.0	75.6
4	3:30-4:30	287.0	207.5	59552.5	42423.0	40.3
5	4:30-5:30	134.0	368.7	49405.8	41579.0	18.8
6	5:30-6:30	82.7	559.2	46245.8	42370.0	9.1
7	6:30-7:30	64.2	655.7	42095.9	38945.0	8.1
8	7:30-8:30	54.1	712.9	38567.9	38084.0	1.3
9	8:30-9:30	48.5	748.7	36312.0	36766.0	-1.2
10	9:30-10:30	45.2	734.3	33190.4	36541.0	-9.2
11	10:30-11:30	44.3	692.8	30691.0	34726.0	-11.6
12	11:30-12:30	42.4	622.0	26372.8	27420.0	-3.8
13	12:30-13:30	36.5	545.3	19903.5	24737.0	-19.5
14	13:30-14:30	40.4	468.0	18907.2	24691.0	-23.4
15	14:30-15:30	46.8	396.5	18556.2	24177.0	-23.2
16	15:30-16:30	53.2	326.8	17385.8	23664.0	-26.5
17	16:30-17:30	60.6	277.2	16798.3	23132.0	-27.4
18	17:30-18:30	73.9	229.6	16967.4	22628.0	-25.0
19	18:30-19:30	88.3	190.8	16847.6	21748.0	-22.5
20	19:30-20:30	101.0	158.7	16028.7	21559.0	-25.7
21	20:30-21:30	120.0	139.5	16740.0	22085.0	-24.2
22	21:30-22:30	146.0	113.5	16571.0	20395.0	-18.7
23	22:30-23:30	164.0	99.2	16268.8	19836.0	-18.0
24	23:30-24:30	179.0	91.0	16283.6	19002.0	-14.3

Test 2

Prototype Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-4:19	0.0	384.3	0.0	0.0	0.0
2	4:19-5:43	47.5	523.6	24871.0	31458.0	-20.9
3	5:43-6:38	75.6	490.8	37104.5	32513.0	14.1
4	6:38-7:25	58.6	538.0	31526.8	28859.0	9.2
5	7:25-8:09	49.6	536.6	26615.4	25551.0	4.2
6	8:09-8:49	43.2	482.0	20822.4	21352.0	-2.5
7	8:49-9:29	41.8	473.4	19788.1	20104.0	-1.6
8	9:29-10:09	39.7	536.8	21311.0	21879.0	-2.6
9	10:09-10:49	39.2	459.2	18000.6	18641.0	-3.4
10	10:49-11:30	39.7	492.3	19544.3	20201.0	-3.3
11	11:30-12:14	40.9	442.0	18077.8	18902.0	-4.4
12	12:14-13:04	43.0	472.0	20296.0	20938.0	-3.1
13	13:04-14:00	46.0	473.4	21776.4	22466.0	-3.1
14	14:00-15:07	49.0	507.1	24847.9	26245.0	-5.3
15	15:07-16:28	43.7	444.6	19429.0	21181.0	-8.3
16	16:28-18:15	50.2	478.3	24010.7	25972.0	-7.6
17	18:15-20:51	75.9	455.0	34534.5	35421.0	-2.5
18	20:51-24:30	131.0	403.9	52910.9	47567.0	11.2

Isco Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-1:30	0.0	81.1	0.0	0.0	0.0
2	1:30-2:30	0.0	48.0	0.0	0.0	0.0
3	2:30-3:30	0.0	91.6	0.0	0.0	0.0
4	3:30-4:30	0.0	207.6	0.0	0.0	0.0
5	4:30-5:30	79.2	369.1	29232.7	22686.0	28.9
6	5:30-6:30	77.5	531.4	41183.5	37056.0	11.1
7	6:30-7:30	56.4	642.8	36253.9	34842.0	4.1
8	7:30-8:30	43.9	722.2	31704.6	33750.0	-6.1
9	8:30-9:30	39.4	784.4	30905.4	33603.0	-8.0
10	9:30-10:30	36.8	743.5	27360.8	30182.0	-9.3
11	10:30-11:30	36.5	695.2	25374.8	28441.0	-10.8
12	11:30-12:30	38.4	611.4	23477.8	26284.0	-10.7
13	12:30-13:30	40.5	547.7	22181.9	24964.0	-11.1
14	13:30-14:30	45.0	469.5	21127.5	23185.0	-8.9
15	14:30-15:30	44.5	397.1	17671.0	21155.0	-16.5
16	15:30-16:30	38.9	333.9	12988.7	15115.0	-14.1
17	16:30-17:30	45.6	279.6	12749.8	14379.0	-11.3
18	17:30-18:30	55.1	232.2	12794.2	14136.0	-9.5
19	18:30-19:30	67.3	189.6	12760.1	13628.0	-6.4
20	19:30-20:30	84.6	161.1	13629.1	13591.0	0.3
21	20:30-21:30	102.0	135.9	13861.8	13323.0	4.0
22	21:30-22:30	123.0	116.1	14277.8	13045.0	9.4
23	22:30-23:30	136.0	104.2	14171.2	12766.0	11.0
24	23:30-24:30	150.0	97.9	14682.0	13188.0	11.3

Test 3

Prototype Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-4:21	0.0	379.3	0.0	0.0	0.0
2	4:21-5:43	0.0	537.2	0.0	0.0	0.0
3	5:43-6:40	0.0	529.1	0.0	0.0	0.0
4	6:40-7:28	0.0	545.6	0.0	26890.0	-100
5	7:28-8:10	32.5	502.8	16341.0	20843.0	-21.6
6	8:10-8:50	47.6	482.2	22952.7	19350.0	18.6
7	8:50-9:29	43.4	474.9	20610.7	20634.0	-0.1
8	9:29-10:10	41.7	541.2	22568.0	13522.0	66.9
9	10:10-10:49	37.7	457.7	17255.3	17044.0	1.2
10	10:49-11:30	40.3	486.7	19614.0	20659.0	-5.1
11	11:30-12:15	43.8	467.9	20494.0	25530.0	-19.7
12	12:15-13:05	47.2	472.5	22302.0	29989.0	-25.6
13	13:05-14:01	56.2	461.2	25919.4	36306.0	-28.6
14	14:01-15:08	71.6	467.0	33437.2	42414.0	-21.2
15	15:08-16:29	95.9	455.9	43720.8	32182.0	35.9
16	16:29-18:16	65.9	444.5	29292.6	25972.0	12.8
17	18:16-21:04	113.0	474.5	53618.5	51798.0	3.5
18	21:04-24:30	187.0	357.3	66815.1	67741.0	-1.4

Isco Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-1:30	0.0	60.9	0.0	0.0	0.0
2	1:30-2:30	0.0	53.0	0.0	0.0	0.0
3	2:30-3:30	0.0	95.8	0.0	0.0	0.0
4	3:30-4:30	0.0	215.7	0.0	0.0	0.0
5	4:30-5:30	0.0	378.2	0.0	0.0	0.0
6	5:30-6:30	0.0	539.7	0.0	0.0	0.0
7	6:30-7:30	0.0	694.5	0.0	6039.0	-100
8	7:30-8:30	41.0	677.2	27764.0	30559.0	-9.1
9	8:30-9:30	38.7	786.3	30429.8	32467.0	-6.3
10	9:30-10:30	31.7	746.1	23651.4	26347.0	-10.2
11	10:30-11:30	32.0	689.2	22054.4	22872.0	-3.6
12	11:30-12:30	39.7	605.7	24046.3	27599.0	-12.9
13	12:30-13:30	46.0	539.7	24826.2	31257.0	-20.6
14	13:30-14:30	60.1	462.7	27808.3	32578.0	-14.6
15	14:30-15:30	75.3	389.4	29321.8	32283.0	-9.2
16	15:30-16:30	93.5	326.9	30565.2	31182.0	-1.7
17	16:30-17:30	42.4	271.7	11520.1	20794.0	-44.6
18	17:30-18:30	61.6	221.7	13656.7	15241.0	-10.4
19	18:30-19:30	90.5	188.0	17014.0	17736.0	-4.1
20	19:30-20:30	119.0	157.6	18754.4	18937.0	-1.0
21	20:30-21:30	143.0	132.2	18904.6	19298.0	-2.0
22	21:30-22:30	171.0	111.4	19049.4	19123.0	-0.4
23	22:30-23:30	190.0	108.4	20596.0	21475.0	-4.1
24	23:30-24:30	209.0	85.3	17827.7	19115.0	-6.8

Test 4

Prototype Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-4:15	0.0	367.2	0.0	0.0	0.0
2	4:15-5:38	0.0	486.6	0.0	0.0	0.0
3	5:38-6:35	0.0	510.6	0.0	0.0	0.0
4	6:35-7:20	0.0	745.2	0.0	0.0	0.0
5	7:20-8:04	0.0	289.5	0.0	0.0	0.0
6	8:04-8:44	0.0	485.0	0.0	0.0	0.0
7	8:44-9:24	0.0	527.6	0.0	0.0	0.0
8	9:24-10:04	0.0	492.4	0.0	5771.0	-100
9	10:04-10:44	45.7	514.3	23503.5	31331.0	-25.0
10	10:44-11:24	55.9	450.8	25199.7	28183.0	-10.6
11	11:24-12:09	60.7	482.6	29293.8	31781.0	-7.8
12	12:09-12:59	63.3	488.2	30903.1	33992.0	-9.1
13	12:59-13:55	67.6	481.0	32515.6	35512.0	-8.4
14	13:55-14:57	74.1	443.1	32833.7	34754.0	-5.5
15	14:57-16:13	85.5	467.8	39996.9	42287.0	-5.4
16	16:13-17:50	106.0	461.1	48876.6	53032.0	-7.8
17	17:50-20:22	128.0	479.1	61324.8	62564.0	-2.0
18	20:22-24:50	152.0	463.7	70482.4	75584.0	-6.8

Isco Sampler

Bottle	Time	Conc. (ppm)	Flow (L)	Br- Det. (mg)	Br- Inj. (mg) (%)	Error
1	0:00-1:30	0.0	73.9	0.0	0.0	0.0
2	1:30-2:30	0.0	52.1	0.0	0.0	0.0
3	2:30-3:30	0.0	92.9	0.0	0.0	0.0
4	3:30-4:30	0.0	209.2	0.0	0.0	0.0
5	4:30-5:30	0.0	372.0	0.0	0.0	0.0
6	5:30-6:30	0.0	534.0	0.0	0.0	0.0
7	6:30-7:30	0.0	645.2	0.0	0.0	0.0
8	7:30-8:30	0.0	728.9	0.0	0.0	0.0
9	8:30-9:30	0.0	753.7	0.0	0.0	0.0
10	9:30-10:30	31.7	788.8	25005.0	26980.0	-7.3
11	10:30-11:30	57.7	696.6	40193.8	43344.0	-7.3
12	11:30-12:30	64.0	625.0	40000.0	41871.0	-4.5
13	12:30-13:30	65.3	541.4	35353.4	38823.0	-8.9
14	13:30-14:30	70.2	475.0	33345.0	36314.0	-8.2
15	14:30-15:30	80.4	400.7	32216.3	32743.0	-1.6
16	15:30-16:30	90.5	336.6	30462.3	33453.0	-8.9
17	16:30-17:30	106.0	280.4	29722.4	32259.0	-7.9
18	17:30-18:30	129.0	232.3	29966.7	30356.0	-1.3
19	18:30-19:30	146.0	189.9	27725.4	27761.0	-0.1
20	19:30-20:30	105.0	160.6	16863.0	17374.0	-2.9
21	20:30-21:30	126.0	134.6	16959.6	17659.0	-4.0
22	21:30-22:30	152.0	114.7	17434.4	17698.0	-1.5
23	22:30-23:30	178.0	106.2	18903.6	18912.0	-0.0
24	23:30-24:30	192.0	90.8	17433.6	19244.0	-9.4

VITA

Kenneth John Hurley was born in Greene County, Tennessee on September 29, 1969. He attended McDonald Elementary School and graduated from West Greene High School in May 1987. The following September he entered the University of Tennessee, Knoxville, and in May 1992 received the degree of Bachelor of Science in Agricultural Engineering. In June 1992, he reentered the University of Tennessee and in May 1996 received a Master of Science degree in Agricultural Engineering.

He is presently employed as an Environmental Engineer for ENSA Environmental, Inc., located in Louisville, Kentucky.

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