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A Study of Ion Profiles for Mahoning River Surface Waters: 1963-1988

by

Janet Einfalt

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in Chemistry

Daryl W. Mincey 11/28/89
Advisor Date

Sally M. Hotchkiss December 11, 1989
Dean of the Graduate School Date

YOUNGSTOWN STATE UNIVERSITY

Graduate School

THESIS

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TITLE: A STUDY OF ION PROFILES FOR
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ABSTRACT

A STUDY OF ION PROFILES FOR MAHONING RIVER SURFACE WATERS: 1963-1988

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MASTER OF SCIENCE

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The Mahoning River in northeastern Ohio has become a reflection of a population's economic growth and decline with its significance in environmental studies warranted by its use and abuse through the past decades. Chemical analyses of the river water and sediment throughout the peak years of steel production and then through the years following the industrial demise in the Mahoning Valley provide useful information about the effects and consequences of uncontrolled human-made pollution in a dynamic system such as a river. However, these analyses have been sporadic and uncontrolled in that method equivalency and standardizations have not been maintained. Differences in testing though will always occur with constantly improving technology. Ion analysis of water samples is especially valuable in diagnosing a river's condition in that both industrial and municipal pollution can often be indicated with the determination of ion concentrations. With the recent explosion in technology including improvements in column efficiency and analysis time, ion chromatography has become the tool of choice for a wide range of ion analyses. For long-term, longitudinal environmental studies which involve repetitive work the advantages of using ion chromatography over the traditional wet lab methods are tremendous. The project presented in this paper involves the analysis of eight ions, five anions and three cations, from Mahoning River surface water samples. The procedure used in determining ion concentrations will demonstrate the efficiency, speed and reliability of the ion chromatography system. Results will be compared to previous data showing the value of this method in water testing and the need for its permanent incorporation into standard test procedures such as those dictated by the U.S. Environmental Protection Agency.

ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. Daryl Mincey, my advisor, and Dr. James Mike for their help in this project and to Dr. Scott Martin for providing the water samples and information on the Mahoning River.

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LIST OF SYMBOLS

SYMBOL	DEFINITION
k'	Capacity factor
K_a	Dissociation constant of an acid
K_b	Dissociation constant of a base
K	Distribution coefficient
HETP	Height Equivalent per Theoretical Plate
$[H^+]$	Hydrogen ion concentration
pH	$-\log [H^+]$
pK_a	$-\log K_a$
pK_b	$-\log K_b$
MPa	Megapascals
µL	Microliters
µm	Micrometers
µS	Microsiemens
min	Minutes
N.D.	No detection
#	Number
N	Number of theoretical plates
ppm	Parts per million
psi	Pounds per square inch
R	Resolution
α	Selectivity factor
S.D.	Standard deviation

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CHAPTER 1

INTRODUCTION

HISTORICAL PERSPECTIVE

The Mahoning River and Industry

The Mahoning River rises in northeasterly Ohio near Alliance and drains an area of 1,131 square miles of which 1,076 sq. miles are in northeastern Ohio and 55 sq. miles in western Pennsylvania[1,2]. It flows from Alliance through Youngstown into Pennsylvania where it joins the Shenango River below New Castle to form the Beaver River[2].

The Mahoning River has been an area of focus for pollution monitoring due to its key role in northeastern Ohio and Pennsylvania industries. Heavy industries, such as steel and iron, have relied on an abundant flow of water nearby for the necessary process of cooling but also as a convenient disposal site for unwanted substances and waste. The Mahoning Valley region in northeastern Ohio has had a varying history of success and decline in industry in the past decades and is a reflection of the struggles the United States has had to face in an increasing industrial and competitive world. These fluctuations are, however, also an indication of the disastrous effects of pollution due to the community's self-interest and apathy toward the environment as the Mahoning River received a notorious reputation as containing anything but water. The vast number of industries utilizing the river in the heyday of steel production is shown in Figure 1. This map was part of a 1977 U.S. Environmental Protection Agency (EPA) study of wasteload allocation[3].

Between Warren and Lowellville, Ohio, 25 miles of the Mahoning River was used by 15 major plants of 9 steel companies which operated a total of 63 rolling mills. In addition, 35 other major industries that included plastics, glass manufacturing and electrical industries utilized the river[2].

Studies of the Mahoning River

Several studies since the 1940s have focused on the quality of water at sites along the Mahoning River[1,2]. The chemical and physical properties of water include pH, temperature, and mineral and ion concentrations[1]. Ion concentrations are good indicators of the health of the river and the extent of pollution. Sodium and potassium ions occur naturally at low concentrations (> 15ppm) and in approximately equal proportions with sodium increasing dramatically as pollution increases[1]. Ammonium is an indicator for municipal waste of inadequately treated water as sewage treatment plants did not until recently effectively remove ammonia from the water flow reentering the river. Fluoride concentration in natural waters is usually very low; readings around 1.0 ppm indicate fluoridation of public water supplies[1]. High nitrate concentrations show sewage contamination since it is a product of the final stage of oxidation in the nitrogen cycle. Nitrate also originates from industrial processing wastes, fertilizers and return drainage from irrigation[1]. Phosphate has long been the focus for domestic pollution with the use of products such as detergents being linked to the death of fresh water aquatic life through the overgrowth of algae with eutrophication. In unpolluted fresh waters the total phosphate content as phosphorus from mineral sources of phosphate is usually only fractions of 1 ppm[1]. Sulfate concentration can indicate industrial pollution resulting from the dumping of untreated sulfuric acid used in the pickling process of steel[2]. It is also a sign of mine drainage as it is formed from the oxidation of sulfides[1].

Probably the most significant indicator of pollution of river waters is chloride concentration. In unpolluted fresh waters the concentration is normally in the range of a few ppm[1]. [illegible] show sewage and industrial waste pollution as well as the high amounts of $CaCl_2$ used to salt the city [illegible] snow and rains wash the salt into storm sewers connected directly to the Mahoning River[1,2]. Industries use large amounts of hydrogen chloride in acid wash processes with the chloride-filled waste dumped directly into the river.

The Use of Ion Concentrations

The importance of ion determinations in a study of a water system such as the Mahoning River is evident from the wide variety of information that can be gathered from analyzing ion concentrations. In the past ion analysis has been performed with traditional wet chemical methods or techniques such as flame photometry which involve individual ion determinations. For example, the 1974 EPA Methods recommended determining potassium concentrations with a colorimetric

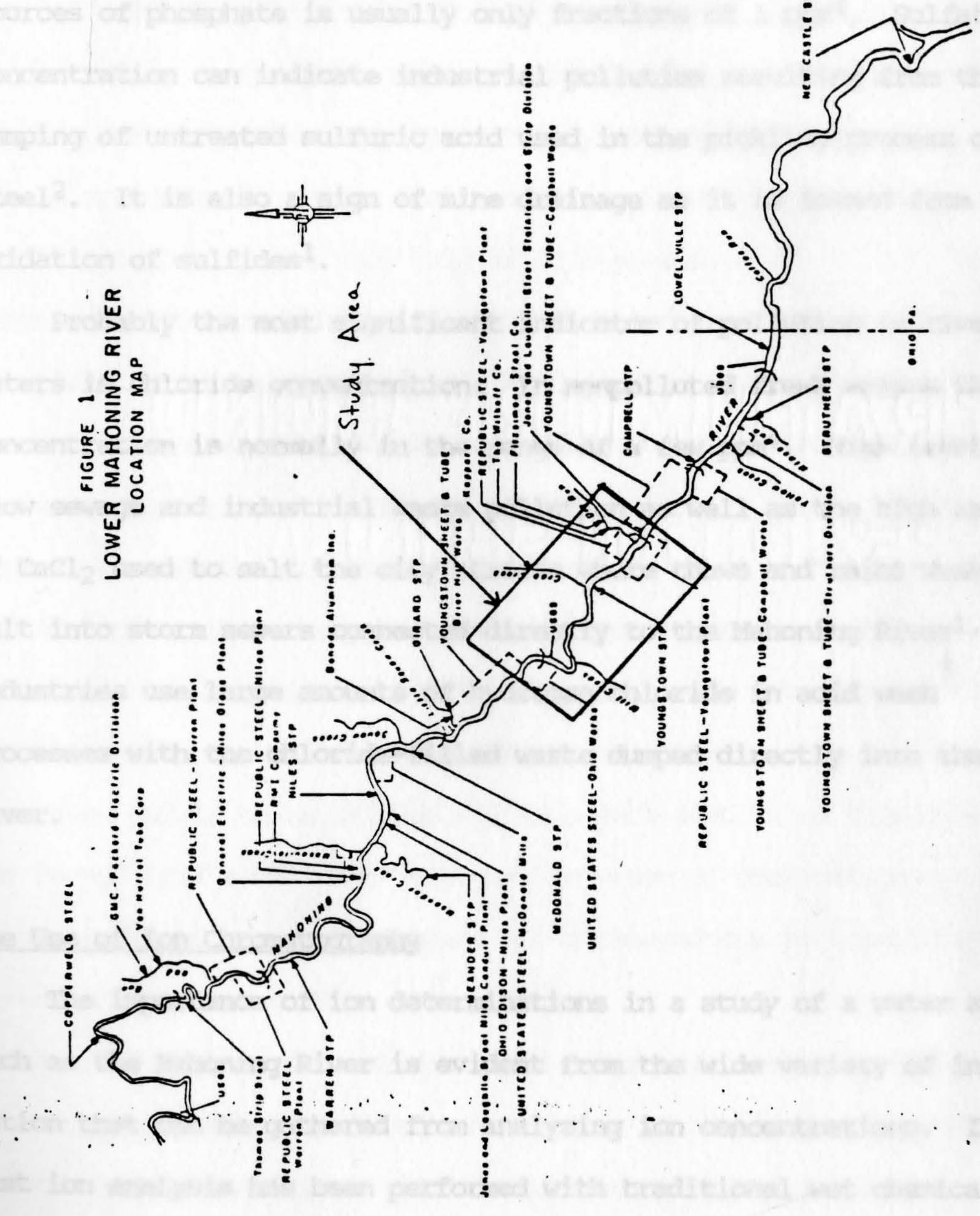


FIGURE 1
LOWER MAHONING RIVER
LOCATION MAP

been the focus for domestic pollution with the use of products such as detergents being linked to the death of fresh water aquatic life through the overgrowth of algae with eutrophication. In unpolluted fresh waters the total phosphate content as phosphorus from mineral sources of phosphate is usually only fractions of 1 ppm[4]. Sulfate concentration can indicate industrial pollution resulting from the dumping of untreated sulfuric acid used in the pickling process of steel[2]. It is also a sign of mine drainage as it is formed from the oxidation of sulfides[1].

Probably the most significant indicator of pollution in river waters is chloride concentration. In nonpolluted fresh waters the concentration is normally in the range of a few ppm[4]. High levels show sewage and industrial waste pollution as well as the high amounts of $CaCl_2$ used to salt the city streets where thaws and rains wash the salt into storm sewers connected directly to the Mahoning River[1,2]. Industries use large amounts of hydrogen chloride in acid wash processes with the chloride-filled waste dumped directly into the river.

The Use of Ion Chromatography

The importance of ion determinations in a study of a water system such as the Mahoning River is evident from the wide variety of information that can be gathered from analyzing ion concentrations. In the past ion analysis has been performed with traditional wet chemical methods or techniques such as flame photometry which involve individual ion determinations. For example, the 1974 EPA Methods recommended determining potassium concentrations with a colorimetric or flame photometric method, nitrate by a brucine colorimetric or cadmium reduction method and chloride with a silver nitrate or automated colorimetric-ferricyanide method[5]. To determine several ions, such as those mentioned in the water studies, took tremendous time and work since each ion required a unique method of analysis.

In 1975 with the publication of the article, "Novel Ion Exchange Chromatographic Methods with Conductivity Detection," by Small, Stevens and Bauman[6], modern ion chromatography was born. The significant development that this article presented was eluent-ion suppression which eliminated the eluent conductance problem that had been plaguing the use of conductivity detection. With the high capacity ion-exchange resins in use at that time, eluent electrolytes, were very concentrated to allow shortened retention times. This produced an overwhelming background signal in relation to the more dilute sample. Eluent suppression dramatically lessened this background allowing widespread use of conductivity detection for ion analysis[7]. Its applications now range from organic acids to transition metals to oxyhalides and from such samples as toothpaste or beer to polluted air[8]. Not only has the range of applications widened but the ease and speed of analysis has increased due to improvements in many components, such as the columns.

As a simple matrix a water sample can readily be analyzed by ion chromatography, thus, applications to water pollution study should be common. However, a lack of method equivalence to the published methods of the EPA and the American Public Health Association/American Water Works Association has stifled ion chromatography use[8]. Equivalent methods should be used when doing studies which require following the guidelines and regulations of these agencies[8]. But the EPA has especially been indecisive in its choice of methods. In a 1979 EPA manual ion chromatography is listed in test methods for inorganic anions[9]. However, in another 1979 EPA manual, ion chromatography is not mentioned in the test methods for inorganic nonmetallics where the traditional wet lab procedures are detailed[10]. The latest revision of this manual, printed in 1983, also includes no ion chromatography methods[11]. As will be shown in the project for this paper, ion chromatography is a practical and efficient method for ion analysis of water samples in a pollution study and should be uniformly incorporated into environmental analysis methods.

ION CHROMATOGRAPHY THEORY

Column Theory

Chromatography involves the separation of sample components due to differences in the equilibrium distribution between two different phases, the mobile and the stationary. Sample components migrate in the mobile phase through the chromatographic system with the velocity of migration of a component dependent upon its equilibrium distribution between the phases. A slower migration occurs for components having distribution coefficients favoring the stationary phase compared to those favoring the mobile phase. Separation results from different migration velocities due to the difference in equilibrium distributions[12].

Ion chromatography involves the separation and determination of anions and cations using a liquid mobile phase and a porous resin bead stationary phase packed into a column. Separation depends upon each component's unique affinity for the stationary phase[12]. A distribution coefficient, K, represents this affinity and is defined as the equilibrium concentration of the component in the stationary phase divided by its concentration in the mobile phase, or[13]

$$K = (X)_s / (X)_m$$

Retention or the capacity factor, k', is related to the time that a component is retained on the separator column and is defined as the number of column volumes needed to elute the component[13]. Thus, retention can be expressed as

$$k' = (V_1 - V_0) / V_0$$

where V_1 is the retention volume for the component and V_0 is the void volume. The ability to resolve the various components reflects the efficiency of the column whereas the selectivity indicates the ratio of column volumes required to elute two different peaks. The selectivity is defined as

$$\alpha = (V_2 - V_0)/(V_1 - V_0) = k'_2 / k'_1 = K_2 / K_1$$

where V_1 is the retention volume for component 1 and V_2 is the retention volume for component 2. Selectivity is also related to the capacity factor and the distribution coefficient as the ratio of these values for the two components[13].

Column efficiency indicates the sharpness of peak bands and is defined with N, the number of theoretical plates, as:

$$N = 16\ (t_r /\ w_b)^2$$

where t_r is the retention time and w_b is the width of the peak at the baseline. If the peak width is measured at half maximum, which gives a more accurate value, for a Gaussian peak[13], then:

$$N = 5.54\ (t_r\ /\ w_{1/2})^2 = (t_r\ /\ w_{0.6})^2$$

For expressing the length of column required for one theoretical plate, HETP or height equivalent per theoretical plate is utilized and is defined as

$$HETP = L_{(mm)}\ /\ N$$

where L equals the column length in millimeters. HETP can be affected by several factors as shown in the following equation derived by van Deemter,

$$HETP = Au^{0.33} + B\ /\ u + Cu + Du$$

where u is the linear velocity of the mobile phase. Term A indicates how the analyte is positioned in the column packing material; term B shows the amount of analyte diffusion into the column pores; term C shows the longitudinal diffusion of analyte into the eluent; term D indicates the stationary phase diffusion. Of significance, though, is the van Deemter equation's implication that column efficiency decreases as the flow rate or linear velocity of the eluent increases[13].

Resolution, R, or the degree of separation of two peaks is illustrated in Figure 2 for peaks 1 and 2 where V is the retention volume and w equals the width of the peak at the baseline[12]. Resolution is related to N, α, and k' as

$$R = 1/4\ (N)^{1/2}\ \left[(\alpha - 1)/\alpha\right]\ \left[k'/(k'+1)\right]$$

and accordingly to efficiency, selectivity, and capacity as[13]

$$R = (\text{efficiency})^{1/2}(\text{selectivity})(\text{capacity})$$

The Ion Chromatograph and Modes

The basic components of an ion chromatograph include:

1. Eluent pump and liquid containers
2. Sample injection valve
3. Ion-exchange separating column
4. Suppressor column coupled to conductivity detector, meter and output device
5. Regenerating pump with electronic timer and control[8].

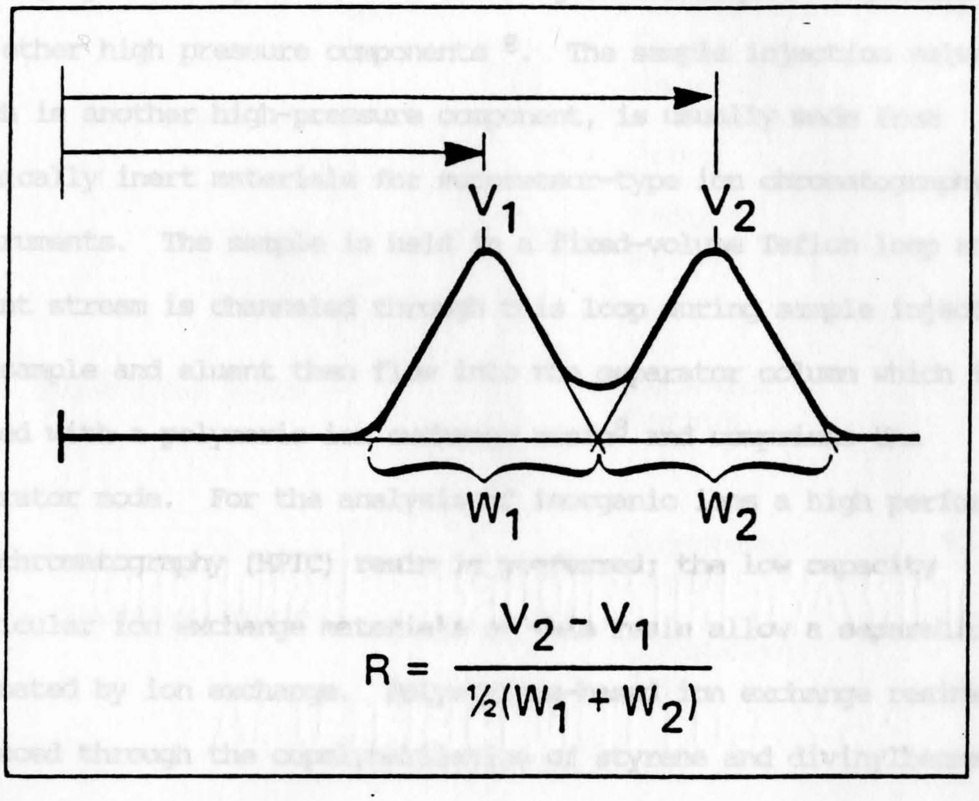


Figure 2.

This set-up is divided into four modes, the delivery, separation, detection and data, as illustrated in Figure 3[12]. In the delivery, the eluent pumping system pushes the eluting ions through the columns and detector at a constant flow rate ranging typically from 0.7 to 4.0 mL/min. The problem of background noise can be reduced by the use of pulse dampers though a mechanical pressure gauge also minimizes pulsing by allowing continuous checking of the liquid "tightness" of the other high pressure components [8]. The sample injection valve, which is another high-pressure component, is usually made from chemically inert materials for suppressor-type ion chromatography instruments. The sample is held in a fixed-volume Teflon loop and the eluent stream is channeled through this loop during sample injection. The sample and eluent then flow into the separator column which is filled with a polymeric ion exchange resin[8] and comprises the separator mode. For the analysis of inorganic ions a high performance ion chromatography (HPIC) resin is preferred; the low capacity pellicular ion exchange materials of this resin allow a separation dominated by ion exchange. Polystyrene-based ion exchange resins are produced through the copolymerization of styrene and divinylbenzene (DVB). The divinylbenzene allows crosslinking of polystyrene (PS) chains together with the resulting rigidity enabling the material to withstand the viscous forces generated by forcing the eluent through the column. With greater crosslinking, the resin swells less in liquid and less separation occurs. Thus, polystyrene comprises the base of the resin bead and forms an inert hydrophobic core which is then coated with ionic groups for the ionic exchange. For cations the core surface contains sulfonic acid groups covalently bonded to the

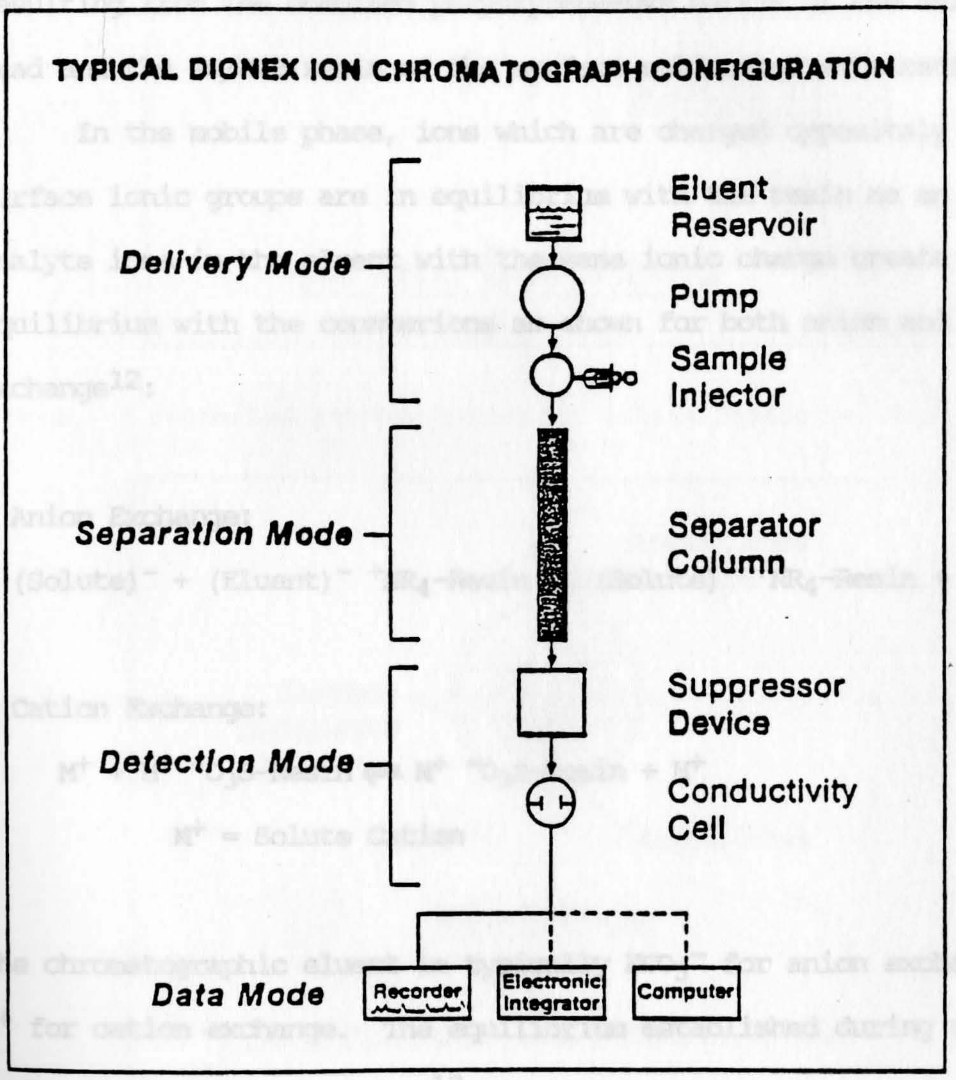

TYPICAL DIONEX ION CHROMATOGRAPH CONFIGURATION
Delivery Mode
Eluent Reservoir
Pump
Sample Injector
Separation Mode
Separator Column
Detection Mode
Suppressor Device
Conductivity Cell
Data Mode
Recorder
Electronic Integrator
Computer

Figure 3.

copolymer as shown in Figure 4[12]. For anions sulfonic groups are also bonded to the core with small (0.1-10 µm) totally porous anion exchange beads attached as shown in Figure 5[12]. These beads are aminated and held by coulombic forces and Van der Waals forces resulting from the combined polystyrene-DVB matrix of the aminated bead and the PS/DVB resin of the surface sulfonated substrate[8].

In the mobile phase, ions which are charged oppositely to the surface ionic groups are in equilibrium with the resin as an ion pair. Analyte ions in the eluent with the same ionic charge create an equilibrium with the counterions as shown for both anion and cation exchange[12]:

Anion Exchange:

$$(\text{Solute})^- + (\text{Eluent})^-\ {}^+NR_4\text{-Resin} \rightleftharpoons (\text{Solute})^-\ {}^+NR_4\text{-Resin} + (\text{Eluent})^-$$

Cation Exchange:

$$M^+ + H^+\ {}^-O_3S\text{-Resin} \rightleftharpoons M^+\ {}^-O_3S\text{-Resin} + H^+$$

M^+ = Solute Cation

The chromatographic eluent is typically HCO_3^- for anion exchange and H^+ for cation exchange. The equilibrium established during anion exchange can be expressed as[12]

Resin Solute Eluent

$$K = (R_4N^+\ X^-)\ (HCO_3^-)\ /\ (R_4N^+\ HCO_3^-)\ (X^-)$$

Resin Eluent Solute

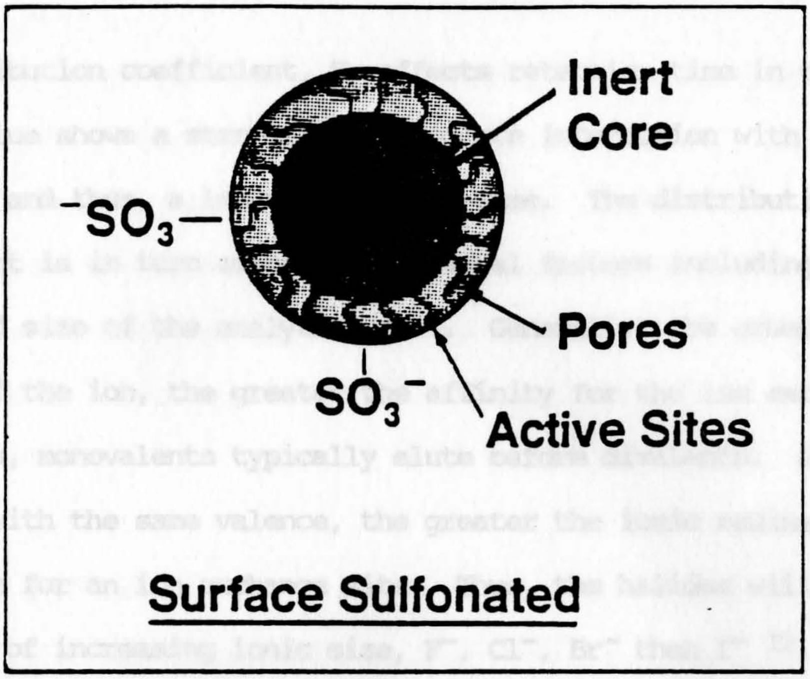


Figure 4. Pictorial Representation of Cation Separator Resin

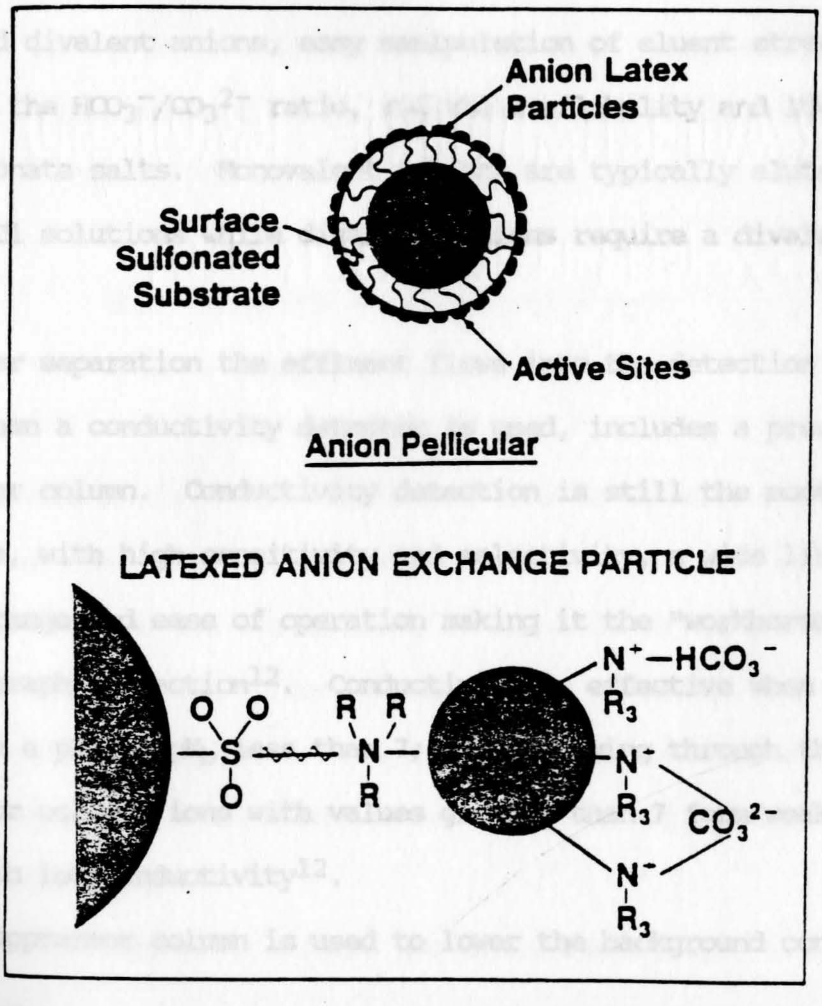


Figure 5. Pictorial Representation of Anion Separator Resin

The distribution coefficient, K, affects retention time in that a higher value shows a stronger ionic solute interaction with the ion exchanger and thus, a longer retention time. The distribution coefficient is in turn affected by several factors including the charge and size of the analyte ions[12]. Generally, the greater the valence of the ion, the greater the affinity for the ion exchange site; thus, monovalents typically elute before divalents. Similarly, for ions with the same valence, the greater the ionic radius, the more attraction for an ion exchange site. Thus, the halides will elute in the order of increasing ionic size, F^-, Cl^-, Br^- then I^- [12].

The anion eluent commonly used for HPIC is a bicarbonate-carbonate mixture. The advantages include ready separation of both mono- and divalent anions, easy manipulation of eluent strength by changing the HCO_3^-/CO_3^{2-} ratio, and the availability and low cost of the carbonate salts. Monovalent cations are typically eluted with dilute HCl solutions while divalent cations require a divalent eluting ion[12].

After separation the effluent flows into the detection mode, which, when a conductivity detector is used, includes a preceding suppressor column. Conductivity detection is still the most widely used mode, with high sensitivity and selectivity, a wide linear dynamic range and ease of operation making it the "workhorse" of ion chromatography detection[12]. Conductivity is effective when detecting ions with a pK_a or pK_b less than 7; after flowing through the suppressor column, ions with values greater than 7 form weak acids and bases with low conductivity[12].

A suppressor column is used to lower the background conductivity of the eluent which contains highly conductive species, hydrogen ions in cation exchange and carbonate ions in anion exchange. Also, the suppressor converts solute ions to their acid and hydroxide forms. Thus, detection sensitivity is increased with decreased eluent and increased solute conductivity due to the high mobilities of H^+ and OH^- in water. With a bicarbonate/carbonate eluent, reactions in the anion suppressor are[12]:

$$2(H^+\text{-Resin}) + Na_2CO_3 \rightarrow 2(Na^+\text{-Resin}) + H_2CO_3$$

$$(H^+\text{-Resin}) + NaHCO_3 \rightarrow (Na^+\text{-Resin}) + H_2CO_3$$

$$(H^+\text{-Resin}) + \text{Cation-}X^- \rightarrow (\text{Cation-Resin}) + H^+X^-$$

The eluent ions have been converted to the weakly dissociated acid H_2CO_3 due to the constant inflow of H^+ ions from the regenerant solution[14]. With an HCl eluent, reactions in the cation suppressor are

$$HCl + \text{Resin-OH} \rightarrow \text{Resin-Cl} + H_2O$$

$$M^+Cl^- + \text{Resin-OH} \rightarrow \text{Resin-Cl} + M^+OH^-$$

The high conductivity of the HCl eluent ions is eliminated with the formation of water with the constant supply of hydroxide ions from the regenerant solution and the affinity of chloride to the resin[12]. In essence, the suppressor column is the counter component to the separator column. For anion exchange, the suppressor is basically a cation exchange column; for cation exchange, the suppressor is an anion exchange column.

The first suppressor columns for ion chromatography were of a packed-bed type, though such drawbacks as off-line regeneration and band-broadening due to diffusion into the pores by weak acid analytes (e.g. HNO_2) created a less-than-ideal system[13]. The introduction of fiber suppressors allowed continuous regeneration of the column and eliminated the "water dip" problem which occurs as packed-bed suppressors become expended and the water dip moves forward in retention time[14]. However, fiber suppressors have a limited ion exchange capacity and cannot suppress more concentrated eluents resulting in the necessity of an almost exclusive use of the bicarbonate/carbonate eluent[13]. Micromembrane suppressors (MMS), which were introduced in 1985, eliminated these drawbacks with the high ion exchange capacity of the packed-bed suppressor and the continuous regeneration capability of the fiber suppressor. Both the fiber suppressor and the MMS contain semipermeable membranes with the regenerant flowing countercurrent to the eluent. For cation analysis, hydroxide ions from the regenerant exchange with the chloride ions of the eluent while the cations are unable to pass through the membrane. For anion analysis, hydrogen ions exchange with sodium and other cations through the membrane while the anions are excluded from passage. The MMS uses variously sized ion exchange screens: a fine screen for the eluent which minimizes the void volume and analyte dispersion and a coarse screen for the regenerant which allows the needed ion exchange capacity and regenerant flow. These screens and ion exchange membranes are stacked and laminated together with the resulting close contact allowing a high exchange capacity[13].

After the suppressor column the effluent enters the conductivity cell which contains two oppositely charged electrodes separated by the effluent flow[12]. Detection is based upon the measurement of electrical conductance in microsiemens, µS, between the electrodes resulting from the ions in solution. For low concentrations conductivity is directly proportional to the concentration of the ions in solution with such factors as the total ionic concentration and the temperature of the solution affecting this linearity. For weak electrolytes the degree of dissociation reflects the fraction of total solute available for carrying electrical current. Deviations in detector linearity occur at higher concentrations due to a decrease in the ratio of ionized to non-ionized species. For strong electrolytes which are completely dissociated in solution (at infinite dilutions), ionic mobility affects detection linearity. Higher concentrations of a strong electrolyte lessen the ionic mobility in solution and thus, conductivity is decreased[12]. For ion chromatography analysis, the linear range is usually between 0.05 and 100 or 200 ppm[8]. Temperature also affects conductivity as an increase causes an increase in ion conductance. Temperature variations can be accounted for by the normalization of conductivities to 25°C; chromatographs are often equipped with temperature compensation devices[15].

After the analytes have been detected, the resulting data is easily handled through electronic integration as detector output is sent directly to an integrator which measures peak area or height and retention time. These results can be be displayed on a recorder or computer screen for rapid interpretation. With standardized conditions, both qualitative information from retention times and quantitative results from peak area or height as compared to known concentrations can be readily obtained[12].

CHAPTER 2

MATERIALS AND METHODS

MATERIALS AND APPARATUS

Solvents and Reagents

For the anion eluent solid Na_2CO_3 and $NaHCO_3$ were used. For the cation eluent double distilled HCl (6 M) was used as well as DL-2,3-diaminopropionic acid monohydrochloride (DAP.HCl). For the anion regenerant double-distilled H_2SO_4 was used. For the cation regenerant tetrabutylammonium hydroxide (TBAOH, 55% solution) obtained from Southwestern Analytical Chemicals in Austin,Texas was used. All dilutions, preparations and cleaning of glassware were done with ultrapure deionized water.

Samples

All water samples were collected by the Youngstown State University Civil Engineering Department under the supervision of Dr. Scott Martin. The samples were collected at five dates: July 13, August 4, August 30, September 29, and November 3, 1988. Six collection sites were used:

1. Lowellville Bridge, Washington Avenue
   in Lowellville
2. Bridge Street in Struthers
3. Cedar Street in Youngstown

4. McKinley Street in MacDonald
5. Main Avenue in Warren
6. Leavitt Road in Leavittsburg

Sample numbers corresponded to the order as listed above. These sites are shown in Figure 6[16]. Samples were collected by the Wildco method using a Grab cup which was lowered in the river just below the surface of the water. These surface water samples are considered to be at 0 feet in depth. The samples were then stored in plastic bottles and refrigerated at approximately 4°C after collection.

Apparatus

The Dionex 2000i/SP ion chromatograph system was used. A diagram of the interior of a Dionex chromatography module is shown in Figure 7[17]. Detailed instructions from the Dionex Corporation for the operation of the system were followed[17]. For the separator columns a HPIC FAST SEP CATION 1 column and a HPIC FAST SEP ANION 1 column were installed according to instructions[18,19]. These columns were designed for rapid determinations of alkali metals and alkaline earths for cations and mono- and divalent anions[19]. However, specifications of the resin structure for the columns were unavailable from the manufacturer, the Dionex Corp. The runs were extremely fast compared to the previously used cation and anion columns which were the HPIC-CS1 and HPIC-AS4, respectively. Twelve min runs were reduced to 2.5-3.0 min with the new columns; the savings in time were immense and resolution of the peaks was consistently good.

A conductivity detector was integrated into the system.

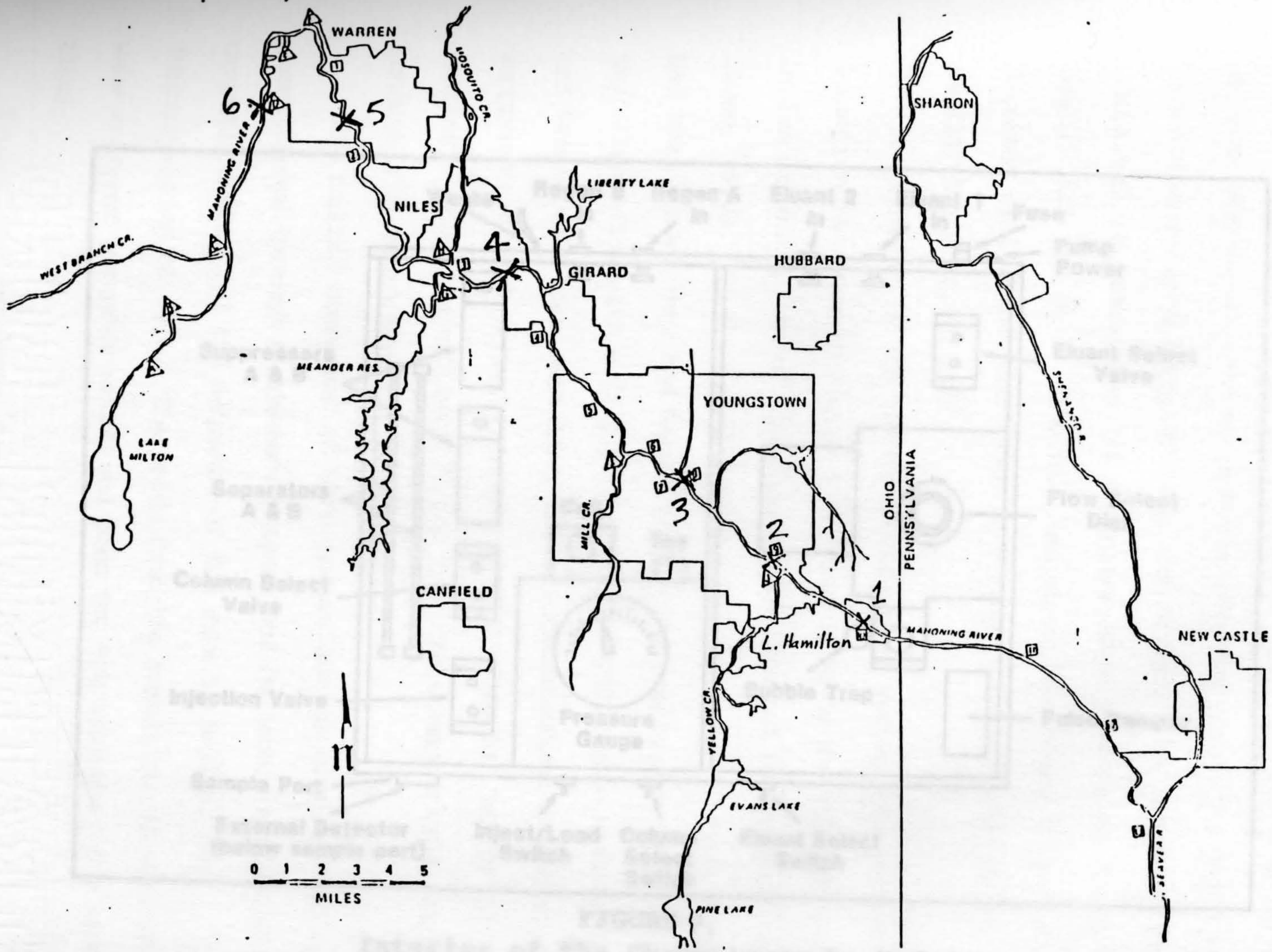


Figure 6. Map of Mahoning River and Collection Sites.

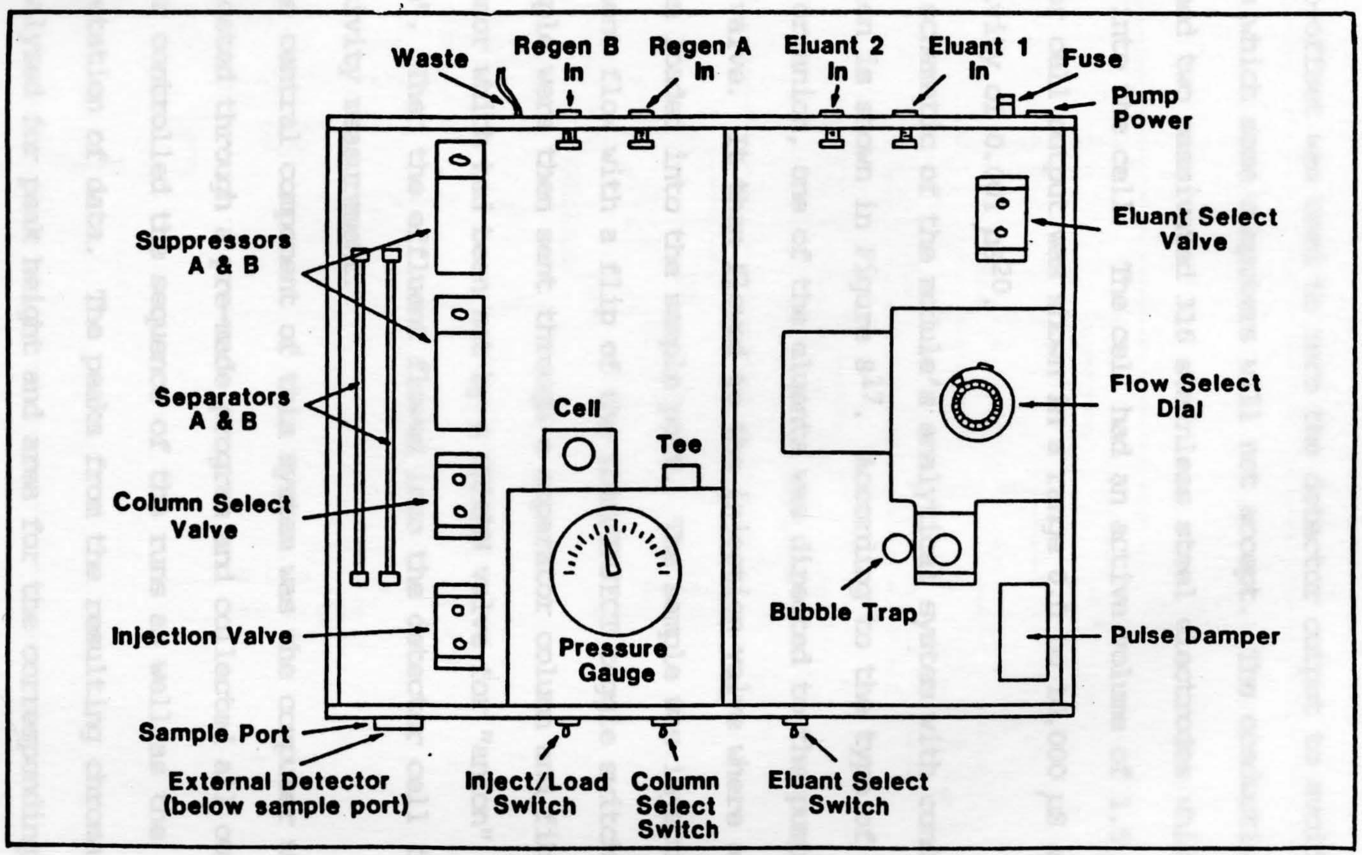


FIGURE 7.
Interior of the Chromatography Module

Temperature compensation which eliminated baseline variations caused by temperature changes of the solution was accomplished with a temperature compensation select switch which was user-controlled[20]. An auto-offset was used to zero the detector output to avoid negative signals which some computers will not accept. The conductivity cell contained two passivated 316 stainless steel electrodes which were sealed into the cell. The cell had an active volume of 1.5 µL. The detector cell output was shown in a range 0.0 to 10,000 µS and with a sensitivity of 0.001 µS[20].

A schematic of the module's analytical system with conductivity detection is shown in Figure 8[17]. According to the type of analysis, cation or anion, one of the eluents was directed to the pump by the eluent valve. It then flowed to the injection valve where a sample had been loaded into the sample port. The sample was injected into the eluent flow with a flip of the LOAD/INJECT toggle switch. Eluent and sample were then sent through a separator column and fiber suppressor which had been set by a COLUMN valve for "anion" or "cation". Then the effluent flowed into the detector cell for conductivity measurement.

The central component of this system was the computer which communicated through a pre-made program and collected all output. The computer controlled the sequence of the runs as well as the interpretation of data. The peaks from the resulting chromatograms were analyzed for peak height and area for the corresponding retention times.

Typical chromatograms for the cation and anion analyses are shown in Figures 9-10. Specific ions were identified by retention times

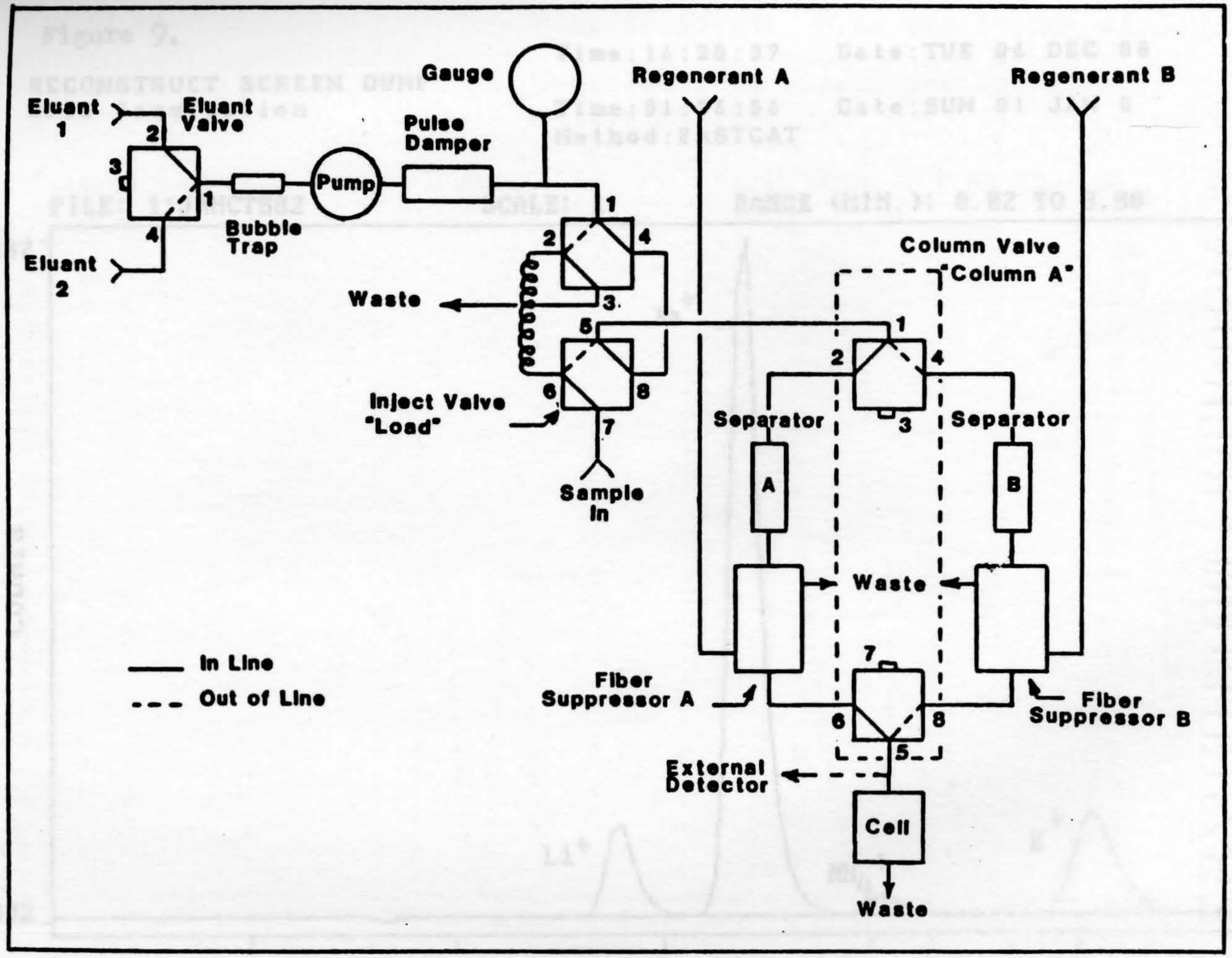


FIGURE 8.
Schematic of the Analytical System
with Conductitivity Detection

Figure 9.

RECONSTRUCT SCREEN DUMP
Data Acquisition

Time:16:20:37 Date:TUE 06 DEC 88

Time:01:36:56 Date:SUN 01 JAN 0
Method:FASTCAT

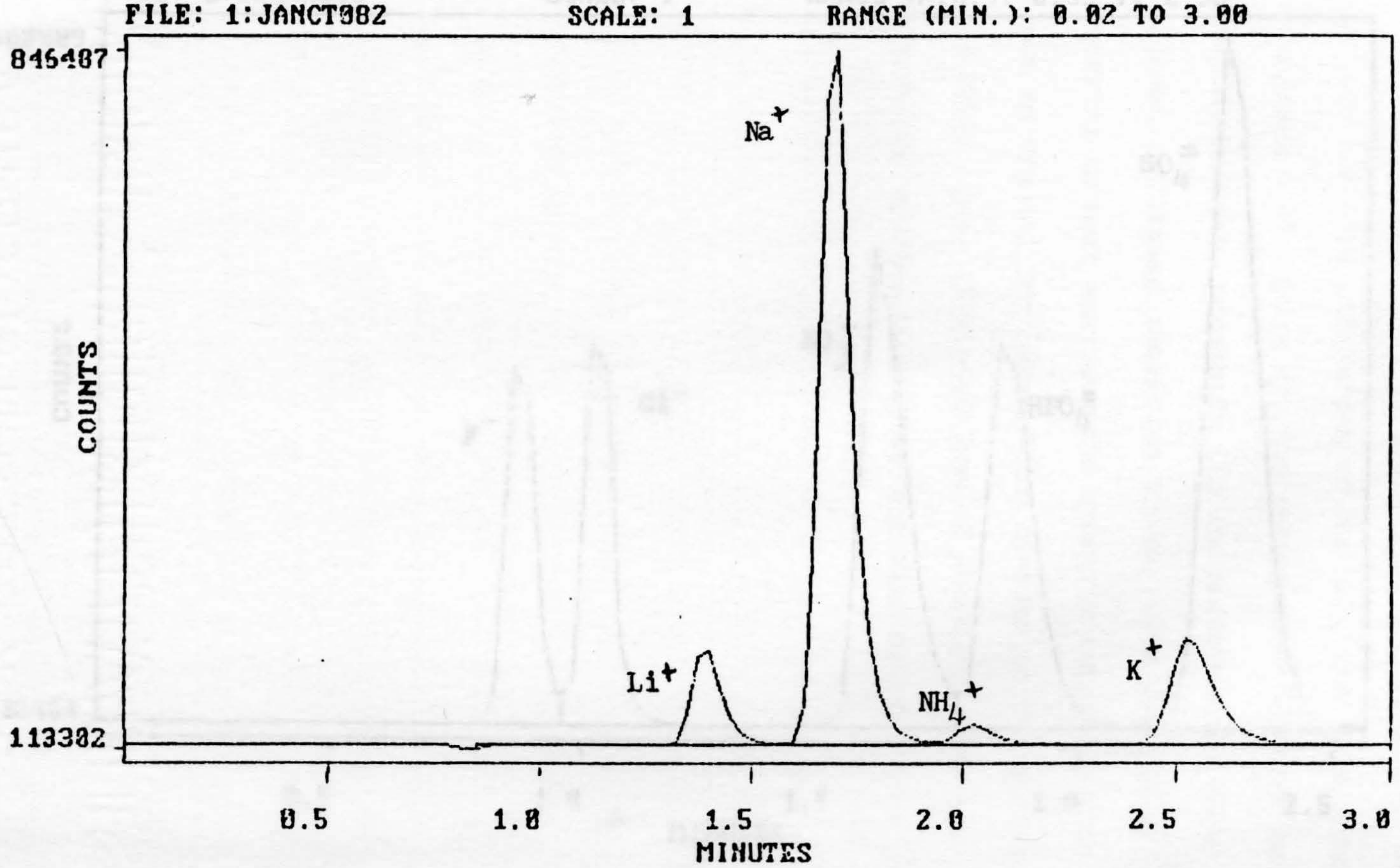
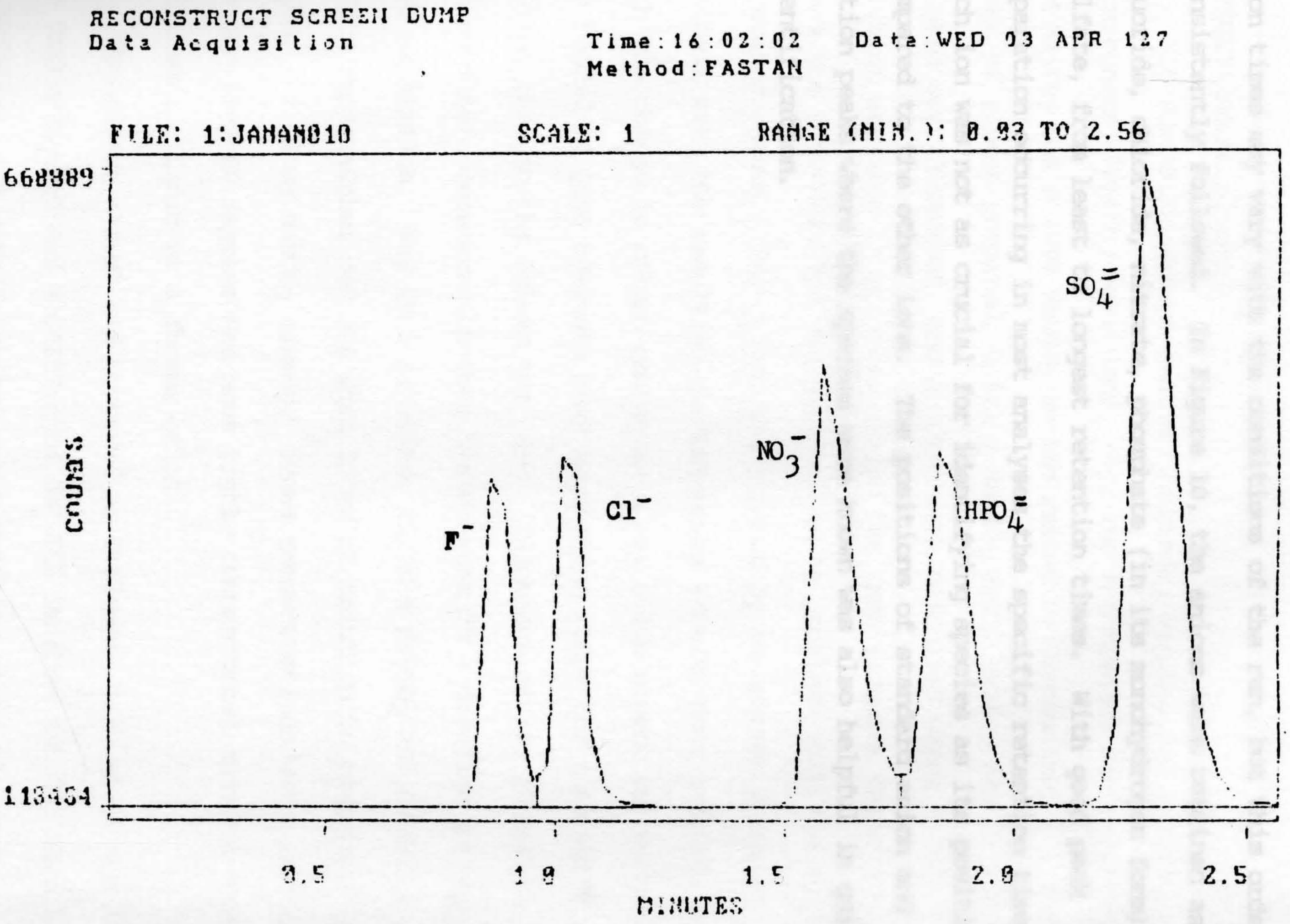


Figure 10.



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RECONSTRUCT SCREEN DUMP          Time.11:02:55    Date:TUE 29 NOV 88
Data Acquisition                 Time:16:02:02    Date:WED 03 APR 127
                                 Method:FASTAN

FILE: 1:JANAN010          SCALE: 1          RANGE (MIN.): 0.83 TO 2.56
```

with the order of retention used as a guide. For example, in Figure 9, cations were retained on the column in the order lithium, sodium, ammonium and potassium, from least to longest retention times. Retention times may vary with the conditions of the run, but this order was consistently followed. In Figure 10, the anions were retained as fluoride, chloride, nitrate, phosphate (in its monohydrogen form) and sulfate, from least to longest retention times. With good peak separation occurring in most analyses the specific retention time of each ion was not as crucial for identifying species as its position compared to the other ions. The positions of standard anion and cation peaks where the species were known was also helpful in quick identification.

EXPERIMENTAL METHODS

Preparation of Eluents

For the anion eluent sodium carbonate, Na_2CO_3, and sodium bicarbonate, $NaHCO_3$, were used. For the recommended concentrations of 2mM Na_2CO_3 and 0.15mM $NaHCO_3$ as instructed by Dionex Corp.[21], for each liter of eluent prepared, 0.212 g Na_2CO_3 and 0.0126 g $NaHCO_3$ were weighed out, dissolved, and diluted with deionized water. This solution was used in all runs except the last (samples dated 11-3-88) where the concentration was changed due to problems with the anion separator column. The column was altered by an unknown cause or accident with the resulting chromatograms showing poor resolution. With the change in column character a new anion eluent concentration was needed to give adequate peak separation since the ions were eluting through the column too fast. Dilutions of 10, 15 and 20 % of the original concentration were tested with 20 % dilution giving good peak separation. For 20 % dilution, 0.170 g Na_2CO_3 and 0.0101 g $NaHCO_3$ were weighed out for each liter of solution to prepare a 1.6 mM Na_2CO_3 / 0.12 mM $NaHCO_3$ eluent. These concentrations were used only for the 11-3-88 samples and some highly concentrated chloride samples which were diluted by a factor of 20.

The cation eluent was prepared as follows: 3.33 mL of 6 M HCl was micropipetted and 0.04217 g of DAP.HCl weighed out for each liter of solution made with deionized water used for dilution, thus resulting in a 20 mM HCl / 0.3 mM DAP.HCl eluent as recommended by the

Dionex Corporation[22]. These eluent concentrations were used for all cation analyses.

Preparation of Regenerants

The anion regenerant consisted of 0.7 mL of concentrated (16M) H_2SO_4 per liter of solution with deionized water used for dilution. This 11.2 mM solution was used in all anion analyses as recommended by the Dionex instructions[21].

The cation regenerant for samples dated 7-13-88, 8-4-88 and 8-30-88 consisted of tetramethylammonium hydroxide (TMAOH) in a 0.1 M solution. Tetrabutylammonium hydroxide (TBAOH) replaced TMAOH in the 0.1 M solution[18] for the 9-29-88 and 11-3-88 samples after the Dionex Corp. cited certain advantages with the use of TBAOH including lower background conductivity due to less diffussion through the suppressor membrane of the larger sized TBAOH molecules[23]. The 0.1 M solution was prepared by diluting 48.54 mL of the stock TBAOH (2.06M) with deionized water per liter of regenerant.

Preparation of Standards

Standards for cations and anions were prepared from stock solutions of 1000 ppm except for potassium (10,000 ppm). Three standards for each ion were prepared with concentrations based on the expected range of sample values. The concentrations of the six anion and cation standard solutions for the eight ions are shown in the Table 1.

Since only 100 mL of each standard solution was prepared, micropipettes were used for measuring the volumes of stock solutions to

Table 1. Anion and Cation Standards

	ANION STANDARDS (ppm)		
ION	# 1	# 2	# 3
Fluoride	1.0	2.0	4.0
Chloride	1.5	3.0	6.0
Nitrate	5.0	10.0	20.0
Phosphate	7.5	15.0	30.0
Sulfate	7.5	15.0	22.5

	CATION STANDARDS (ppm)		
ION	# 1	# 2	# 3
Sodium	12.5	25.0	37.5
Ammonium	1.0	2.0	3.0
Potassium	4.0	8.0	12.0

ensure accuracy. Thus, for a concentration of 1 ppm fluoride in the anion standard #1, 100 µL of the 1000 ppm stock solution was micropipetted to a 100 mL flask and after the addition of the other stock solutions, the mixture was diluted to 100 mL with deionized water. These standard solutions were used for all analyses. They were stored in plastic bottles to prevent loss of ions from the solution and were kept in a refrigerator except during analysis.

Preparation of Samples

Sample preparation was accomplished by the YSU Civil Engineering Department under the supervision of Dr. Martin. After collection, the water samples were filtered in a two-step process: first, through a Fisher G-4 glass fiber-filter with an effective pore size of approximately 1.0 µm; then, through a Gelman GA-6 membrane with a pore size equalling 0.45 µm. The samples were then ready for analysis. Like the standards the samples were stored in a refrigerator when not being analyzed, in plastic bottles to prevent loss of ions. Sample filtration is a crucial step before analysis with ion chromatography in that potentially damaging substances which can clog and destroy the column are eliminated from the water sample before it is injected into the IC column.

Ion Chromatography Method

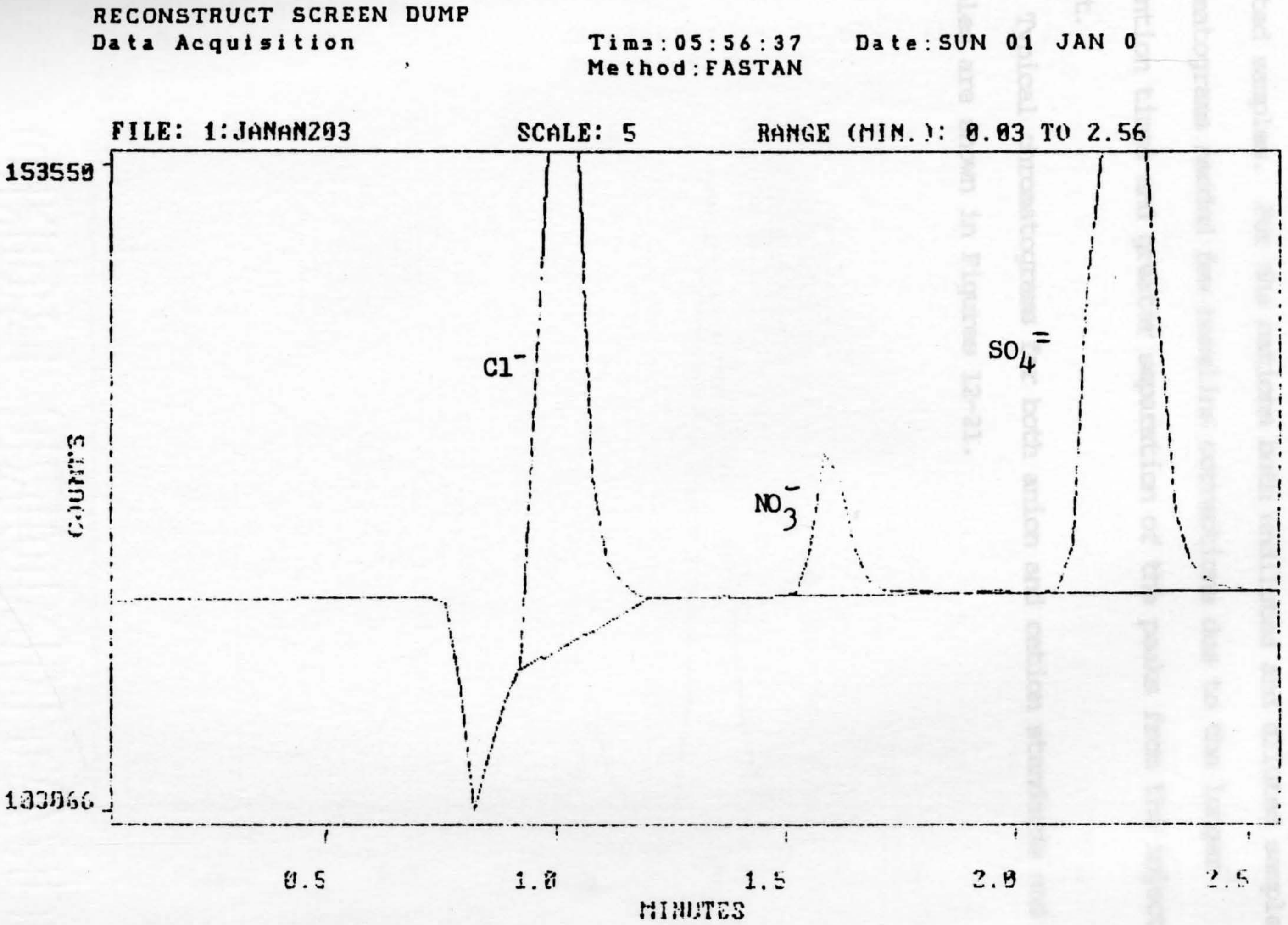
Instructions for the 2000i/SP Dionex system from the company were followed for the operation of the chromatograph module and computer data acquisition program[17]. The flow rate of the eluent for all cation and anion analyses was kept at approximately 2 mL / min though this was crudely measured since no flow rate device existed on the instrument. However, for each set of runs of standards and samples the flow rate was assumed to be constant. Pump pressure was kept at approximately 800 psi (5.5 MPa) for all analyses though this reading fluctuated in a range between 650-900 psi (4.5-6.0 MPa). Samples dated 7-13-88, 8-4-88 and 8-30-88 were analyzed using a 50 µL injection loop for both cations and anions. When TBAOH replaced TMAOH for the cation regenerant detection became more sensitive and the standard and sample peaks for sodium showed column saturation. A 20 µL loop was then used with the resulting sodium peaks for the standards within range. A 20 µL loop was then used for all subsequent analyses. An open-tipped syringe was used for injection of all standards and samples, with deionized water used for rinsing the syringe between injections.

The instrument was run through a warm-up period of at least 30 minutes to allow the system to equilibrate. For a cation or anion run each of the three standards was analyzed three times with computer printouts of the resulting peak heights and peak areas checked. After linearity of the standards with respect to concentration versus peak height was established, each sample was analyzed twice with additional runs done if the peak heights were grossly different.

Valid analysis of the ions can occur only if sample concentrations are within a reasonable range for interpretation, which in this project is within the range of the standard concentrations. Dilution became necessary for all samples in both cation and anion analysis due to the tremendous variation in ion concentration for the eight species. Thus, each sample was analyzed four times -- once in its undiluted form for cations, then for anions, then diluted for cations, then diluted for anions. Sodium sample concentrations were consistently higher than the highest standard (37.5 ppm) so all raw sodium peak data reflect dilution by a factor of four. Chloride and sulfate sample concentrations were also repeatedly higher than acceptable so dilution by a factor of ten was used. However, for samples dated 11-3-88 and several highly concentrated chloride ($>$ 6 ppm) samples from the other collection dates dilution by a factor of 20 was necessary for analysis. Dilutions were prepared with deionized H_2O. For a 4-fold dilution, 2.5 mL of sample was mixed with 7.5 mL H_2O; for a 10-fold dilution, 1 mL of sample with 9 mL H_2O; for a 20-fold dilution, 1 mL of sample with 19 mL H_2O. All dilutions were done in sterile, disposable cups with the mixture swirled. The diluted samples were then injected and run identically to the undiluted samples.

All resulting chromatograms were examined for straight baselines to ensure validity of the data. Baseline corrections were done with the system's computer by manipulation of the parameters for analysis. For the anions undiluted samples tended to give horizontal baselines with no correction needed after the initial run. Diluted samples, however, gave enormous slanting negative peaks at the injection point with baseline correction often needed. This slanting baseline is shown in Figure 11. The emergence of the fluoride and chloride peaks with the injection point is a consequence of the fast separator column used and the significant difference in conductivity between the eluent and the diluted sample which causes the deep injection point. A remedy to this problem would be the use of a slower column which would

Figure 11.



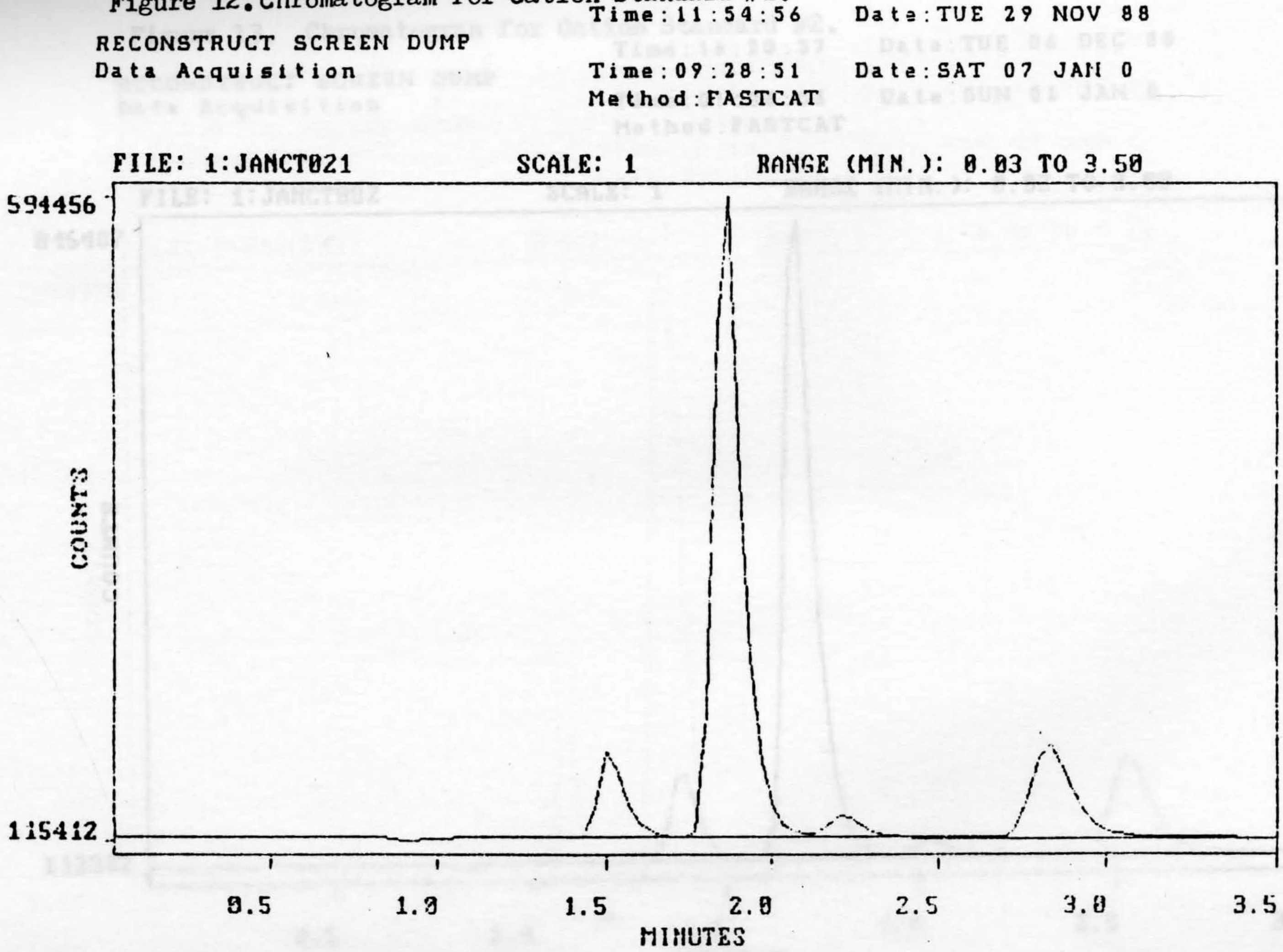
```
                                   Time:12:19:29    Date:TUE 29 NOV 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                   Tima:05:56:37    Date:SUN 01 JAN 0
                                   Method:FASTAN

FILE: 1:JANAN203          SCALE: 5        RANGE (MIN.): 0.03 TO 2.56
```

separate the fluoride and chloride peaks from the injection point but would also increase the run time. The advantage of the 2.5 min run time far outweighs the inconvenience of baseline correction for diluted samples. For the cations both undiluted and diluted sample chromatograms needed few baseline corrections due to the longer retention times and greater separation of the peaks from the injection point.

Typical chromatograms for both anion and cation standards and samples are shown in Figures 12-21.

Figure 12. Chromatogram for Cation Standard #1.



Time:11:54:56 Date:TUE 29 NOV 88

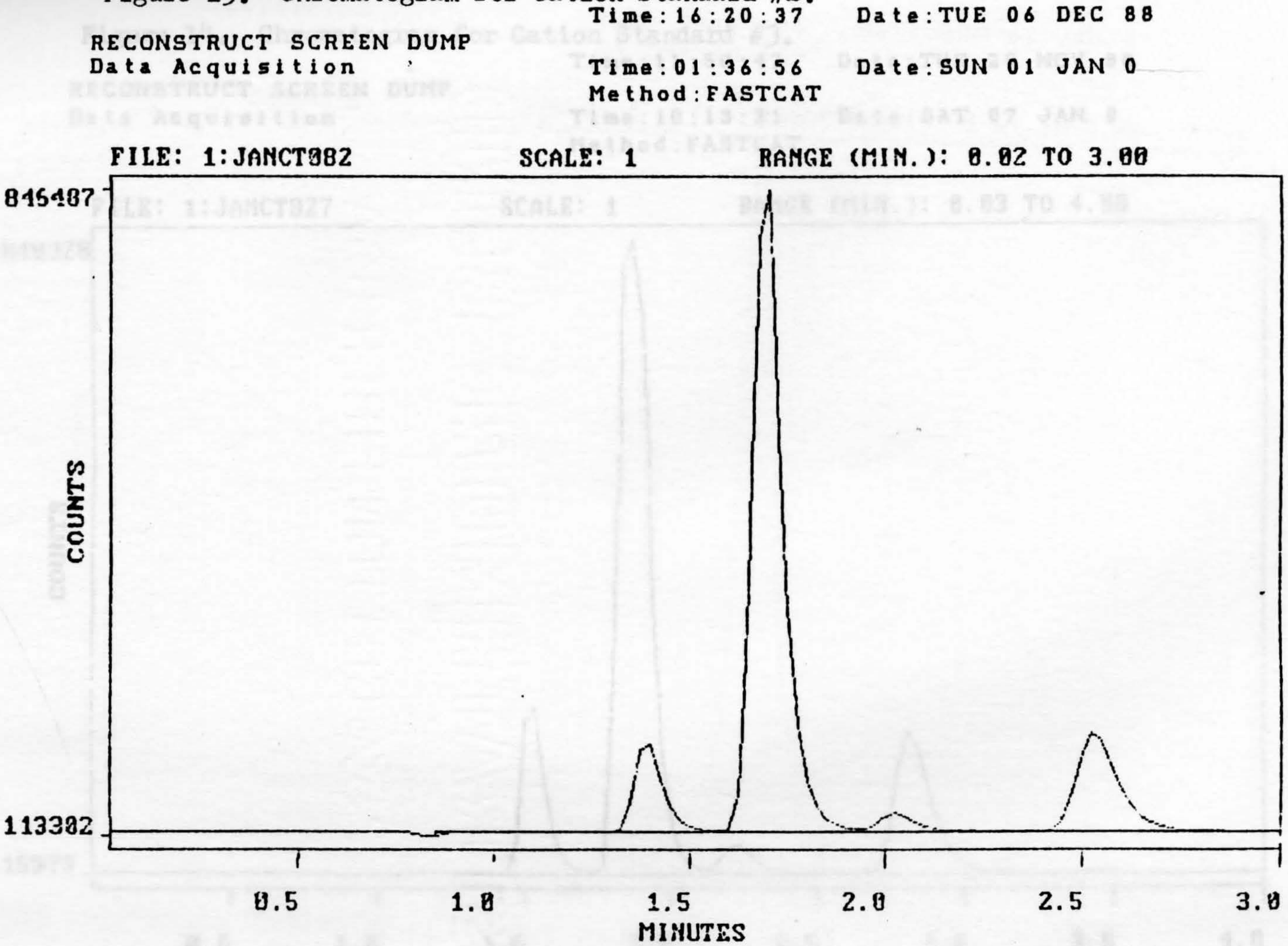
RECONSTRUCT SCREEN DUMP

Data Acquisition Time:09:28:51 Date:SAT 07 JAN 0

Method:FASTCAT

FILE: 1:JANCT021 SCALE: 1 RANGE (MIN.): 0.03 TO 3.50

Figure 13. Chromatogram for Cation Standard #2.



Time:16:20:37 Date:TUE 06 DEC 88

RECONSTRUCT SCREEN DUMP

Data Acquisition

Time:01:36:56 Date:SUN 01 JAN 0

Method:FASTCAT

FILE: 1:JANCT082 SCALE: 1 RANGE (MIN.): 0.02 TO 3.00

Figure 14. Chromatogram for Cation Standard #3.

```
                                        Time:11:50:47    Date:TUE 29 NOV 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                        Time:10:13:21    Date:SAT 07 JAN 0
                                        Method:FASTCAT

FILE: 1:JANCT027              SCALE: 1         RANGE (MIN.): 0.03 TO 4.00
```

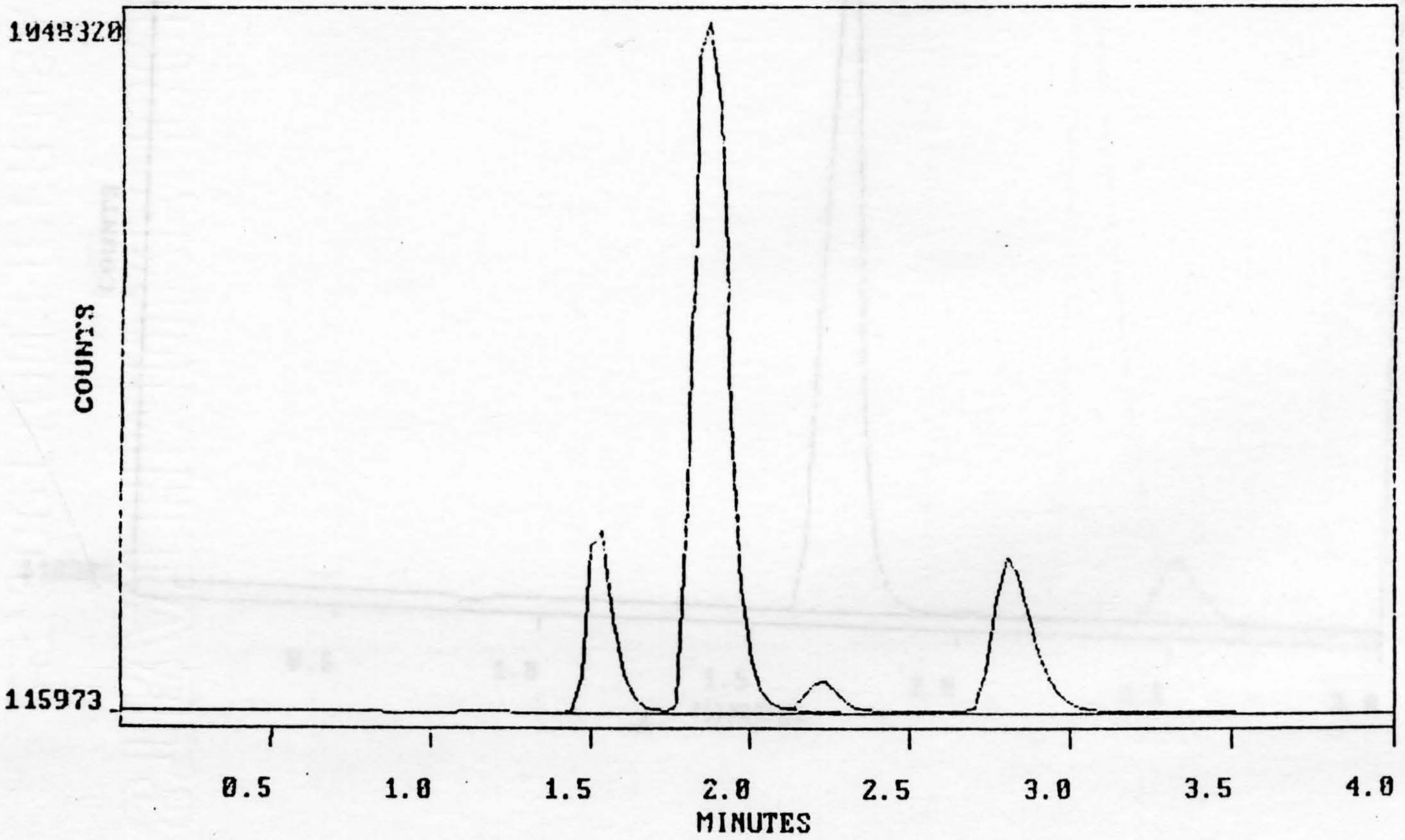
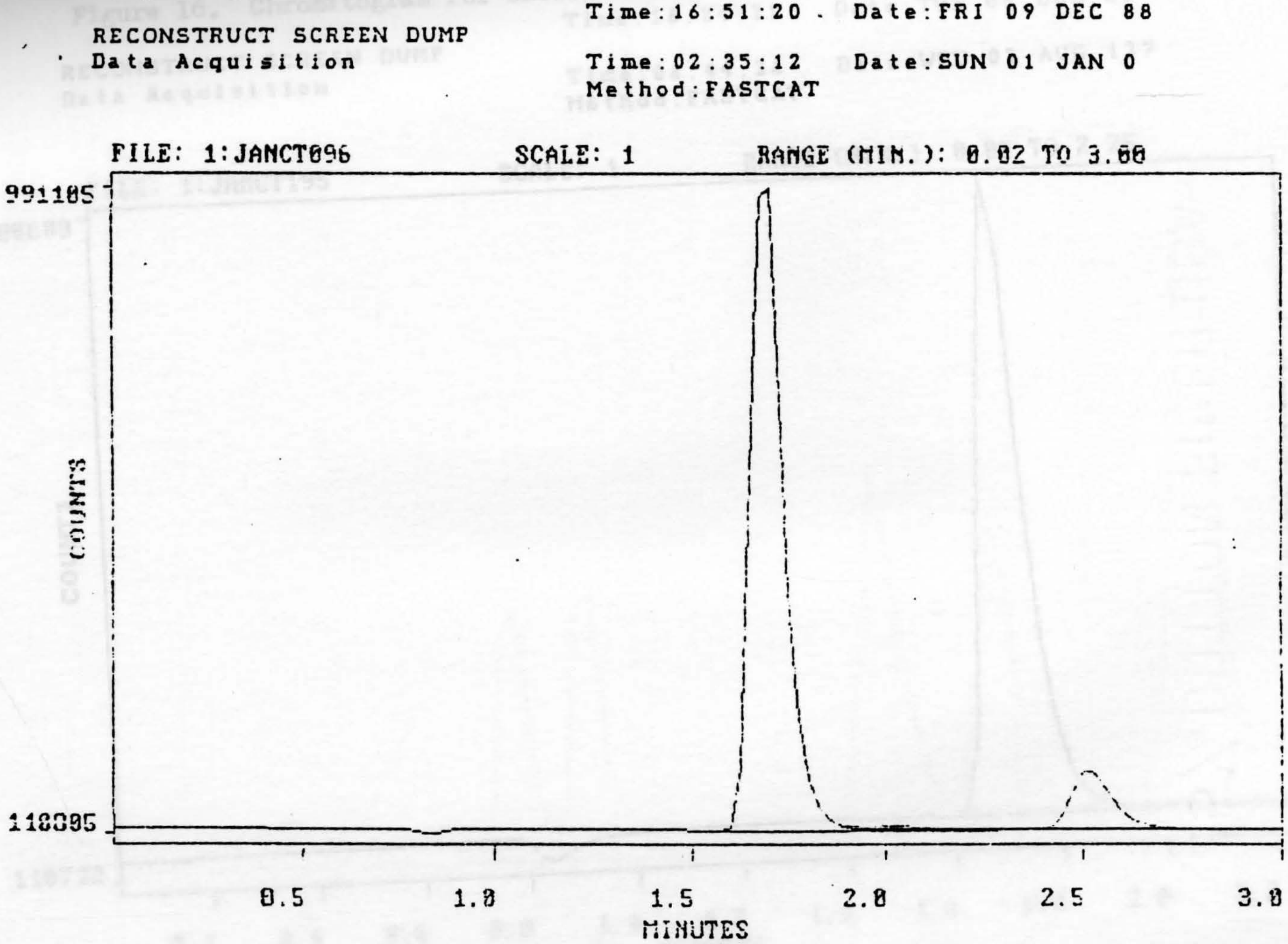


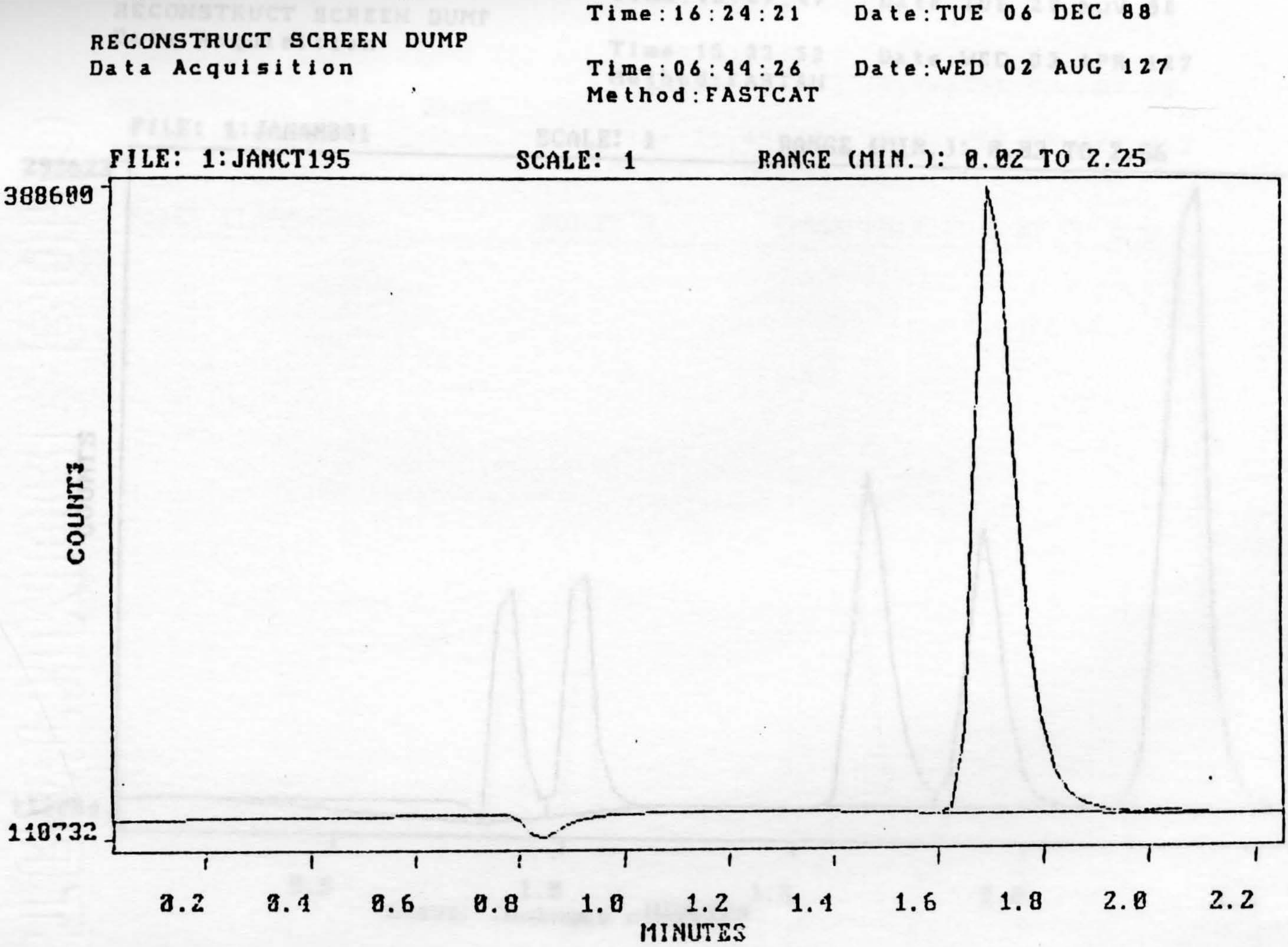
Figure 15. Chromatogram for Cations in Undiluted Sample.



```
                                   Time:16:51:20 . Date:FRI 09 DEC 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                   Time:02:35:12   Date:SUN 01 JAN 0
                                   Method:FASTCAT

FILE: 1:JANCT096          SCALE: 1          RANGE (MIN.): 0.02 TO 3.00
```

Figure 16. Chromatogram for Cations in Diluted Sample.



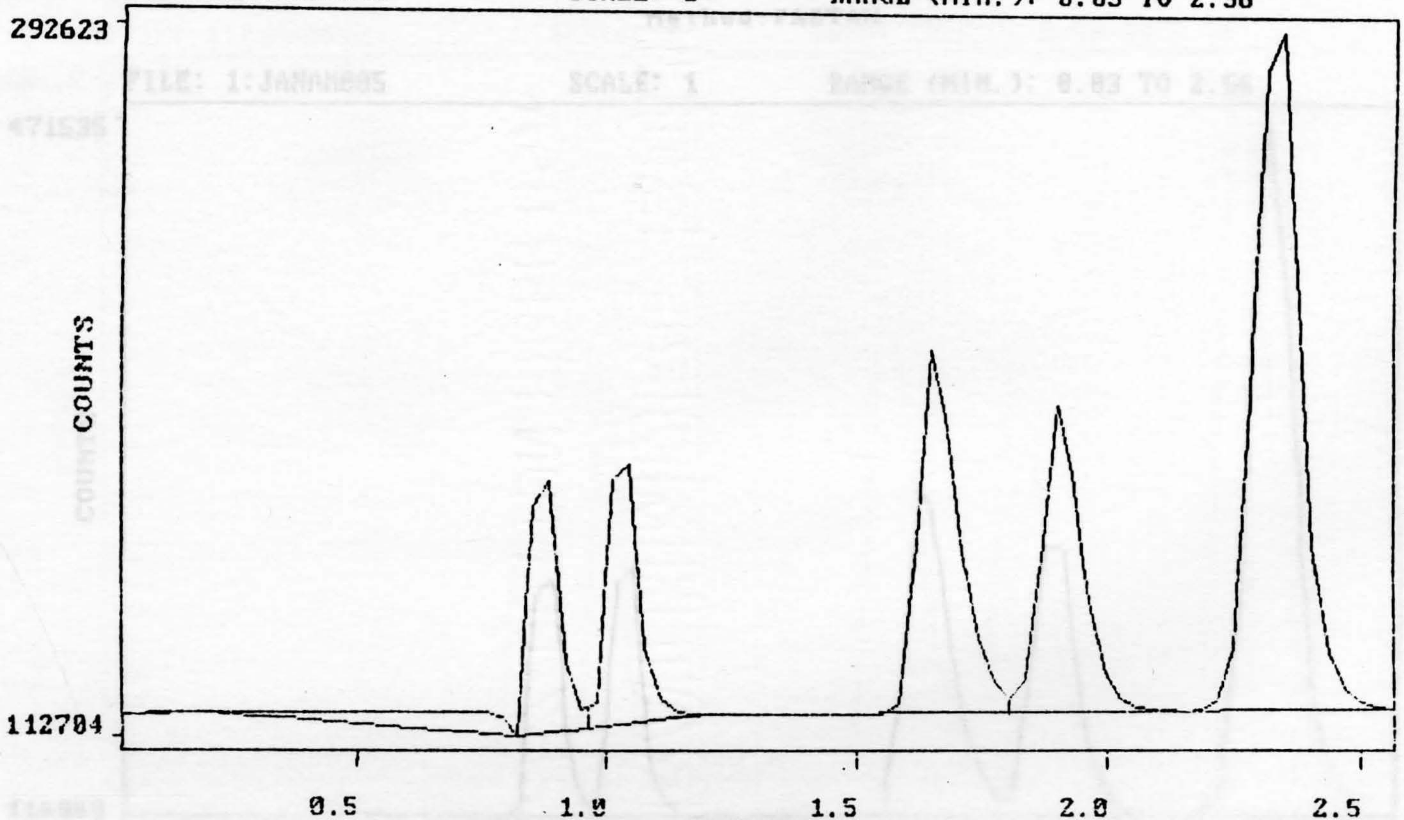
```
                                   Time:16:24:21    Date:TUE 06 DEC 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                   Time:06:44:26    Date:WED 02 AUG 127
                                   Method:FASTCAT

FILE: 1:JANCT195              SCALE: 1          RANGE (MIN.): 0.02 TO 2.25
```

Figure 17. Chromatogram for Anion Standard #1.

```
                                   Time:10:29:49    Date:TUE 29 NOV 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                   Time:15:32:52    Date:WED 03 APR 127
                                   Method:FASTAN

FILE: 1:JANAN001            SCALE: 1         RANGE (MIN.): 0.03 TO 2.56
```



```
ERROR: Unknown command
```

Figure 18. Chromatogram for Anion Standard #2.

```
                                Time:10:58:15   Date:TUE 29 NOV 88
RECONSTRUCT SCREEN 'DUMP
Data Acquisition                Time:15:45:38   Date:WED 03 APR 127
                                Method:FASTAN
```

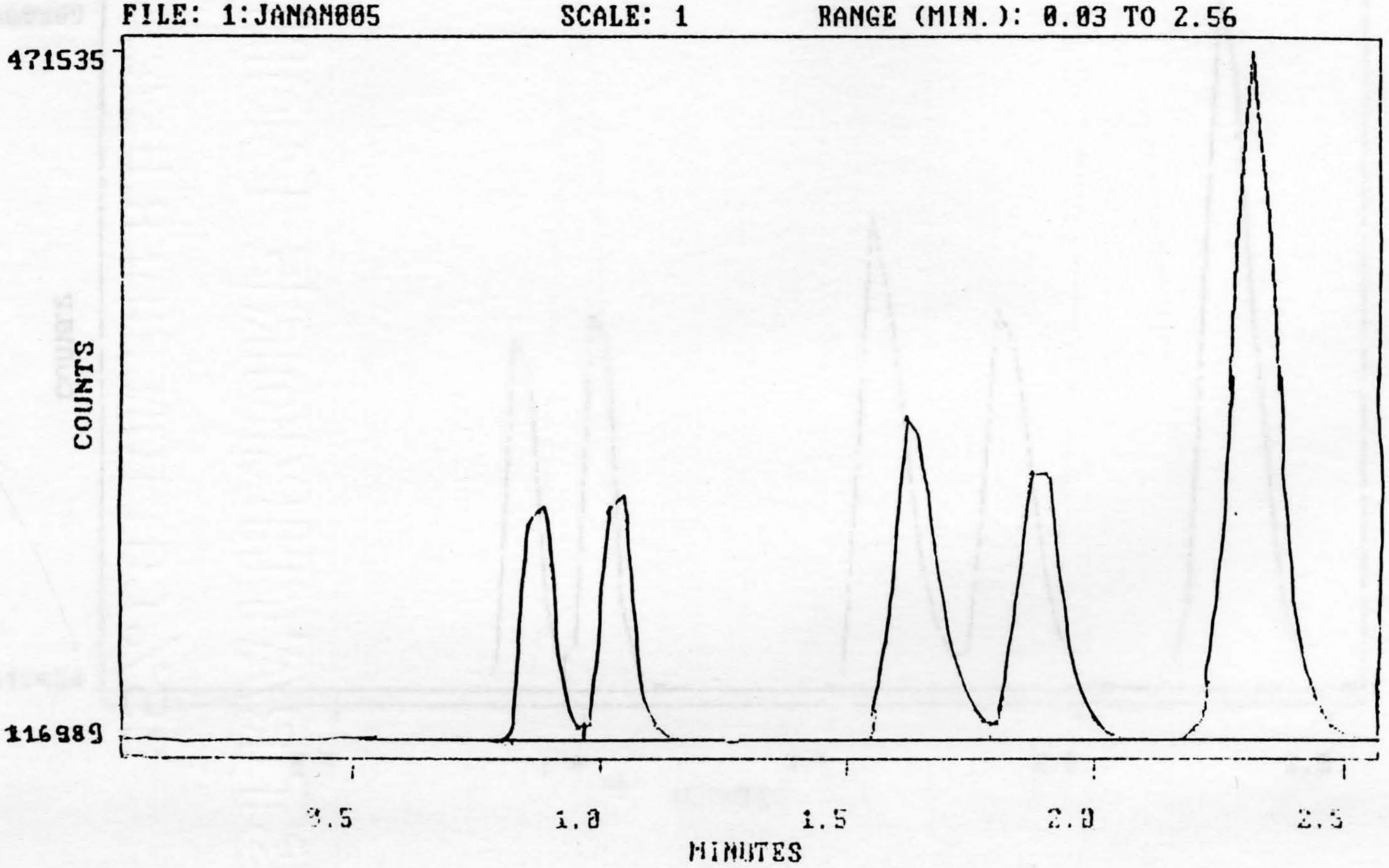
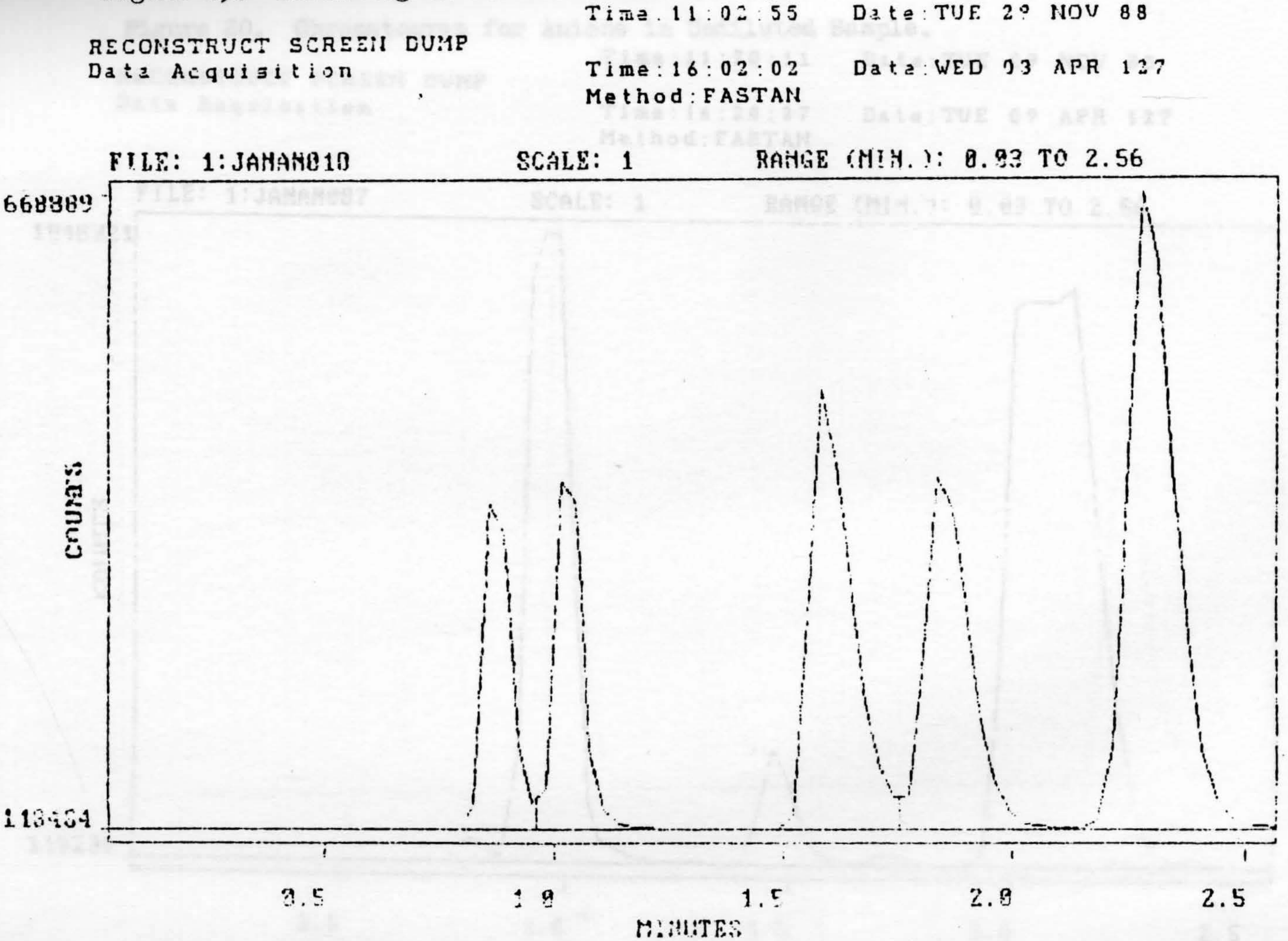


Figure 19. Chromatogram for Anion Standard #3.



```
                                   Time.11:02:55   Date:TUE 29 NOV 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                   Time:16:02:02   Data:WED 03 APR 127
                                   Method:FASTAN

 FILE: 1:JANAN010           SCALE: 1        RANGE (MIN.): 0.93 TO 2.56
```

Figure 20. Chromatogram for Anions in Undiluted Sample.

```
                                    Time:11:20:11   Date:TUE 29 NOV 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                    Time:16:24:27   Date:TUE 09 APR 127
                                    Method:FASTAN
```

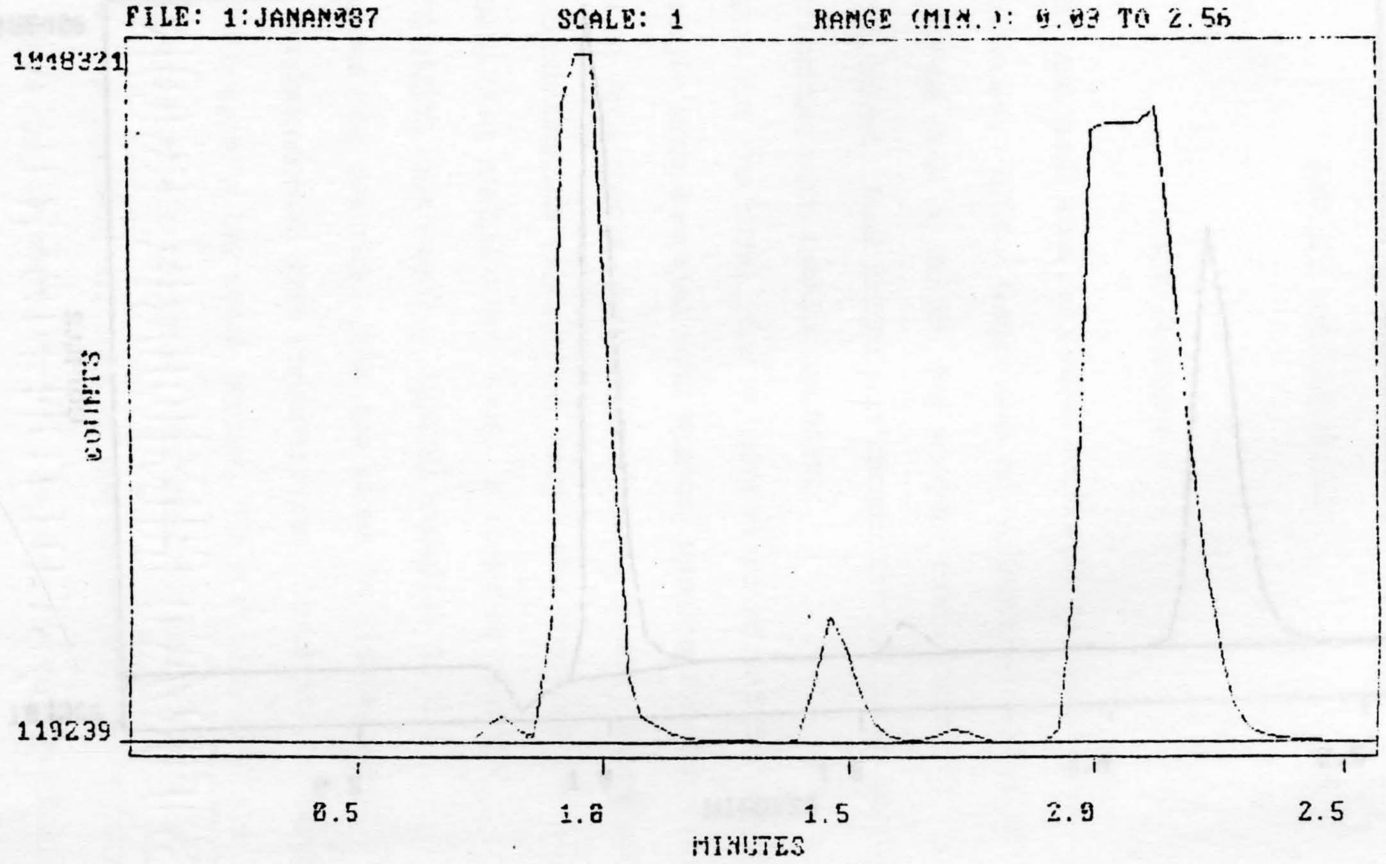
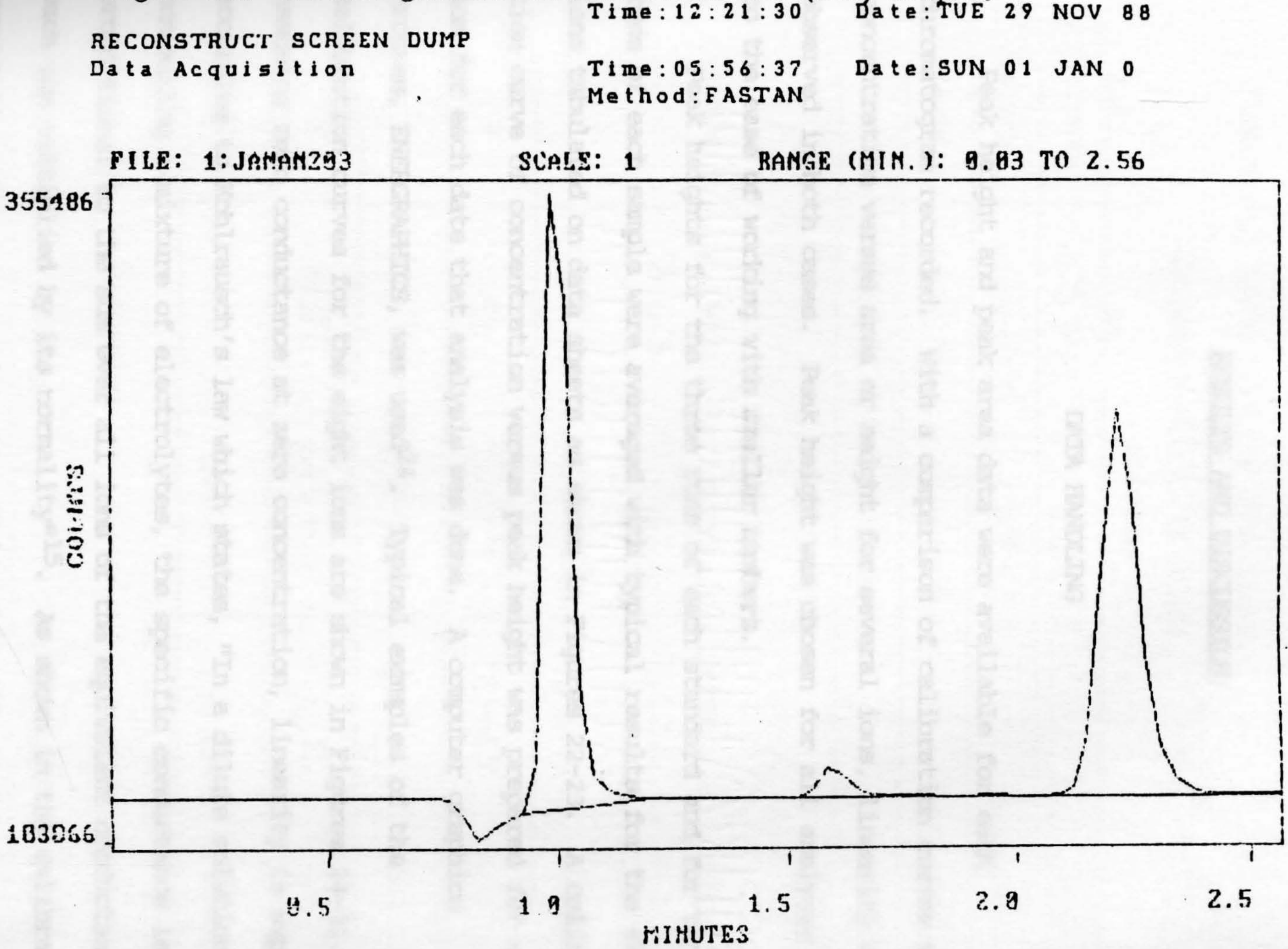


Figure 21. Chromatogram for Anions in Diluted (10X) Sample.



```
                                        Time:12:21:30   Date:TUE 29 NOV 88
RECONSTRUCT SCREEN DUMP
Data Acquisition                        Time:05:56:37   Date:SUN 01 JAN 0
                                        Method:FASTAN

FILE: 1:JANAN203           SCALE: 1          RANGE (MIN.): 0.03 TO 2.56
```

CHAPTER 3

RESULTS AND DISCUSSION

DATA HANDLING

Peak height and peak area data were available for each chromatogram recorded. With a comparison of calibration curves of concentration versus area or height for several ions, linearity was observed in both cases. Peak height was chosen for all analyses due to the ease of working with smaller numbers.

Peak heights for the three runs of each standard and for the two runs of each sample were averaged with typical results for the eight ions tabulated on data sheets as shown in Figures 22-23. A calibration curve of concentration versus peak height was prepared for each ion for each date that analysis was done. A computer graphics program, ENERGRAPHICS, was used[24]. Typical examples of the calibration curves for the eight ions are shown in Figures 24-31. Assuming zero conductance at zero concentration, linearity is expected according to Kohlrausch's law which states, "In a dilute solution containing a mixture of electrolytes, the specific conductance is proportional to the sum over all ions of the equivalent conductance of each ion multiplied by its normality"[15]. As shown in the calibration curves linearity was consistently achieved for the standards. For each calibration curve the regression formula was also computed by the

Figure 22. Typical Cation Data Sheet.

CATIONS
ION CHROMATOGRAPHY PEAK HEIGHT

RUN DATE: 11-19-88
SAMPLE DATE: 11-3-88

	STANDARDS		
ION	#1	#2	#3
LITHIUM	53711	106638	214086
SODIUM	408528	783616	919816
AMMONIUM	11769	21331	29637
POTASSIUM	58496	113794	173599

SAMPLES

SAMPLE #	LITH	SODIUM	AMMON	POTAS
1	3163	457550	16626	112680
2	1678	460556	16904	120104
3	1190	406443	12459	105242
4	1052	367974	25292	110251
5	451	297418	N.R.	76573
6	410	266823	N.R.	73026

N.R. = No Reading

Figure 23. Typical Anion Data Sheet.

ANIONS
ION CHROMATOGRAPHY PEAK HEIGHTS

RUN DATE: 9-2-88
SAMPLE DATE: 8-30-88

	STANDARDS		
ION	#1	#2	#3
FLUORIDE	67830	132978	298553
CHLORIDE	71991	153727	350972
NITRATE	89869	177223	374771
PHOSPHATE	77834	154936	318467
SULFATE	173072	347380	536729

SAMPLES

SAMPLE #	FLUOR	CHLOR	NITRA	PHOSP	SULFA
1	28904	335192	157396	N.R.	191640
2	29988	*369218	143916	N.R.	209383
3	25061	343162	90988	N.R. 1495	214899
4	24808	*365401	70690	N.R.	229692
5	18275	288536	38157	N.R.	205024
6	16750	253114	40882	N.R.	198212

N.R. = No Reading
* refers to samples requiring 20 X dilution.

Figure 24.

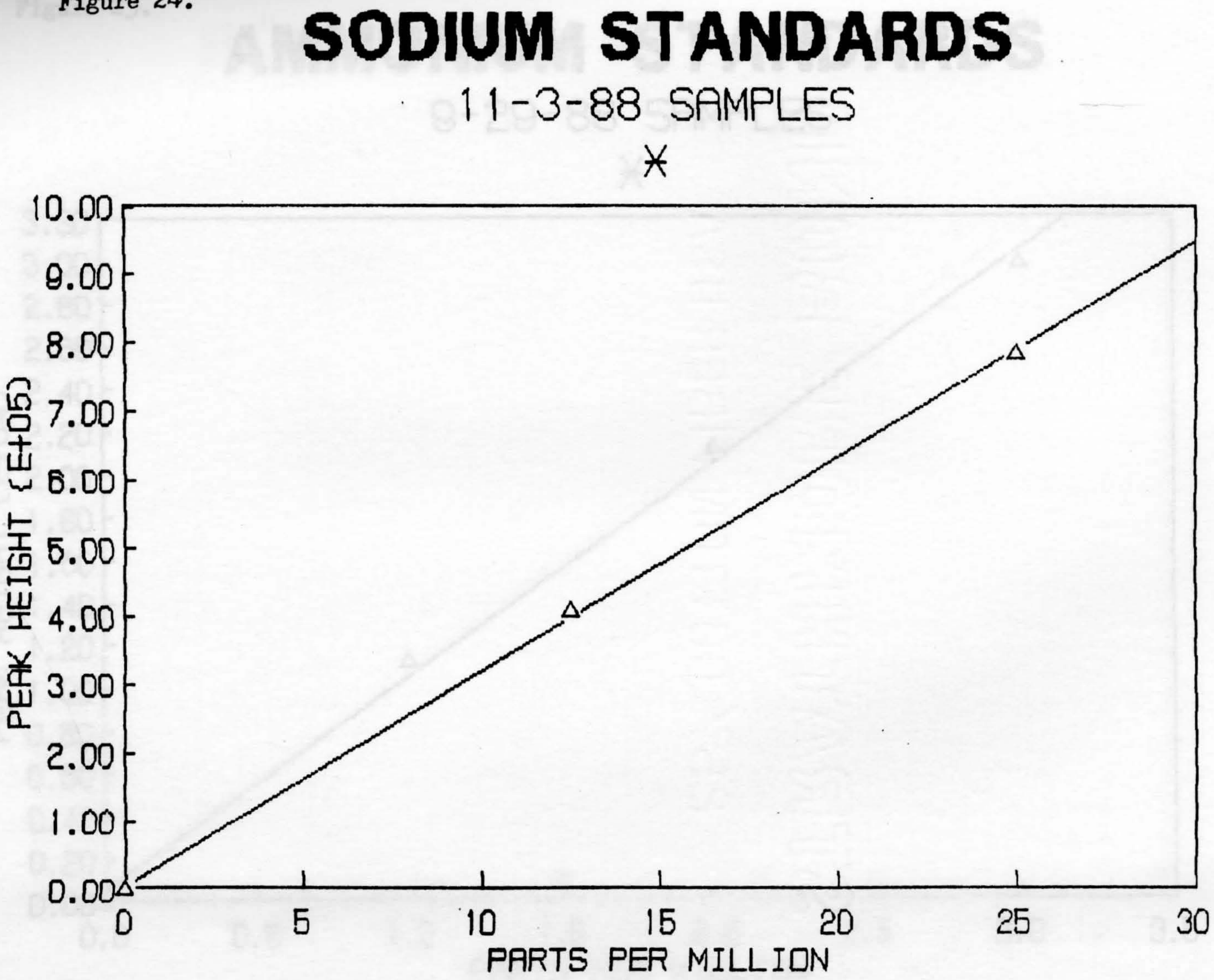

SODIUM STANDARDS
11-3-88 SAMPLES
*
PEAK HEIGHT (E+05)
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
5
10
15
20
25
30
PARTS PER MILLION

Figure 25.

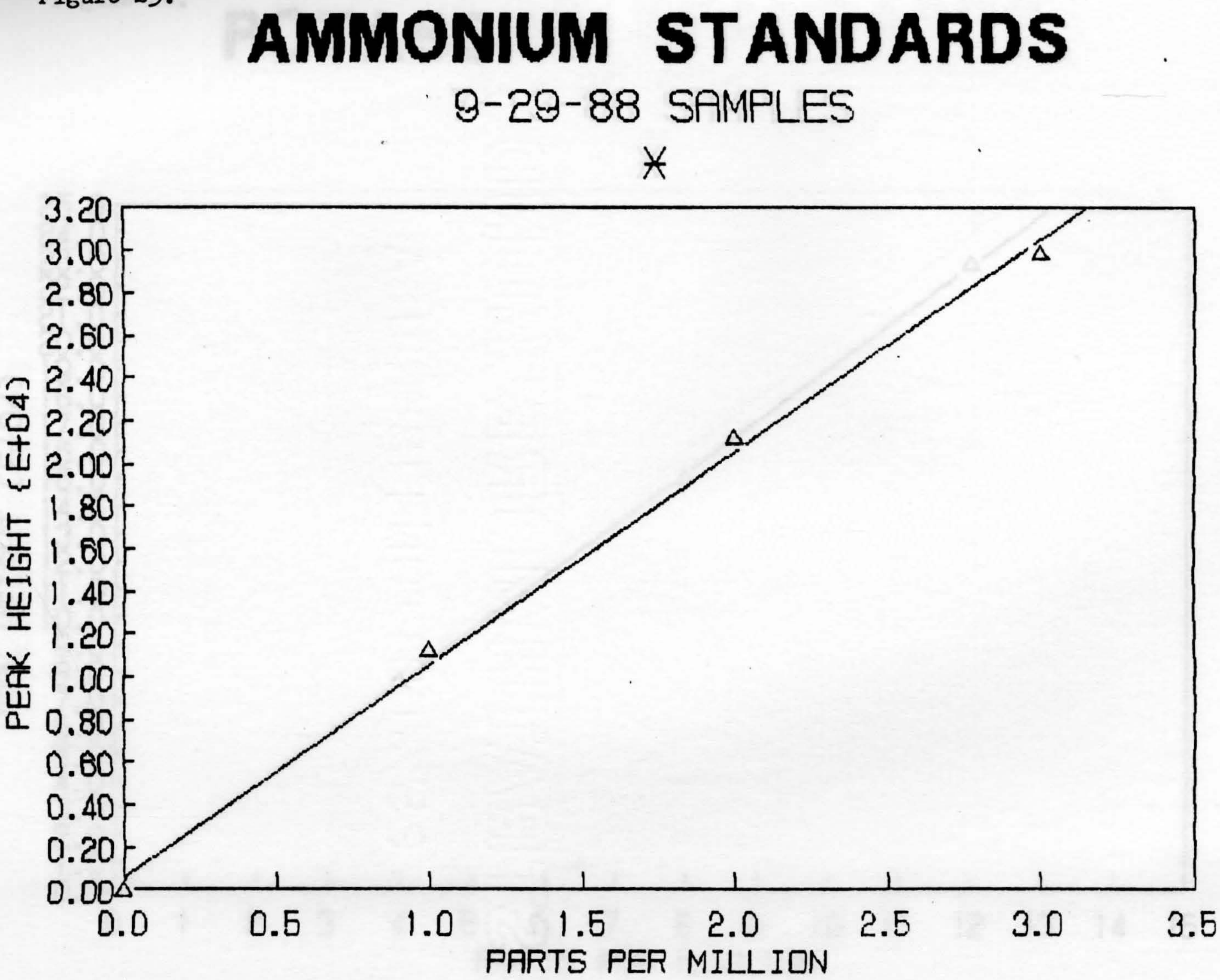

AMMONIUM STANDARDS
9-29-88 SAMPLES
*
PEAK HEIGHT (E+04)
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
PARTS PER MILLION

Figure 26.

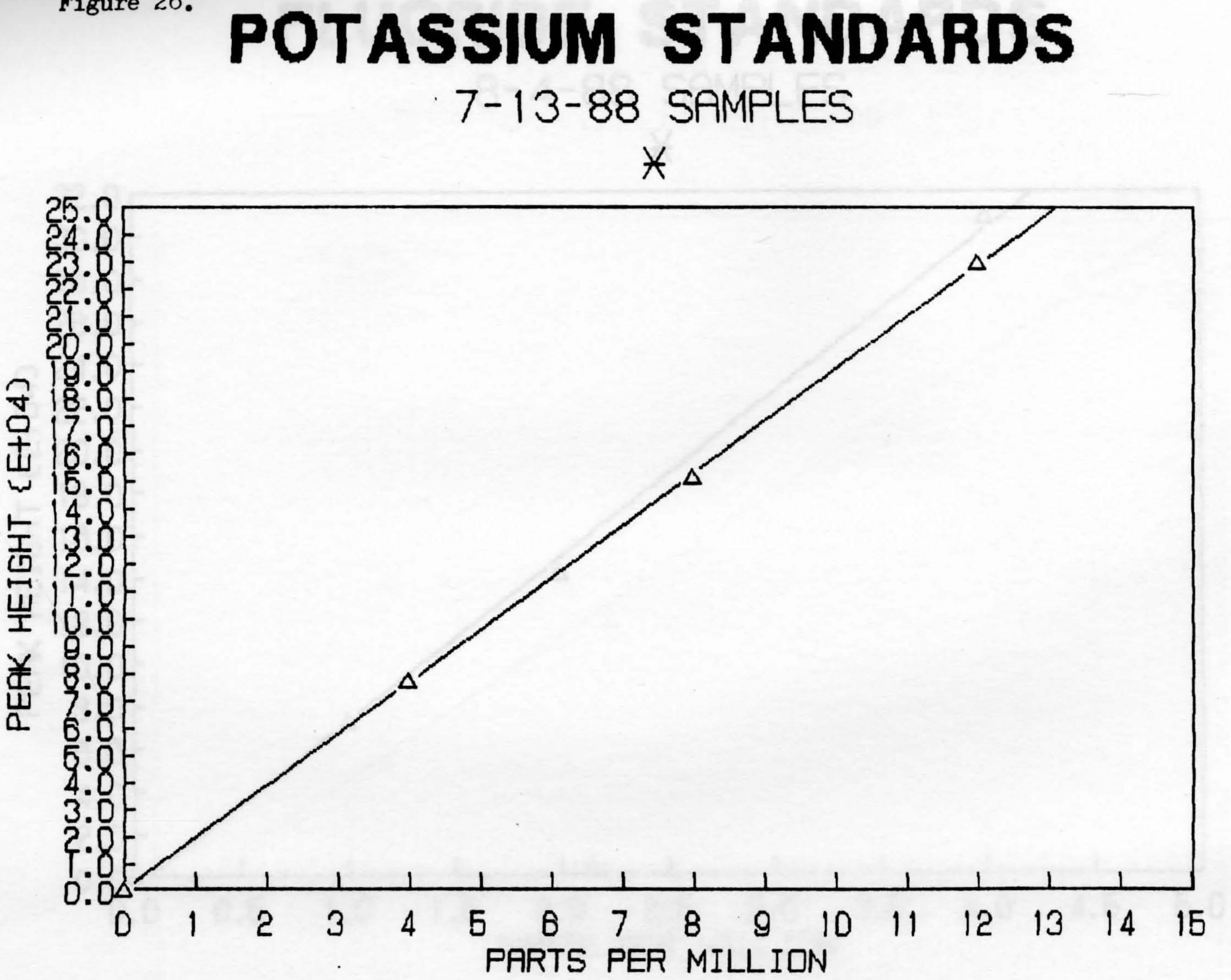

POTASSIUM STANDARDS
7-13-88 SAMPLES
*
PEAK HEIGHT {E+04}
25.0
24.0
23.0
22.0
21.0
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
PARTS PER MILLION

Figure 27.

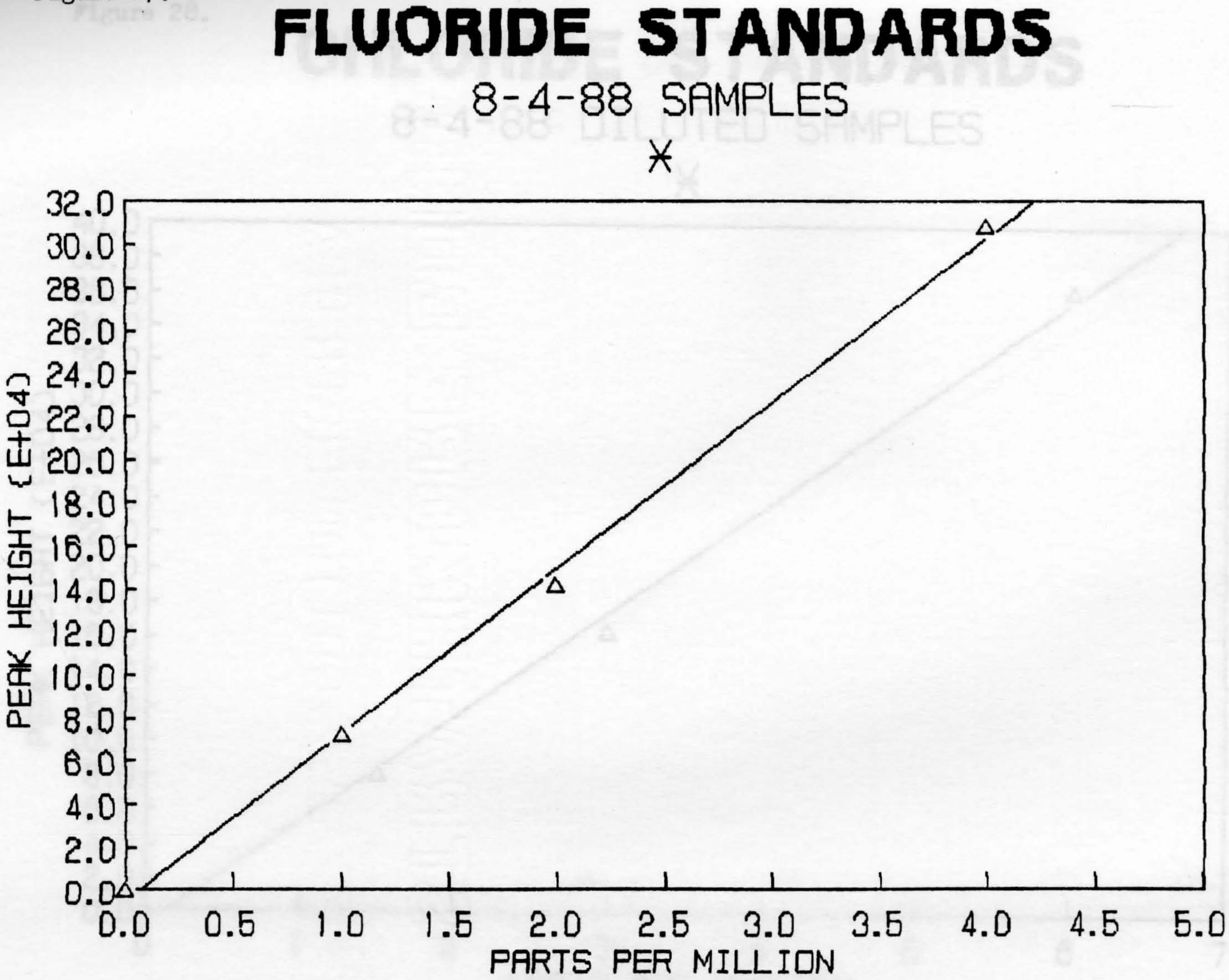

FLUORIDE STANDARDS
8-4-88 SAMPLES
*
PEAK HEIGHT {E+04}
32.0
30.0
28.0
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
PARTS PER MILLION

Figure 28.

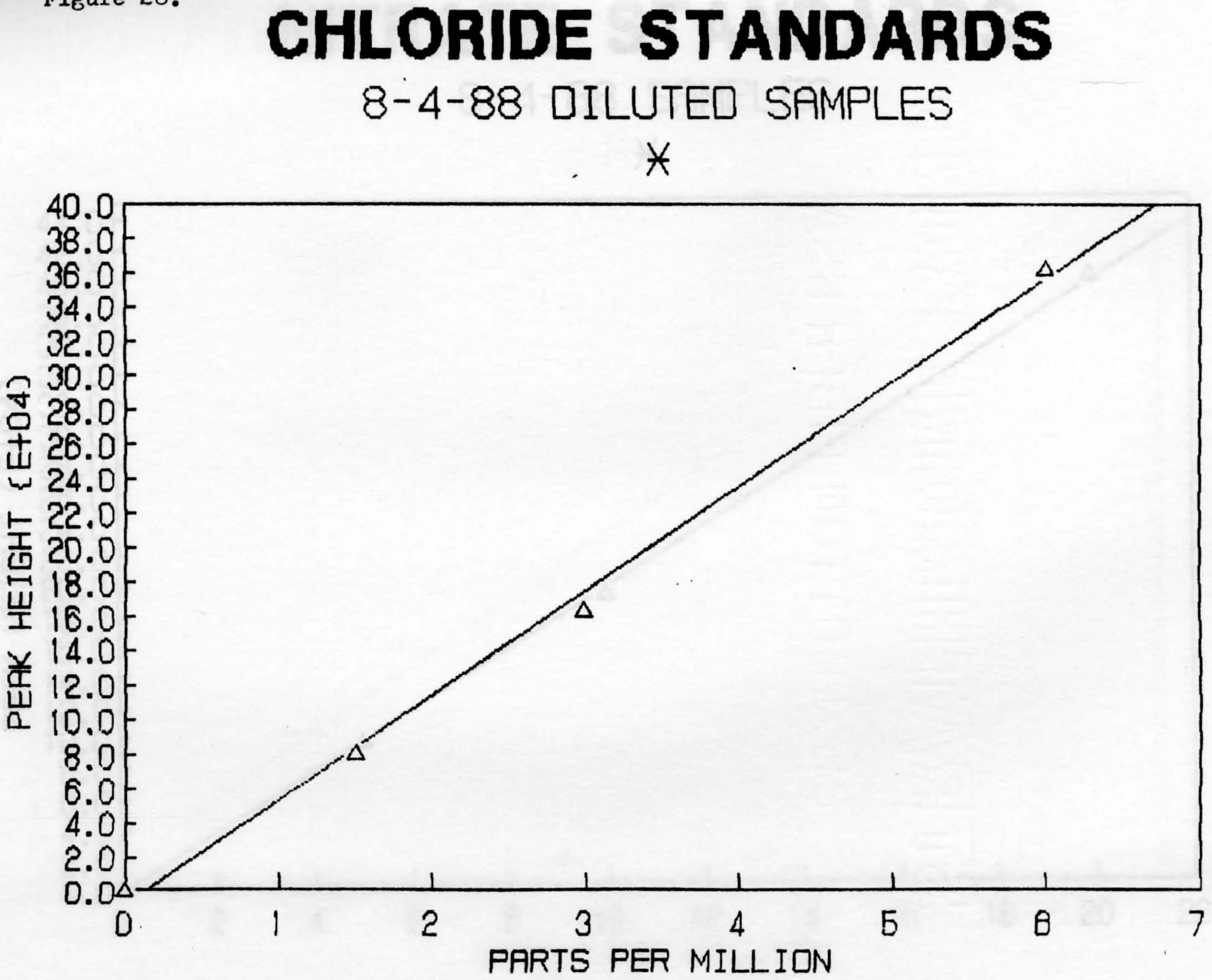

CHLORIDE STANDARDS
8-4-88 DILUTED SAMPLES
PEAK HEIGHT (E+04)
40.0
38.0
36.0
34.0
32.0
30.0
28.0
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
1
2
3
4
5
6
7
PARTS PER MILLION

Figure 29.

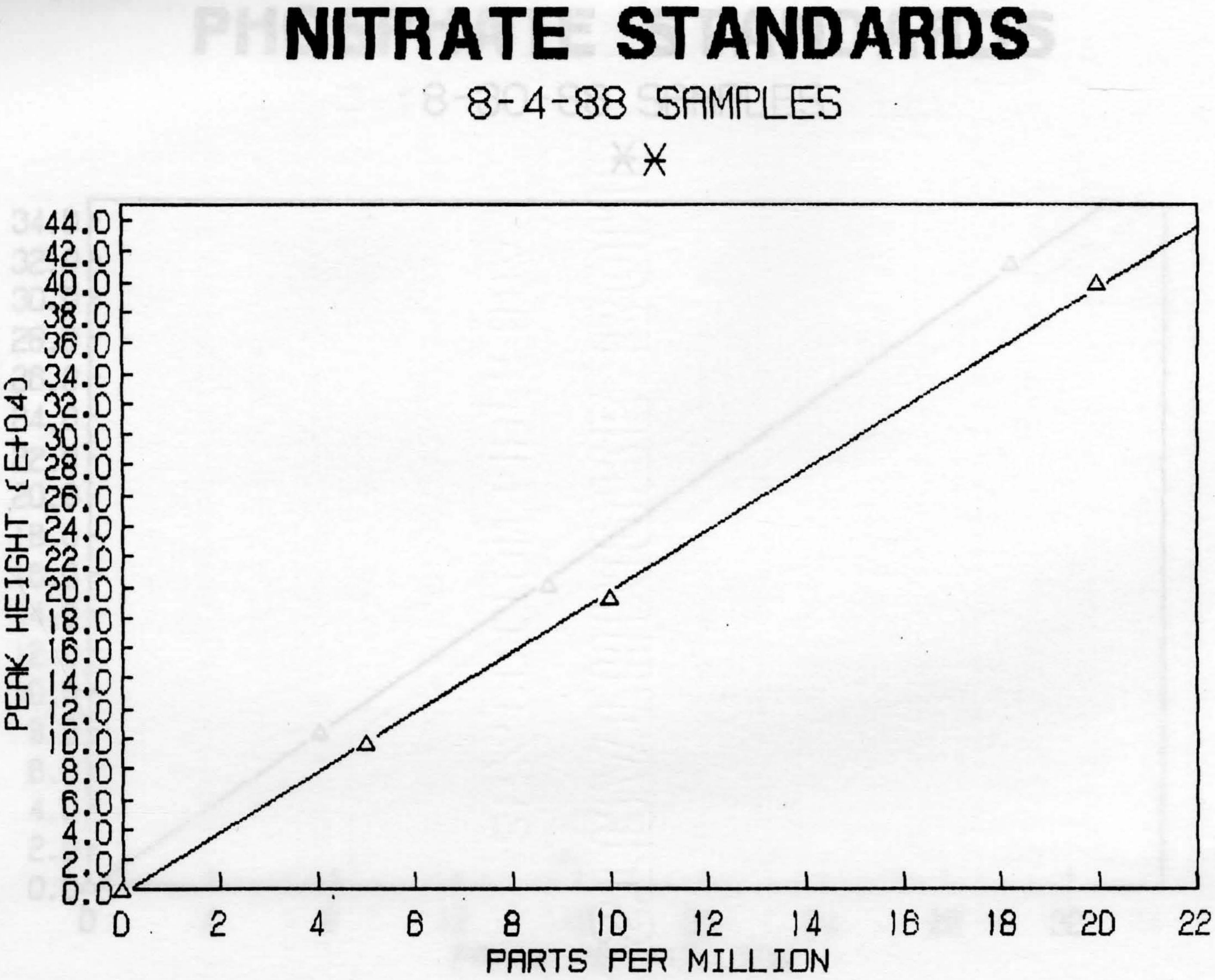

NITRATE STANDARDS
8-4-88 SAMPLES
*
PEAK HEIGHT (E+04)
44.0
42.0
40.0
38.0
36.0
34.0
32.0
30.0
28.0
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
2
4
6
8
10
12
14
16
18
20
22
PARTS PER MILLION

Figure 30.

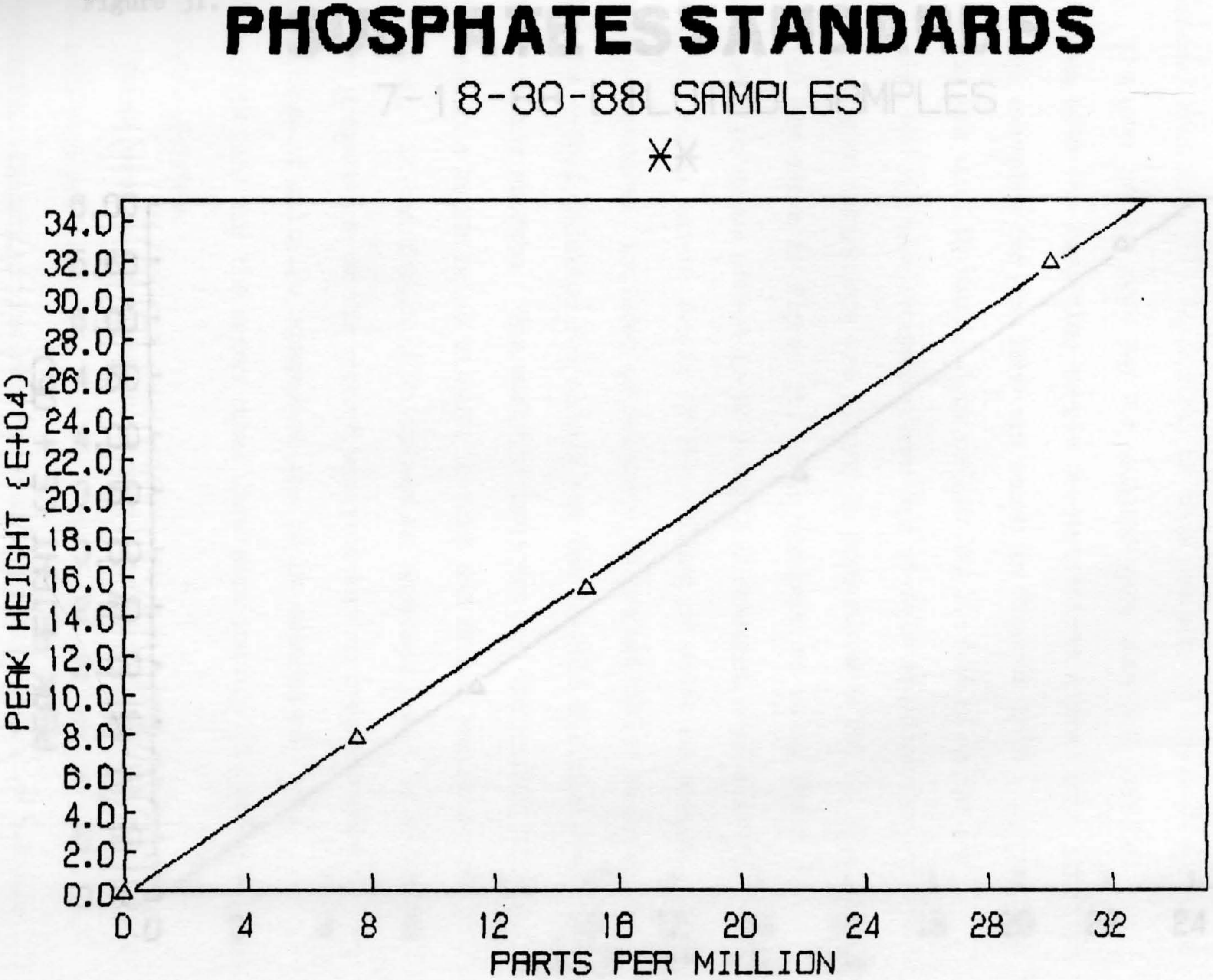
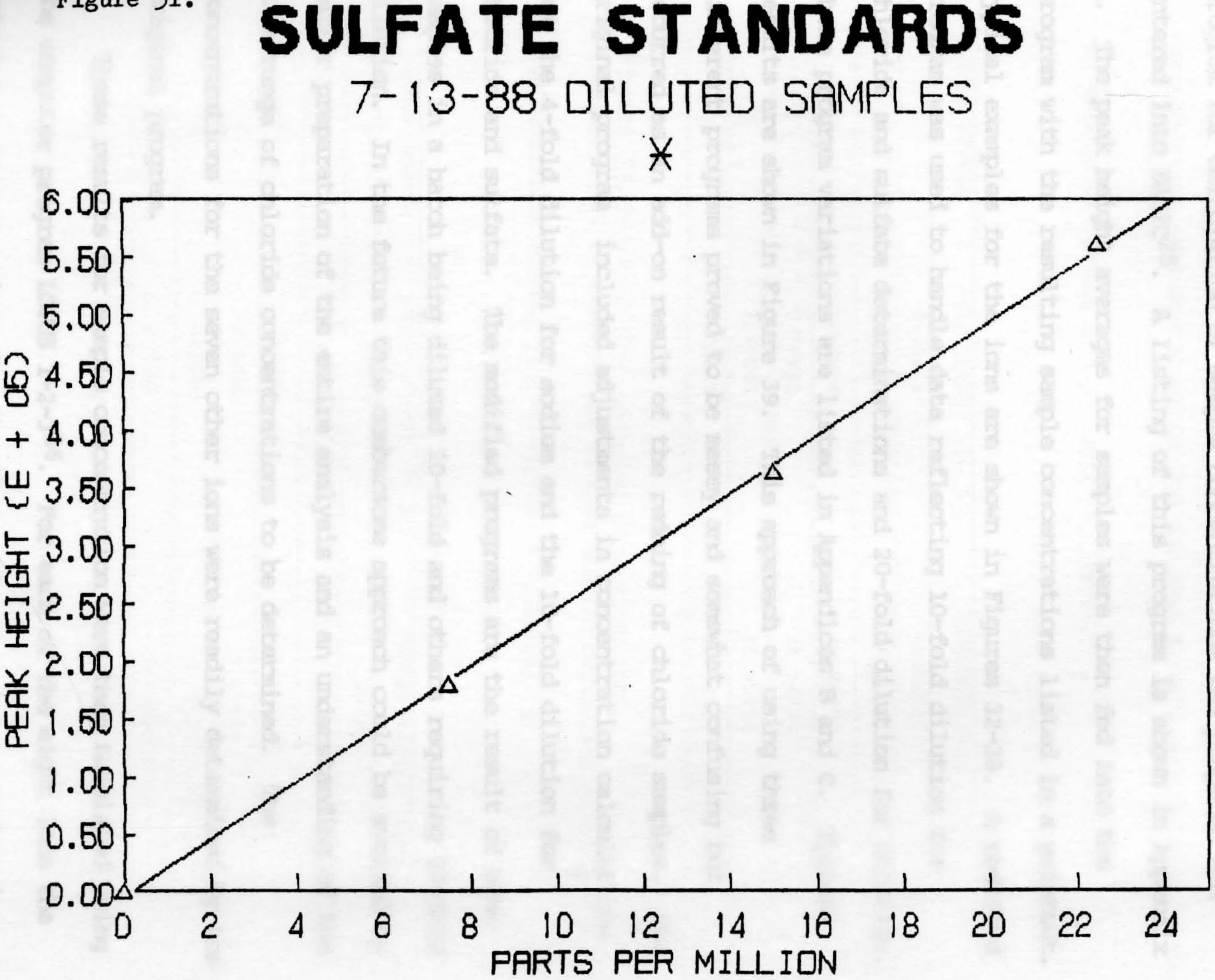

PHOSPHATE STANDARDS
8-30-88 SAMPLES
*
PEAK HEIGHT {E+04}
34.0
32.0
30.0
28.0
26.0
24.0
22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
4
8
12
16
20
24
28
32
PARTS PER MILLION

Figure 31.


SULFATE STANDARDS
7-13-88 DILUTED SAMPLES
*
PEAK HEIGHT (E + 05)
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
2
4
6
8
10
12
14
16
18
20
22
24
PARTS PER MILLION

ENERGRAPHICS program and used in the determination of sample concentration.

For ease and clarity in raw data handling a tailor-made computer program for calculation of sample concentrations was prepared and entered into BASIC[25]. A listing of this program is shown in Appendix A. The peak height averages for samples were then fed into the program with the resulting sample concentrations listed in a printout. Typical examples for the ions are shown in Figures 32-38. A modified program was used to handle data reflecting 10-fold dilution for chloride and sulfate determinations and 20-fold dilution for chloride. These program variations are listed in Appendices B and C. Typical results are shown in Figure 39. This approach of using three different programs proved to be messy and somewhat confusing but occurred as an add-on result of the redoing of chloride samples. The original program included adjustments in concentration calculations for the 4-fold dilution for sodium and the 10-fold dilution for chloride and sulfate. The modified programs are the result of some samples in a batch being diluted 10-fold and others requiring 20-fold dilution. In the future this cumbersome approach could be avoided by better preparation of the entire analysis and an understanding of the wide range of chloride concentrations to be determined. The concentrations for the seven other ions were readily determined by the original program.

These results for sample concentration were then tabulated using the computer program LOTUS 1-2-3[26]. For each of the eight ions the calculated concentrations for the five collection dates at the six sites are shown in Tables 2-9. Collection sites correspond to sample

Figure 32. Printout for Sodium Determinations.

```
CONCENTRATIONS OF SODIUM FOR 9-29-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMPLE DILUTION
BY A FACTOR OF 4

THE REGRESSION FORMULA IS Y =  .0034  +  .2863177  X

__________________________________________________________________
SAMPLE NUMBER          PEAK HEIGHT (E+ 5 )          CONCENTRATION (PPM)
__________________________________________________________________
     1                     3.44418                      48.06941
------------------------------------------------------------------
     2                     3.4062                       47.53881
------------------------------------------------------------------
     3                     2.90986                      40.60469
------------------------------------------------------------------
     4                     2.74818                      38.34594
------------------------------------------------------------------
     5                     2.30992                      32.22323
------------------------------------------------------------------
     6                     2.09177                      29.17557
------------------------------------------------------------------
```

Figure 33. Printout for Ammonium Determinations.

```
CONCENTRATIONS OF AMMONIUM FOR 11-3-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

THE REGRESSION FORMULA IS Y =  .09133  +  .9847285  X

__________________________________________________________________
SAMPLE NUMBER          PEAK HEIGHT  (E+ 4 )          CONCENTRATION (PPM)
__________________________________________________________________
     1                     1.6626                       1.595638
------------------------------------------------------------------
     2                     1.6904                       1.623869
------------------------------------------------------------------
     3                     1.2459                       1.172476
------------------------------------------------------------------
     4                     2.5292                       2.475677
------------------------------------------------------------------
     5                     0.0000                       NO DETECTION
------------------------------------------------------------------
     6                     0.0000                       NO DETECTION
------------------------------------------------------------------
```

Figure 34. Printout for Potassium Determinations.

```
CONCENTRATIONS OF POTASSIUM FOR 9-29-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

THE REGRESSION FORMULA IS Y = -.00383  +  1.389242  X


SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )          CONCENTRATION (PPM)
------------------------------------------------------------------------
     1                      9.6368                       6.939489
------------------------------------------------------------------------
     2                      9.4922                       6.835404
------------------------------------------------------------------------
     3                      8.783                        6.324909
------------------------------------------------------------------------
     4                      8.208                        5.911015
------------------------------------------------------------------------
     5                      6.4939                       4.677176
------------------------------------------------------------------------
     6                      6.165                        4.440429
------------------------------------------------------------------------
```

Figure 35. Printout for Fluoride Determinations.

```
CONCENTRATIONS OF FLUORIDE FOR 7-13-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

THE REGRESSION FORMULA IS Y = -.62558  +  7.590461  X

_____________________________________________________________________
SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )          CONCENTRATION (PPM)
_____________________________________________________________________
      1                    3.695                        .3692118
---------------------------------------------------------------------
      2                    3.9176                       .5985382
---------------------------------------------------------------------
      3                    2.9946                       .4769382
---------------------------------------------------------------------
      4                    2.926                        .4679005
---------------------------------------------------------------------
      5                    1.8451                       .3254981
---------------------------------------------------------------------
      6                    1.6255                       .296567
---------------------------------------------------------------------
```

Figure 36. Printout for Nitrate Determinations.

```
CONCENTRATIONS OF NITRATE FOR 9-29-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

THE REGRESSION FORMULA IS Y = -.14586  +  1.404752  X

_____________________________________________________________________
SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )          CONCENTRATION (PPM)
_____________________________________________________________________
      1                    19.2402                      13.80034
---------------------------------------------------------------------
      2                    16.5564                      11.88983
---------------------------------------------------------------------
      3                    8.5808                       6.212241
---------------------------------------------------------------------
      4                    7.7228                       5.601457
---------------------------------------------------------------------
      5                    2.2226                       1.686034
---------------------------------------------------------------------
      6                    3.165                        2.356899
---------------------------------------------------------------------
```

Figure 37. Printout for Sulfate Determinations.

```
CONCENTRATIONS OF SULFATE FOR 11-3-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMPLE DILUTION
BY A FACTOR OF 10

THE REGRESSION FORMULA IS Y = -.75891  +  1.369832  X


--------------------------------------------------------------------------------
SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )              CONCENTRATION (PPM)
--------------------------------------------------------------------------------
     1                    16.1344                         123.324
--------------------------------------------------------------------------------
     2                    14.6634                         112.5854
--------------------------------------------------------------------------------
     3                    14.2236                         109.3748
--------------------------------------------------------------------------------
     4                    14.4772                         111.2261
--------------------------------------------------------------------------------
     5                    14.3115                         110.0165
--------------------------------------------------------------------------------
     6                    12.3496                         95.69428
```

Figure 38. Printout for Phosphate Determinations.

```
CONCENTRATIONS OF PHOSPHATE FOR 9-29-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

THE REGRESSION FORMULA IS Y =  .042  +  .7155695  X


--------------------------------------------------------------------------------
SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )              CONCENTRATION (PPM)
--------------------------------------------------------------------------------
     1                    1.7497                          2.386491
--------------------------------------------------------------------------------
     2                    1.3842                          1.875709
--------------------------------------------------------------------------------
     3                    .3931                           .4906582
--------------------------------------------------------------------------------
     4                    .3339                           .4079269
--------------------------------------------------------------------------------
     5                    .034                          NO DETECTION
--------------------------------------------------------------------------------
     6                    .0246                         NO DETECTION
--------------------------------------------------------------------------------
```

Figure 39. Printouts for Chloride Determinations.

```
CONCENTRATIONS OF CHLORIDE FOR 8-4-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMPLE DILUTION
BY A FACTOR OF 20 (INDICATED BY *) OR 10

THE REGRESSION FORMULA IS Y = -.785  +  6.066868  X


____________________________________________________________________
SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )          CONCENTRATION (PPM)
____________________________________________________________________
      1  *
-------------------------------------------------------------------
      2  *
-------------------------------------------------------------------
      3  *
-------------------------------------------------------------------
      4  *
-------------------------------------------------------------------
      5                   29.4286                      49.80099
-------------------------------------------------------------------
      6                   28.2732                      47.89655
-------------------------------------------------------------------
```

```
CONCENTRATIONS OF CHLORIDE FOR 8-4-88 SAMPLES DETERMINED BY ION CHROMATOGRAPHY

CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMPLE DILUTION
BY A FACTOR OF 20 (INDICATED BY *) OR 10

THE REGRESSION FORMULA IS Y = -.785  +  6.066868  X


____________________________________________________________________
SAMPLE NUMBER          PEAK HEIGHT (E+ 4 )          CONCENTRATION (PPM)
____________________________________________________________________
      1  *                13.7025                      59.96975
-------------------------------------------------------------------
      2  *                13.8925                      60.75762
-------------------------------------------------------------------
      3  *                13.2691                      58.17258
-------------------------------------------------------------------
      4  *                13.3348                      58.44501
-------------------------------------------------------------------
      5                   29.4286                      49.80099
-------------------------------------------------------------------
      6                   28.2732                      47.89655
-------------------------------------------------------------------
```

Table 2.

SODIUM CONCENTRATIONS IN PPM

SITE	SAMPLE DATE 7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	44.35	46.00	38.35	48.07	57.78	46.91	6.33
BRIDGE STREET, STRUTHERS	42.44	44.68	40.49	47.54	58.16	46.66	6.21
CEDAR STREET, YOUNGSTOWN	35.19	40.62	37.61	40.60	51.28	41.06	5.50
McKINLEY STREET, McDONALD	36.74	38.49	36.18	38.35	46.39	39.23	3.69
MAIN AVENUE, WARREN	34.70	30.10	33.17	32.22	37.42	33.52	2.45
LEAVITT ROAD, LEAVITTSBURG	27.86	28.63	31.24	29.18	33.53	30.09	2.05

Table 3.

AMMONIUM CONCENTRATION IN PPM

SITE	SAMPLE DATE 7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	0.814	1.061	0.714	0.002	1.596	0.837	0.517
BRIDGE STREET, STRUTHERS	0.992	1.248	0.790	N.D.	1.624	0.931	0.542
CEDAR STREET, YOUNGSTOWN	0.647	0.888	0.527	N.D.	1.172	0.647	0.392
McKINLEY STREET, McDONALD	0.907	0.167	0.621	0.617	2.476	0.957	0.795
MAIN AVENUE, WARREN	N.D.	N.D.	N.D.	N.D.	N.D.	0.000	0.000
LEAVITT ROAD, LEAVITTSBURG	0.292	0.184	0.144	N.D.	N.D.	0.124	0.112

Table 4.

POTASSIUM CONCENTRATIONS IN PPM

SITE			SAMPLE DATE				
	7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	6.66	7.90	5.30	6.94	7.82	6.92	0.94
BRIDGE STREET, STRUTHERS	6.49	7.57	5.35	6.84	8.34	6.92	1.01
CEDAR STREET, YOUNGSTOWN	5.67	8.35	5.53	6.32	7.30	6.64	1.06
McKINLEY STREET, McDONALD	5.55	7.78	5.20	5.91	7.65	6.42	1.08
MAIN AVENUE, WARREN	5.01	5.10	4.55	4.68	5.31	4.93	0.28
LEAVITT ROAD, LEAVITTSBURG	4.40	4.84	4.09	4.44	5.07	4.57	0.34

Table 5.

FLUORIDE CONCENTRATIONS IN PPM

SITE	SAMPLE DATE 7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	0.569	0.561	0.467	0.587	0.761	0.589	0.096
BRIDGE STREET, STRUTHERS	0.599	0.542	0.481	0.552	0.792	0.593	0.106
CEDAR STREET, YOUNGSTOWN	0.477	0.487	0.415	0.520	0.698	0.519	0.095
McKINLEY STREET, McDONALD	0.468	0.432	0.412	0.472	0.679	0.493	0.096
MAIN AVENUE, WARREN	0.325	0.281	0.324	0.344	0.457	0.346	0.059
LEAVITT ROAD, LEAVITTSBURG	0.297	0.270	0.304	0.319	0.447	0.327	0.062

Table 6.

CHLORIDE CONCENTRATION IN PPM

	SAMPLE DATE						
SITE	7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	63.24	59.97	58.64	62.98	83.83	65.73	9.22
BRIDGE STREET, STRUTHERS	60.45	60.76	53.17	60.99	81.01	63.28	9.34
CEDAR STREET, YOUNGSTOWN	52.93	58.17	59.99	61.98	83.79	63.37	10.64
McKINLEY STREET, McDONALD	56.09	58.45	50.00	61.11	71.47	59.42	7.05
MAIN AVENUE, WARREN	57.10	49.80	50.73	51.12	53.20	52.39	2.61
LEAVITT ROAD, LEAVITTSBURG	46.98	47.90	44.72	47.66	47.19	46.89	1.13

Table 7.

NITRATE CONCENTRATIONS IN PPM

SITE	SAMPLE DATE 7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	10.64	9.92	8.59	13.80	15.80	11.75	2.65
BRIDGE STREET, STRUTHERS	9.88	8.74	7.87	11.89	16.10	10.90	2.93
CEDAR STREET, YOUNGSTOWN	6.47	6.96	5.04	6.21	6.95	6.33	0.70
McKINLEY STREET, McDONALD	5.35	4.82	3.96	5.60	4.61	4.87	0.58
MAIN AVENUE, WARREN	5.73	2.95	2.23	1.69	1.79	2.87	1.49
LEAVITT ROAD, LEAVITTSBURG	2.68	1.89	2.37	2.36	2.17	2.29	0.26

Table 8.

SITE	PHOSPHATE CONC. (PPM) SAMPLE DATE 7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	STD
LOWELLVILLE BRIDGE, WASHINGTON AVE	1.57	1.95	N.D.	2.39	2.10	1.60	0.84
BRIDGE STREET, STRUTHERS	1.25	1.46	N.D.	1.88	1.90	1.30	0.69
CEDAR STREET, YOUNGSTOWN	0.55	0.11	0.29	0.49	1.00	0.49	0.30
McKINLEY STREET, McDONALD	0.52	0.08	N.D.	0.41	1.11	0.42	0.40
MAIN AVE., WARREN	N.D.	N.D.	N.D.	N.D.	N.D.	0.00	0.00
LEAVITT ROAD, LEAVITTSBURG	N.D.	N.D.	N.D.	N.D.	N.D.	0.00	0.00

Table 9.

SULFATE CONC. (PPM)
SAMPLE DATE

SITE	7-13-88	8-4-88	8-30-88	9-29-88	11-3-88	MEAN	STD
LOWELLVILLE BRIDGE, WASHINGTON AVE.	94.27	102.94	81.96	110.94	123.32	102.69	14.10
BRIDGE STREET, STRUTHERS	106.15	93.26	89.42	98.89	112.59	100.06	8.42
CEDAR STREET, YOUNGSTOWN	88.32	86.42	91.74	92.95	109.37	93.76	8.15
McKINLEY STREET, McDONALD	79.75	83.59	97.96	87.85	111.23	92.08	11.34
MAIN AVE., WARREN	79.77	81.53	87.59	85.70	110.02	88.92	10.91
LEAVITT ROAD, LEAVITTSBURG	75.59	77.19	84.73	77.31	95.69	82.10	7.50

numbers from the data sheets in order, for example, Lowellville Bridge, Washington Ave. is the site for sample # 1 as Leavitt Road, Leavittsburg is the site of sample # 6. The mean and standard deviation of the five dates for each site are also shown and were calculated with the LOTUS program. For the ion profiles new tables were prepared using the concentration means and standard deviations with the river miles for each site. These results are shown in Tables 10-17. The number of river miles is the distance from the collection site to the mouth of the Mahoning River which is where it meets the Shenango River. Thus, the further upstream the site, the greater the river miles. The river mile figures were determined by Dean Morgan in the YSU Biology Dept.

The SIGMAPLOT computer graphics program[27] was used to prepare graphs of river miles versus ion concentration for each of the eight ions. The source of data for the plots is from Tables 10-17 where files were created to transfer from the LOTUS to the SIGMAPLOT program. These ion profile graphs are shown in Figures 40-47. In addition to data collected in the project, data from previous Mahoning River analyses were studied for comparison. These concentration readings were compiled by the Ohio Environmental Protection Agency from 1963-1988 with the sources and methods of analysis unknown[28]. However, because of the long span of data collection (26 years) a comparison of ion concentrations would seem to be of value. Chloride, as stated, is a good indicator of industrial pollution and was chosen as the focus of the comparisons. First Street in Lowellville was chosen as the site for analysis because it is one of the more polluted regions of the river and chloride concentrations will be in a high

Table 10.

SITE	RIVER MILES	SODIUM CONCENTRATIONS IN PPM MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	14.0	46.91	6.33
BRIDGE STREET, STRUTHERS	17.8	46.66	6.21
CEDAR STREET, YOUNGSTOWN	21.6	41.06	5.50
McKINLEY STREET, McDONALD	31.1	39.23	3.69
MAIN AVENUE, WARREN	39.3	33.52	2.45
LEAVITT ROAD, LEAVITTSBURG	47.4	30.09	2.05

Table 11.

SITE	RIVER MILES	AMMONIUM CONCENTRATIONS IN PPM MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	14.0	0.837	0.517
BRIDGE STREET, STRUTHERS	17.8	0.931	0.542
CEDAR STREET, YOUNGSTOWN	21.6	0.647	0.392
McKINLEY STREET, McDONALD	31.1	0.957	0.795
MAIN AVENUE, WARREN	39.3	0.000	0.000
LEAVITT ROAD, LEAVITTSBURG	47.4	0.124	0.112

Table 12.

SITE	RIVER MILES	POTASSIUM CONCENTRATIONS IN PPM MEAN	S.D.
WASHINGTON AVE.	14.0	6.92	0.94
BRIDGE STREET, STRUTHERS	17.8	6.92	1.01
CEDAR STREET, YOUNGSTOWN	21.6	6.64	1.06
McKINLEY STREET, McDONALD	31.1	6.42	1.08
MAIN AVENUE, WARREN	39.3	4.93	0.28
LEAVITT ROAD, LEAVITTSBURG	47.4	4.57	0.34

Table 13.

SITE	RIVER MILES	FLUORIDE CONCENTRATIONS IN PPM MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	14.0	0.589	0.096
BRIDGE STREET, STRUTHERS	17.8	0.593	0.106
CEDAR STREET, YOUNGSTOWN	21.6	0.519	0.095
McKINLEY STREET, McDONALD	31.1	0.493	0.096
MAIN AVENUE, WARREN	39.3	0.346	0.059
LEAVITT ROAD, LEAVITTSBURG	47.4	0.327	0.062

Table 14.

SITE	RIVER MILES	NITRATE CONCENTRATIONS IN PPM MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	14.0	11.75	2.65
BRIDGE STREET, STRUTHERS	17.8	10.90	2.93
CEDAR STREET, YOUNGSTOWN	21.6	6.33	0.70
McKINLEY STREET, McDONALD	31.1	4.87	0.58
MAIN AVENUE, WARREN	39.3	2.87	1.49
LEAVITT ROAD, LEAVITTSBURG	47.4	2.29	0.26

Table 15.

SITE	RIVER MILES	CHLORIDE CONCENTRATIONS IN PPM MEAN	S.D.
LOWELLVILLE BRIDGE, WASHINGTON AVE.	14.0	65.73	9.22
BRIDGE STREET, STRUTHERS	17.8	63.28	9.34
CEDAR STREET, YOUNGSTOWN	21.6	63.37	10.64
McKINLEY STREET, McDONALD	31.1	59.42	7.05
MAIN AVENUE, WARREN	39.3	52.39	2.61
LEAVITT ROAD, LEAVITTSBURG	47.4	46.89	1.13

Table 16.

SITE	RIVER MILES	SULFATE CONC. (PPM) MEAN	STD
LOWELLVILLE BRIDGE, WASHINGTON AVE.	14.0	102.7	14.1
BRIDGE STREET, STRUTHERS	17.8	100.1	8.4
CEDAR STREET, YOUNGSTOWN	21.6	93.8	8.1
McKINLEY STREET, McDONALD	31.1	92.1	11.3
MAIN AVE., WARREN	39.3	88.9	10.9
LEAVITT ROAD, LEAVITTSBURG	47.4	82.1	7.5

Table 17.

SITE	RIVER MILES	PHOSPHATE CONC. (PPM) MEAN	STD
LOWELLVILLE BRIDGE, WASHINGTON AVE	14.0	1.6	0.8
BRIDGE STREET, STRUTHERS	17.8	1.3	0.7
CEDAR STREET, YOUNGSTOWN	21.6	0.5	0.3
McKINLEY STREET, McDONALD	31.1	0.4	0.4
MAIN AVE., WARREN	39.3	0.0	0.0
LEAVITT ROAD, LEAVITTSBURG	47.4	0.0	0.0

Figure 40.

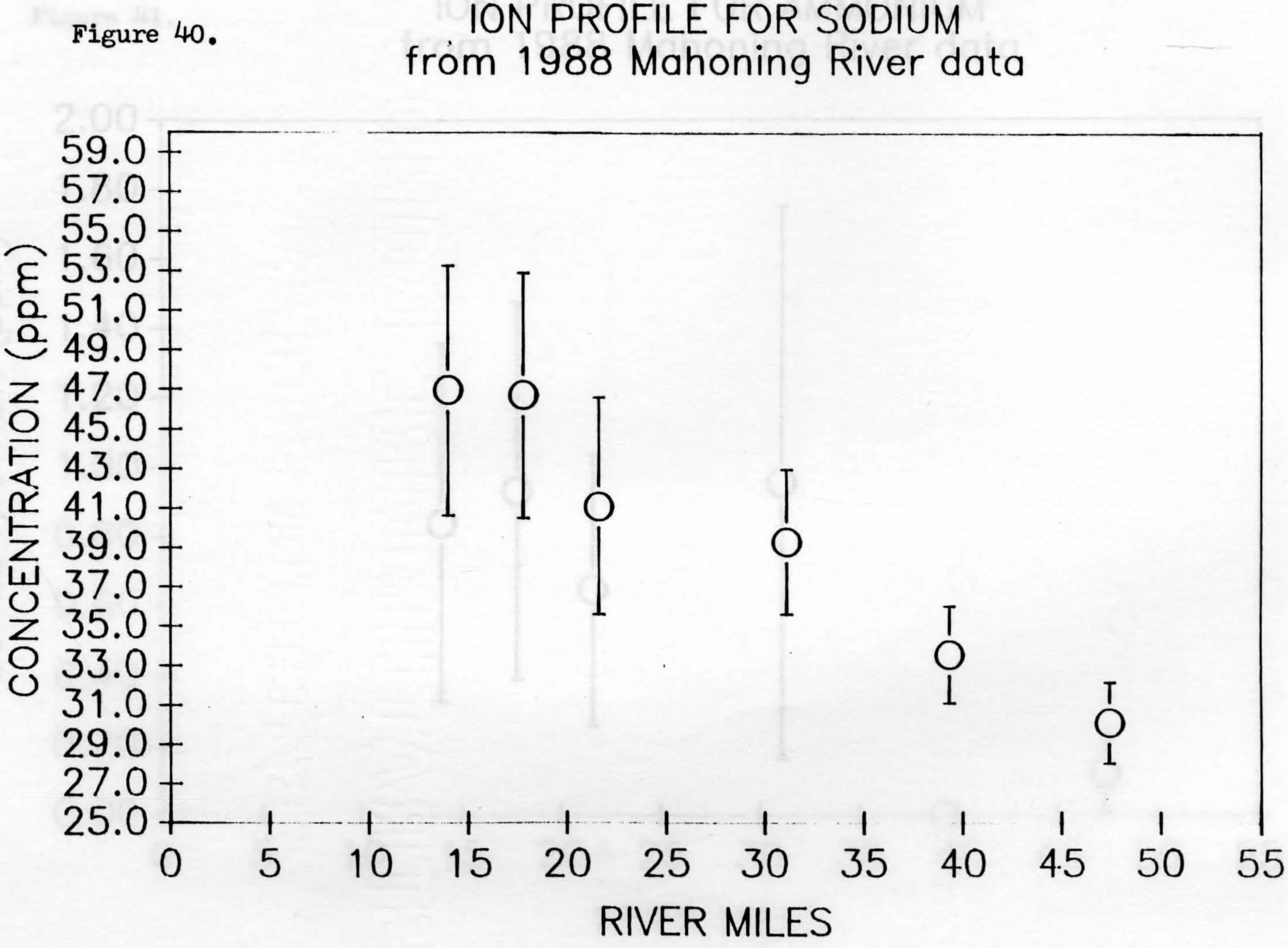
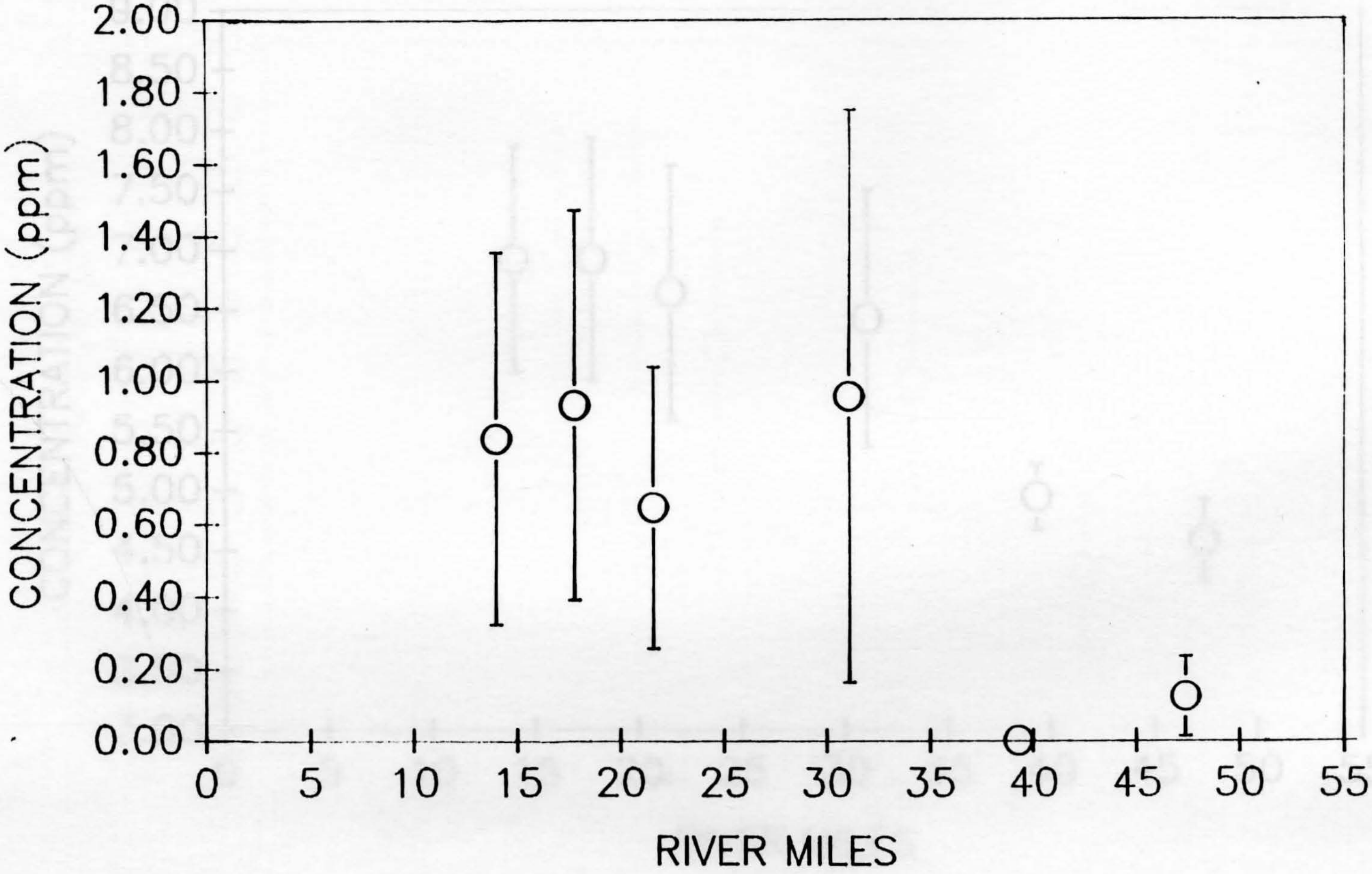
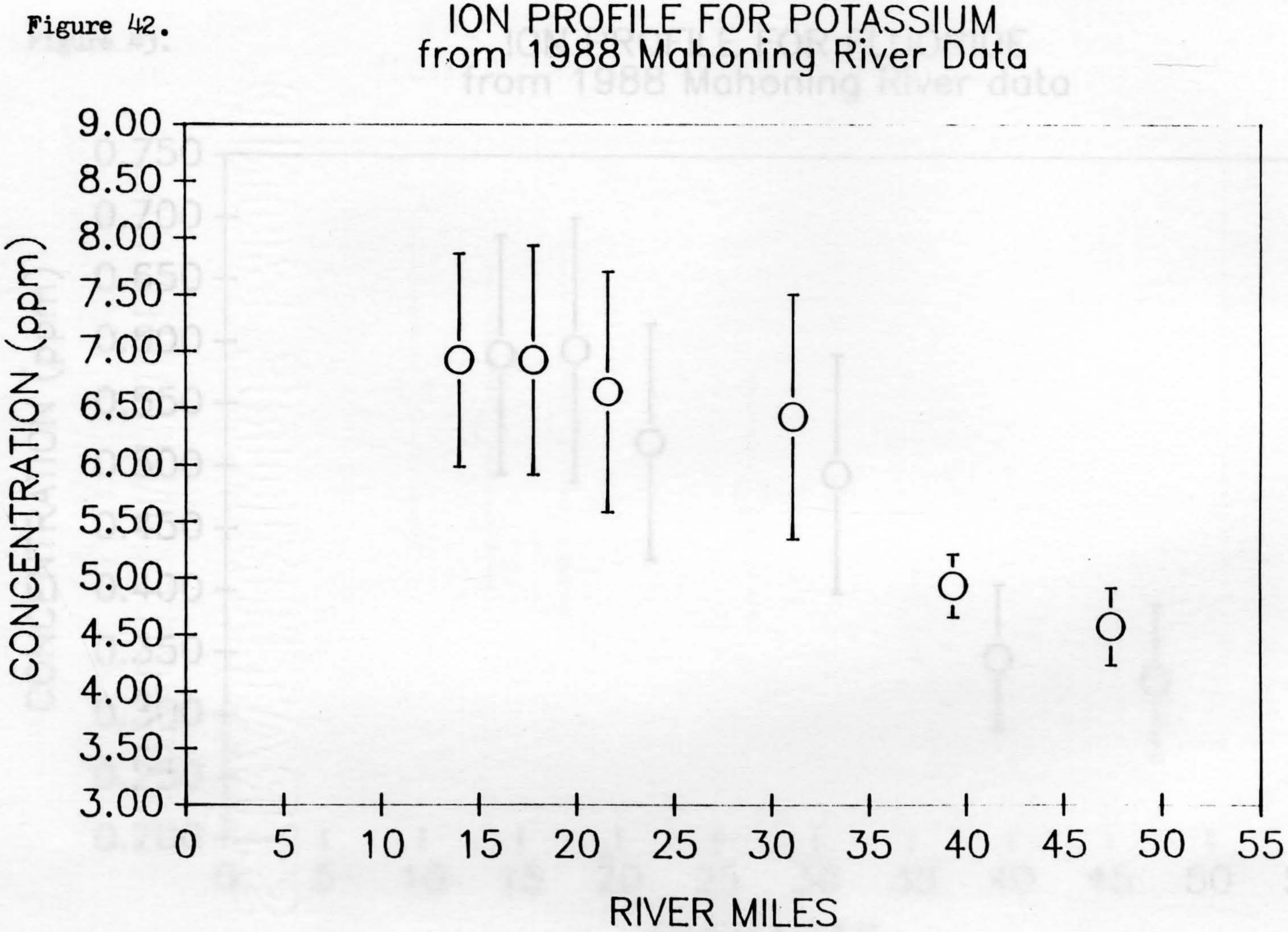

ION PROFILE FOR SODIUM
from 1988 Mahoning River data
CONCENTRATION (ppm)
59.0
57.0
55.0
53.0
51.0
49.0
47.0
45.0
43.0
41.0
39.0
37.0
35.0
33.0
31.0
29.0
27.0
25.0
0
5
10
15
20
25
30
35
40
45
50
55
RIVER MILES

Figure 41.



ION PROFILE FOR AMMONIUM
from 1988 Mahoning River data

Figure 42.


ION PROFILE FOR POTASSIUM
from 1988 Mahoning River Data
CONCENTRATION (ppm)
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
0
5
10
15
20
25
30
35
40
45
50
55
RIVER MILES

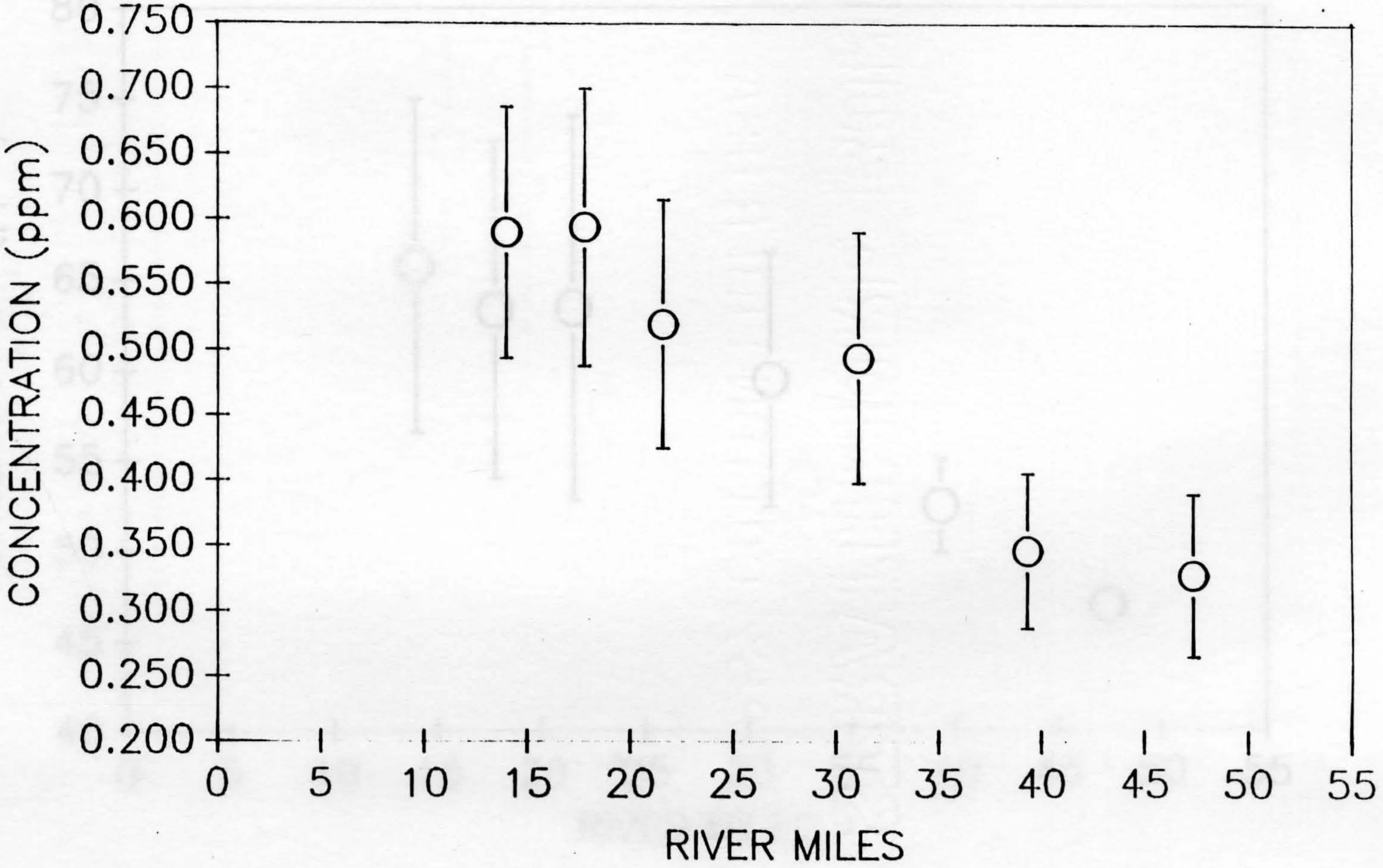


Figure 43. ION PROFILE FOR FLUORIDE from 1988 Mahoning River data

Figure 44.

ION PROFILE FOR CHLORIDE
from 1988 Mahoning River data

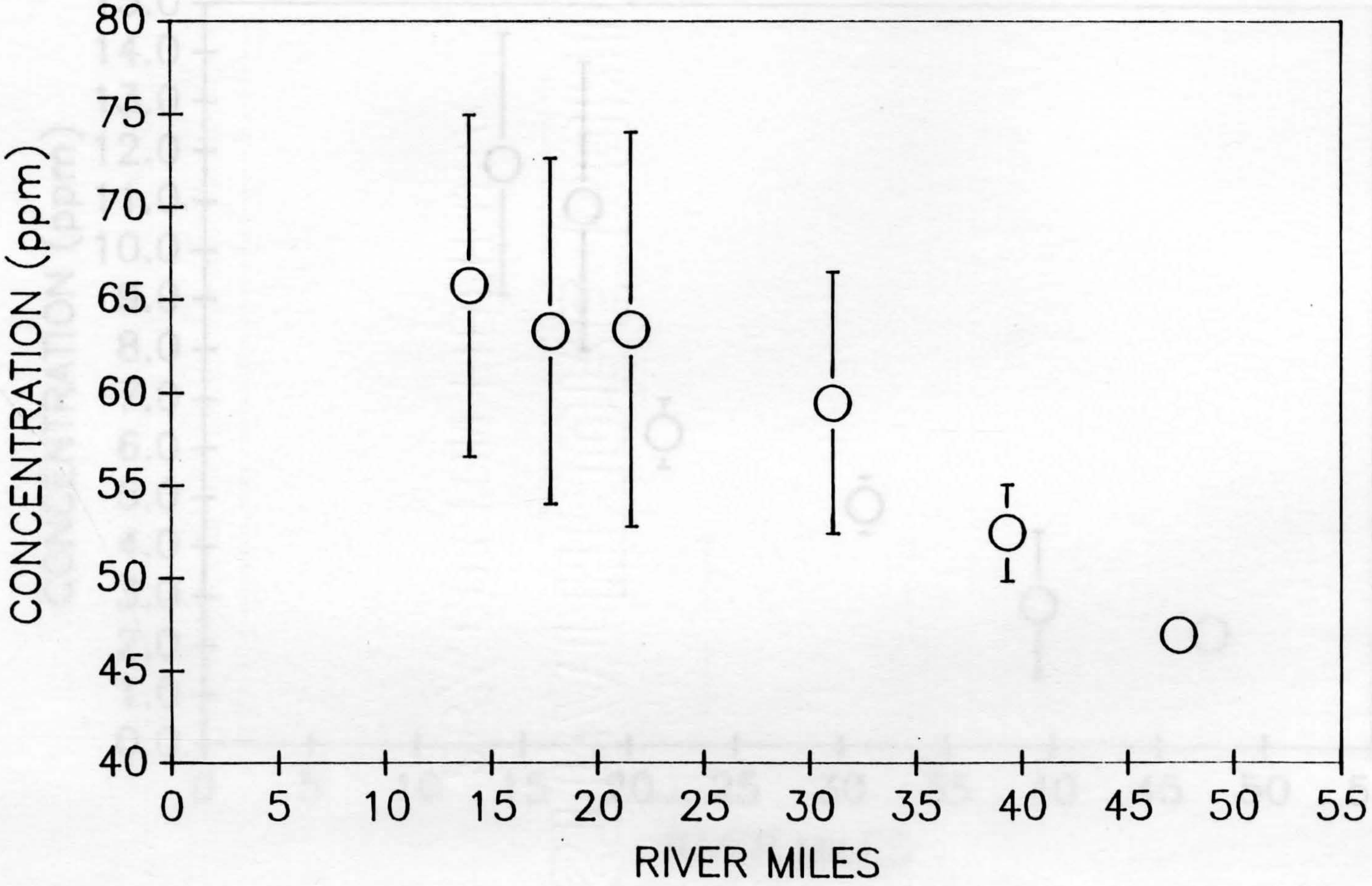


Figure 45.

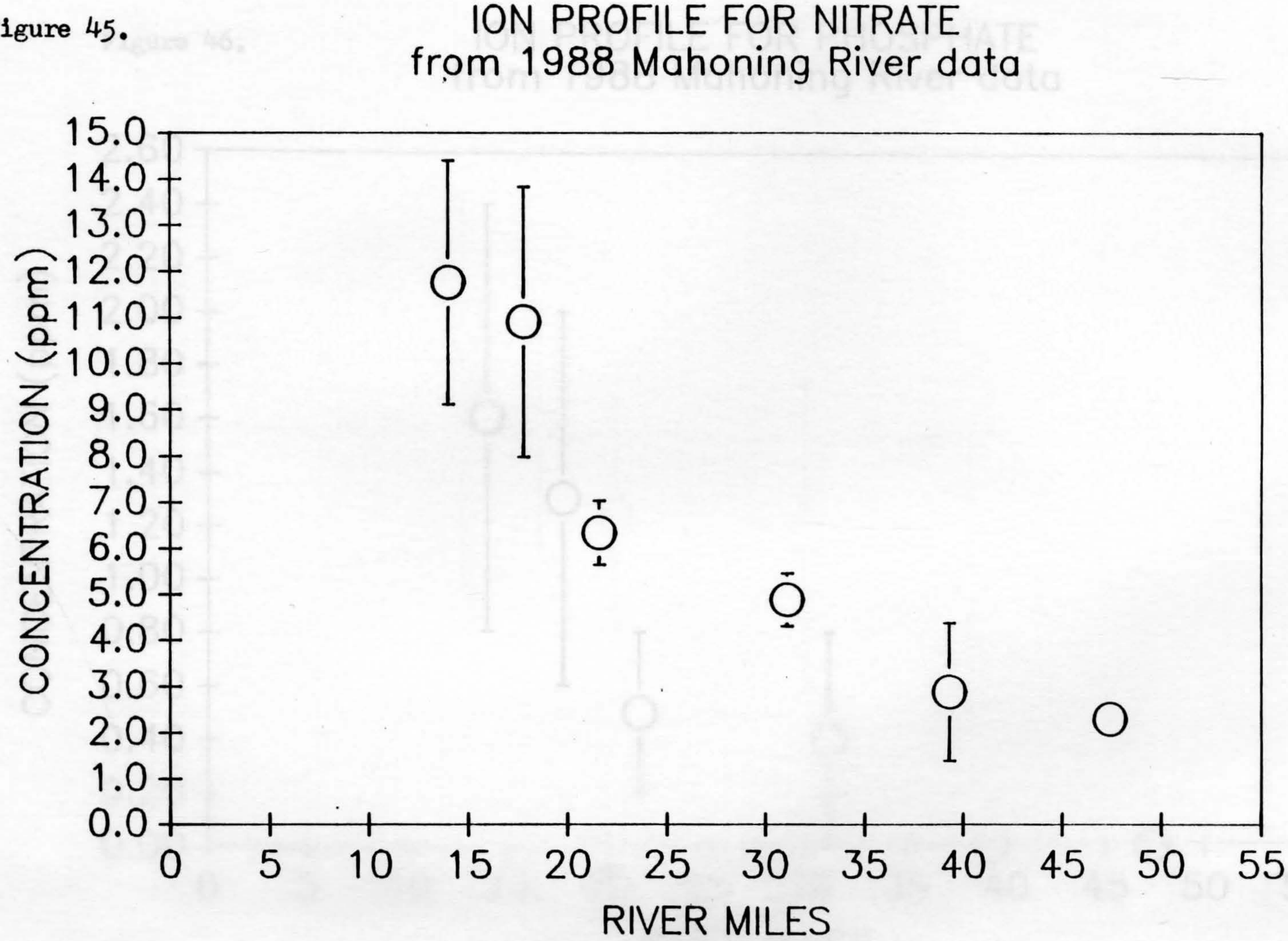

ION PROFILE FOR NITRATE
from 1988 Mahoning River data
CONCENTRATION (ppm)
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
5
10
15
20
25
30
35
40
45
50
55
RIVER MILES

Figure 46.

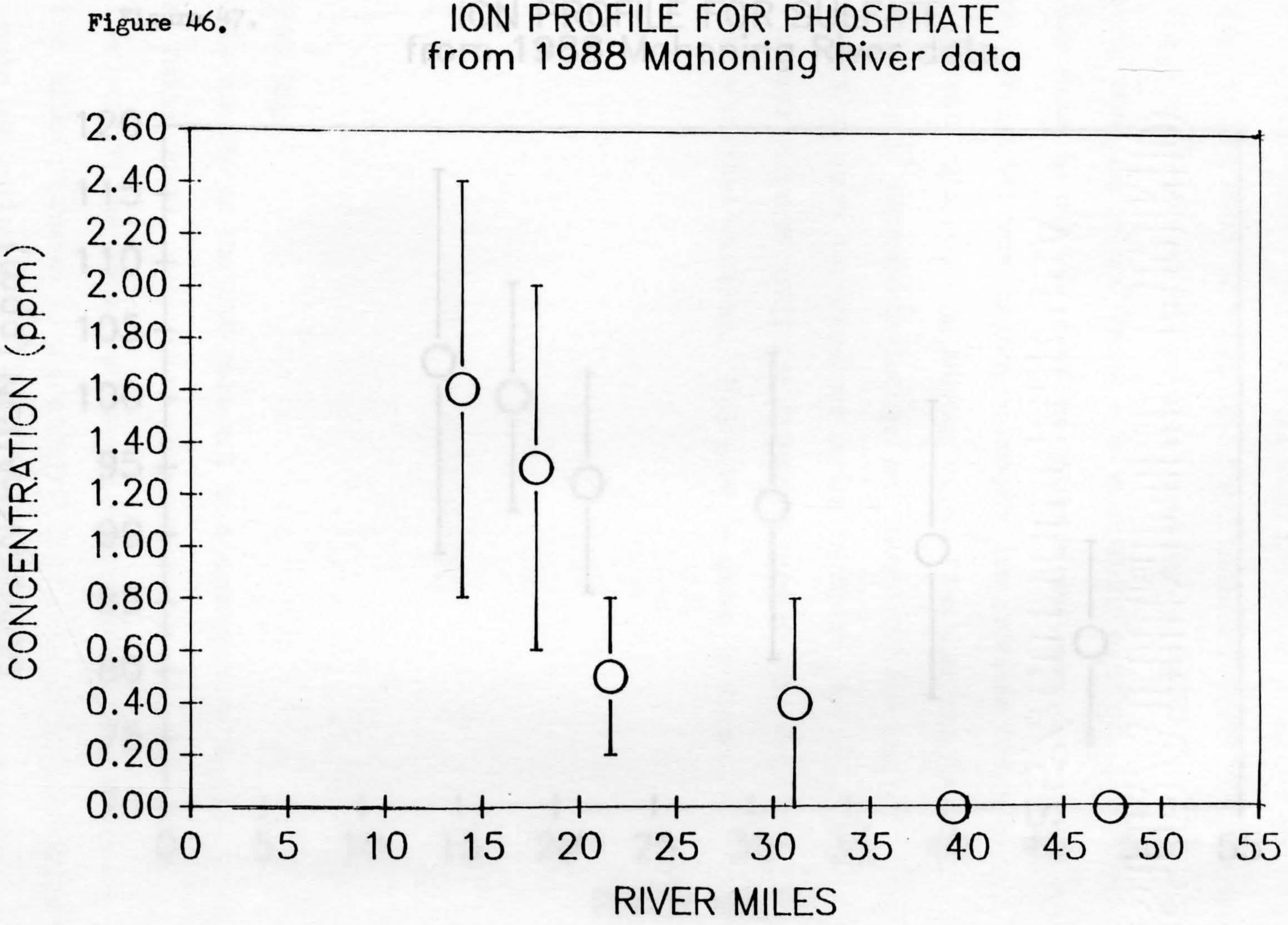
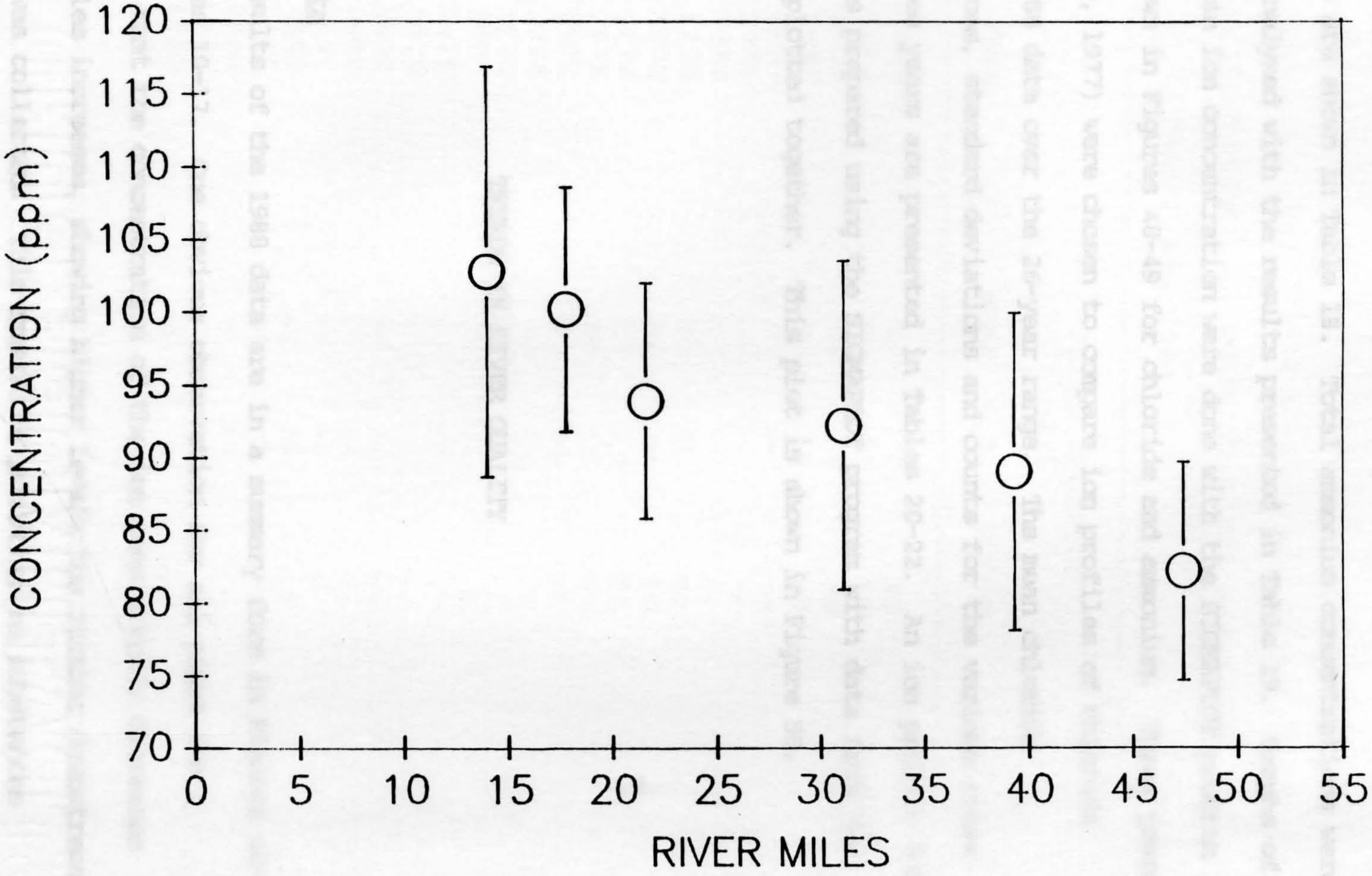

ION PROFILE FOR PHOSPHATE
from 1988 Mahoning River data
CONCENTRATION (ppm)
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
5
10
15
20
25
30
35
40
45
50
55
RIVER MILES

Figure 47.



ION PROFILE FOR SULFATE
from 1988 Mahoning River data

range. Total chloride concentrations for each year where at least four collections occurred were averaged with the mean and standard deviation calculated. These results with the count or number of collections are shown in Table 18. Total ammonium concentrations were similarly analyzed with the results presented in Table 19. Graphs of year vs. mean ion concentration were done with the SIGMAPLOT program and are shown in Figures 48-49 for chloride and ammonium. Three years (1965, 1970, 1977) were chosen to compare ion profiles of chloride with the 1988 data over the 26-year range. The mean chloride concentrations, standard deviations and counts for the various sites for the three years are presented in Tables 20-22. An ion profile for chloride was prepared using the SIGMAPLOT program with data from the four years plotted together. This plot is shown in Figure 50.

TRENDS IN RIVER QUALITY

The 1988 Data

The results of the 1988 data are in a summary form in Figures 40-47 and Tables 10-17. One obvious observation for all eight ion profiles is that the concentration of the ion consistently decreases as river miles increases, showing higher levels the farther downstream the sample was collected. This result is predicted as substances entering a river will travel downstream with the flow until deposition

Table 18. SUMMARY OF MAHONING RIVER EPA DATA
SITE: LOWELLVILLE- FIRST STREET
YEAR: 1963-1988

	TOTAL CHLORIDE (MG/L)		
YEAR	MEAN	S.D.	COUNT
1963	53	20	49
1964	60	21	50
1965	58	13	50
1966	63	24	33
1967	--	--	--
1968	--	--	--
1969	--	--	--
1970	63	25	20
1971	63	50	46
1972	80	24	51
1973	88	16	29
1974	50	24	20
1975	48	11	9
1976	57	13	12
1977	70	33	9
1978	--	--	--
1979	--	--	--
1980	--	--	--
1981	--	--	--
1982	--	--	--
1983	42	10	7
1984	48	7	9
1985	--	--	--
1986	42	8	4
1987	--	--	--
1988	66	9	5

Table 19. SUMMARY OF MAHONING RIVER EPA DATA
SITE: LOWELLVILLE- FIRST STREET
YEAR: 1970-1988

	TOTAL AMMONIUM (MG/L)		
YEAR	MEAN	S.D.	COUNT
1970	2.06	0.43	19
1971	2.05	0.61	49
1972	2.12	0.50	51
1973	1.70	0.46	26
1974	2.73	1.65	23
1975	2.16	1.22	9
1976	2.81	1.07	12
1977	2.56	2.08	11
1978	2.35	1.37	11
1979	1.83	1.09	12
1980	2.33	1.97	15
1981	2.10	1.53	10
1982	2.60	1.23	9
1983	1.33	1.18	12
1984	1.00	0.35	10
1985	1.59	1.11	12
1986	1.05	0.70	12
1987	1.37	0.71	5
1988	0.84	0.52	5

Figure 48. Summary of Mahoning River EPA Data
Site: Lowellville– First St.
TOTAL AMMONIUM

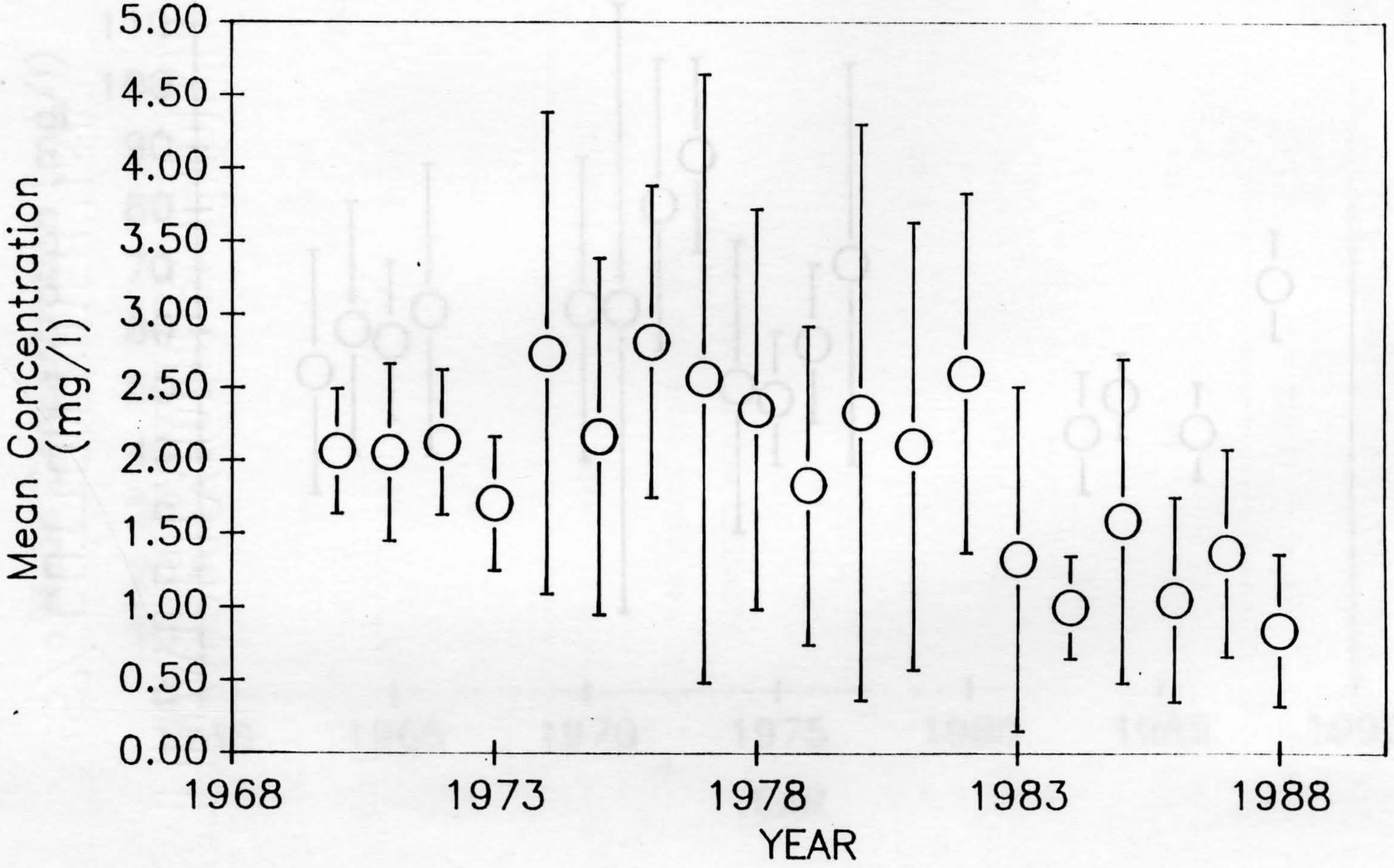


Figure 49.

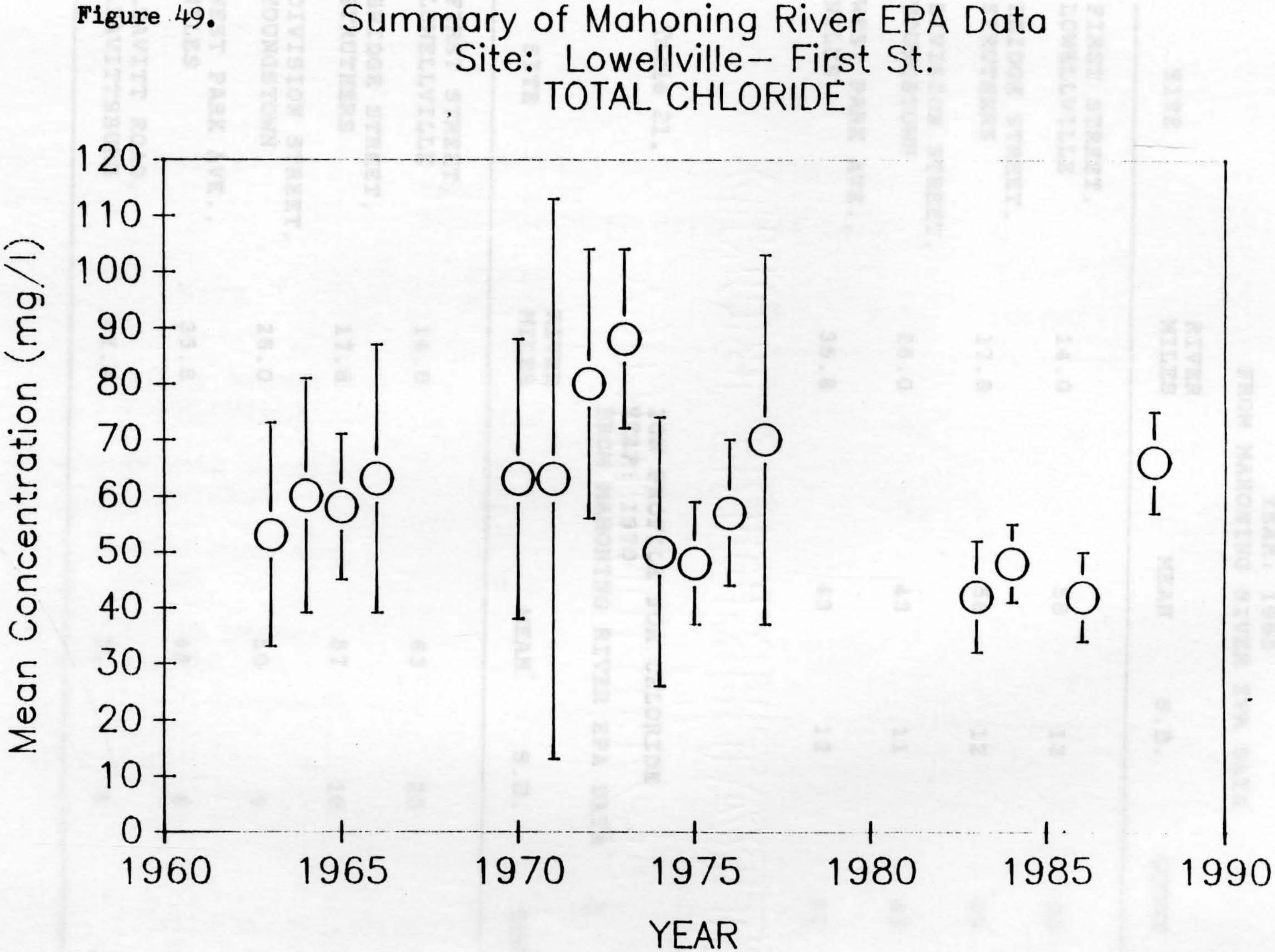

Summary of Mahoning River EPA Data
Site: Lowellville– First St.
TOTAL CHLORIDE
Mean Concentration (mg/l)
0
10
20
30
40
50
60
70
80
90
100
110
120
1960
1965
1970
1975
1980
1985
1990
YEAR

Table 20.

ION PROFILE FOR CHLORIDE
YEAR: 1965
FROM MAHONING RIVER EPA DATA

SITE	RIVER MILES	MEAN	S.D.	COUNT
FIRST STREET, LOWELLVILLE	14.0	58	13	50
BRIDGE STREET, STRUTHERS	17.8	58	12	49
DIVISION STREET, YOUNGSTOWN	26.0	43	11	47
WEST PARK AVE., NILES	35.8	43	12	51

Table 21.

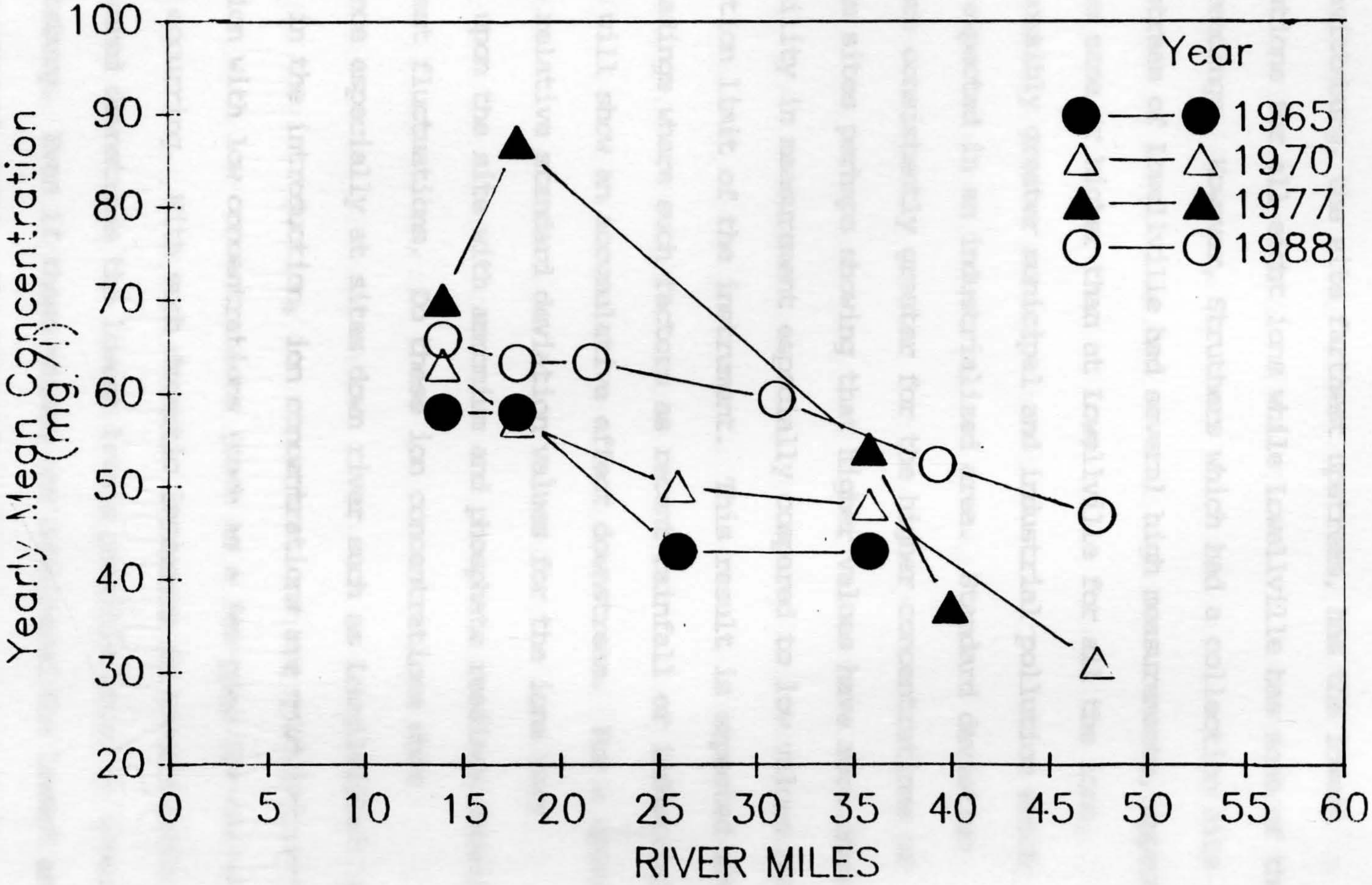
ION PROFILE FOR CHLORIDE
YEAR: 1970
FROM MAHONING RIVER EPA DATA

SITE	RIVER MILES	MEAN	S.D.	COUNT
FIRST STREET, LOWELLVILLE	14.0	63	25	20
BRIDGE STREET, STRUTHERS	17.8	57	10	19
DIVISION STREET, YOUNGSTOWN	26.0	50	9	19
WEST PARK AVE., NILES	35.8	48	5	19
LEAVITT ROAD, LEAVITTSBURG	47.4	31	8	19

Table 22. ION PROFILE FOR CHLORIDE
YEAR: 1977
FROM MAHONING RIVER EPA DATA

SITE	RIVER MILES	MEAN	S.D.	COUNT
FIRST STREET, LOWELLVILLE	14.0	70	33	9
BRIDGE STREET, STRUTHERS	17.8	87	32	5
WEST PARK AVE., NILES	35.8	54	10	7
SOUTH STREET, WARREN	39.9	37	7	7

Figure 50. CHLORIDE PROFILE FOR THE YEARS 1965,1970,1977,1988 from Mahoning River EPA data



or evaporation occurs. The repeated pattern for all the ions demonstrates that whatever is dumped in a river will affect a downstream area more. This result has been confirmed in previous studies^{2}. Thus, Leavittsburg, the site farthest upstream, has the lowest concentrations for all eight ions while Lowellville has some of the highest readings. However, Struthers which had a collection site 3.8 miles upstream of Lowellville had several high measurements, approximately the same or higher than at Lowellville for all the ions, showing possibly greater municipal and industrial pollution which would be expected in an industrialized area. Standard deviation values were consistently greater for the higher concentrations of downstream sites perhaps showing that higher values have more chance of variability in measurement especially compared to low values near the detection limit of the instrument. This result is expected with higher readings where such factors as recent rainfall or industrial discharge will show an accumulative effect downstream. For a specific site, the relative standard deviation values for the ions vary depending upon the site with ammonium and phosphate readings showing the greatest fluctuations. Do these ion concentrations show significance especially at sites down river such as Lowellville? As mentioned in the introduction, ion concentrations are good indicators of pollution with low concentrations (such as a few ppms for chloride) naturally occurring. With such dramatic increases in concentration being measured downstream the lowest levels possible would be observed at Leavittsburg. Even if these values are considered the lowest and indicating natural causes, the tremendous increases at other sites show human-made effects of pollution.

Tables 2-9 show ion concentrations for the five sample dates. The concentrations are consistently higher for the six sites for the 11-3-88 collection date. 1988 was an unusual year for rainfall in this region, as in most of the United States, in that an extensive drought occurred through the summer months. With less rainfall, water levels in the Mahoning River would be lower with higher ion concentrations expected. The high 11-3-88 readings as compared to the other values could indicate the effects of the drought which would be evident after the summer months. However, sudden increases from month to month could show a pollution plug which was "caught" during a sampling. If an industry makes a large discharge of waste or by-products into the river this plug will travel downstream eventually dissipating, but if detected would show unusually high ion concentrations. Since the readings for all eight ions are high for the November sampling, a drought effect is suspected; industries will be discharging only what is used in the processing -- massive amounts of chloride ion, but not all eight ions, would be expected of industries using acid wash processes. The sulfate concentrations in Table 9 show the highest values for all the ions. Sulfur naturally occurs in high concentrations in the Mahoning Valley region and is present in the river as the sulfate ion after oxidation but again the consistent downstream increase of concentration shown in Figure 47 suggests an industrial source where sulfuric acid is being used. For species such as fluoride and phosphate, caution should be used in interpretation of data in that some values ($<$ 1ppm) are near the detection limit and variations between sample dates may not show significance.

The 1988 data indicates some sources of pollution from industrial and municipal causes. Sodium, chloride, and sulfate levels were high and as mentioned, the sources of these ions are readily seen in the Mahoning Valley region. However, potassium, fluoride and phosphate levels were low with the phosphate values showing the most significance in perhaps a lessening of domestic pollution which was of public concern a few years ago.

Composite Analysis

The 1988 data is probably best analyzed with previous data from the Mahoning River. Tables 18 and 19 and Figures 48-50 present data obtained from the 1988 project assimilated with older data summarized by the EPA for the Mahoning River. Table 18 which contains chloride concentrations for the Lowellville site and Table 19 which similarly shows ammonium concentrations demonstrate the tremendous variation in sampling size since 1963 with counts ranging from 51 to 4. Variation also occurs as to when samples were collected, whether in the higher rainfall season, in the spring, or in the drier months. The 1988 samples were collected mostly in the summer months and during the unusual condition of a drought. Despite these differences interpretation of the data is still of interest. As shown in Figure 48, chloride concentration reached peak in the early 1970s with lower levels recorded in the 1980s. The 1988 concentration which is higher then the other 1980s values might be due to the drought which would increase all ion concentrations. Lower chloride levels in the ’80s could be a reflection of less industrial activity after many factories along the river were economically devastated and forced to shut down in the late 1970s. The standard deviations for the peak years are much greater, especially for 1971 with a S.D. equal to 50 ppm, than for later years. This pattern is perhaps due to the greater variation of higher levels in a fluctuating rainfall region such as the Mahoning Valley. Also, improved instrumentation or more accurate procedures can account for this trend. An important observation is, however, that all the mean values are much greater than chloride concentrations in unpolluted fresh waters which as stated are a few ppm. The concentration means range from 42 to 88 ppm showing that even after the decline of the major industries in the Mahoning Valley, the chloride levels are still abnormally high.

Similarly, ammonium concentration, collected from the years 1970 to 1988, show the highest readings in the mid-1970s when the Mahoning Valley community was thriving. As with the chloride concentrations, the standard deviations show tremendous variation in values especially in 1977. Ammonium concentration, as mentioned, is a good indicator of municipal waste. Sewage that has not been properly treated before the flow reenters the river will contribute to high ammonium values. With the building of a new sewage treatment plant in Youngstown in 1988 which can more effectively remove nitrogen from the inflowing water, the low NH_4^+ level for the 1988 reading perhaps indicates this efficiency especially when the value is expected to be higher in a drought year.

Tables 15 and 20-22 show chloride concentrations for different sites for various years. The years, 1965, 1970, 1977 and 1988 present a range for the 26 years with 1977 showing peak industrial activity and 1988 representing the post-industrial era. Unfortunately, data from the mid 1980s was insufficient for analysis. Figure 50 shows a composite of the four ion profiles where similar patterns can be seen. For all four years, the downstream (fewer river miles)-higher concentration trend can be easily discerned. For the peak year, 1977, chloride levels at Lowellville and especially Struthers were the highest showing the tremendous discharges from the industry in Youngstown. As compared to the upstream sites in Niles and Warren, the values show a dramatic increase. The 1988 readings show a leveling-off effect as the chloride concentrations are high but the differences between upstream and downstream sites is not as great. Interestingly, the 1988 values are not the lowest; the 1970 readings indicate less chloride contamination. As observed before, all of the values are well above the chloride concentrations of natural waters.

EVALUATION OF IC SYSTEM

The first impression when studying the various tables and figures that have been presented is that there is a tremendous amount of data to handle. Besides calibration curves for each ion for each run date, data sheets, calculations of ion concentrations, graphs and tables are prepared. With the simultaneous determination of several cations or anions, organization is crucial in the successful handling of the data. At this point the computer becomes the most significant element of the analysis. Since the ion chromatography system is so general in analysis with the capability to allow determinations of a wide range of ions, the burden of specific testing falls on the analyst who should readily transfer as much of this tedious work to the computer as possible. The process used in this project was helped immensely by the data-acquisition computer with a chromatography program and the personal computer but could be improved upon for more efficient analysis and less human error.

The ion chromatography system was reliable in the analysis as shown in the repeated linearity of the calibration curves (Figures 24-31). Except for the column accident, which was quickly diagnosed, and the changing of regenerants (TMAOH to TBAOH) the procedure was routine. Even with the faster columns which allowed run times as short as 2.5 min, the standard and sample peaks on the chromatograms showed consistently good resolution. With this solid basis, the system can only be improved upon with more computer interaction and innovative ideas from the analyst allowing modification of the set-up for the unique requirements of the analysis.

Thus, the ion chromatography system should be a method of choice for analyses that involve repetitive determinations of various ions. In environmental research this scenario is often the case. The EPA and other organizations which set the standards for procedures in testing water will hopefully soon take advantage of the tremendous diversity and speed this system has to offer.

Appendix A: Original BASIC program for the calculation of ion concentrations.

```
100 REM THIS PROGRAM DETERMINES CONCENTRATIONS IN PPM OF SAMPLES USING THE REGR
      ESSION FORMULA OF THE STANDARD CURVE
105 PRINT "PLEASE ENTER THE NAME OF THE ION"
106 INPUT I$
107 PRINT "PLEASE ENTER THE DATE OF THE SAMPLES"
108 INPUT D$
110 PRINT "PLEASE ENTER THE NUMBER OF SAMPLES"
120 INPUT N
130 PRINT "PLEASE ENTER THE Y INTERCEPT"
140 INPUT B
150 PRINT "PLEASE ENTER THE SLOPE VALUES"
160 INPUT R,S
170 M=R/S
175 PRINT "PLEASE ENTER THE EXPONENT FOR PEAK HEIGHT"
176 INPUT P
177 LPRINT "CONCENTRATIONS OF "I$" FOR "D$" SAMPLES DETERMINED BY ION CHROMATOGR
APHY
178 LPRINT CHR$(10)
179 IF I$= "CHLORIDE"  GOTO 340
180 IF I$= "SULFATE" GOTO 340
181 IF I$="SODIUM" GOTO 331
182 LPRINT "THE REGRESSION FORMULA IS Y = " B " + " M " X"
183 LPRINT CHR$(10)
186 LPRINT CHR$(10)
190 LPRINT "____________________________________________________________________"

200 LPRINT "SAMPLE NUMBER       PEAK HEIGHT (E+"P")       CONCENTRATION (PPM)"
210 LPRINT "____________________________________________________________________"

230 FOR J= 1 TO N
240 PRINT "PLEASE ENTER THE PEAK HEIGHT FOR SAMPLE NUMBER " J
250 INPUT H
251 IF H=0! GOTO 320
252 IF H<B GOTO 297
255 IF I$= "CHLORIDE" GOTO 360
256 IF I$="SULFATE" GOTO 360
257 IF I$="SODIUM" GOTO 375
260 C = (H - B)/ M
270 LPRINT "      "J TAB(22) H TAB(48) C
288 LPRINT "--------------------------------------------------------------------"

290 NEXT J
291 LPRINT CHR$(10)
292 LPRINT CHR$(10)
293 LPRINT CHR$(10)
295 END
297 IF I$= "CHLORIDE" GOTO 360
298 IF I$="SULFATE" GOTO 360
299 IF I$="SODIUM" GOTO 375
300 LPRINT "      "J TAB(22) H TAB(48) "NO DETECTION"
310 GOTO 288
320 LPRINT "      "J"               0.0000                        NO DETECTION"
330 GOTO 288
331 LPRINT "CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMP
LE DILUTION BY A FACTOR OF 4"
332 LPRINT CHR$(10)
335 GOTO 182
340 LPRINT "CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMP
LE DILUTION BY A FACTOR OF 10"
345 LPRINT CHR$(10)
350 GOTO 182
360 C= 10*(H-B)/M
370 GOTO 270
375 C= 4*(H-B)/M
376 GOTO 270
```

Appendix B: Modified BASIC program for the calculation of ion concentrations with 10 and 20 X dilution of samples.

```
100 REM THIS PROGRAM DETERMINES CONCENTRATIONS IN PPM OF SAMPLES USING THE REGR
      ESSION FORMULA OF THE STANDARD CURVE
105 PRINT "PLEASE ENTER THE NAME OF THE ION"
106 INPUT I$
107 PRINT "PLEASE ENTER THE DATE OF THE SAMPLES"
108 INPUT D$
110 PRINT "PLEASE ENTER THE NUMBER OF SAMPLES"
120 INPUT N
130 PRINT "PLEASE ENTER THE Y INTERCEPT"
140 INPUT B
150 PRINT "PLEASE ENTER THE SLOPE VALUES"
160 INPUT R,S
170 M=R/S
175 PRINT "PLEASE ENTER THE EXPONENT FOR PEAK HEIGHT"
176 INPUT P
177 LPRINT "CONCENTRATIONS OF "I$" FOR "D$" SAMPLES DETERMINED BY ION CHROMATOGR
APHY
178 LPRINT CHR$(10)
179 IF I$= "CHLORIDE"  GOTO 340
180 IF I$= "SULFATE" GOTO 340
181 IF I$="SODIUM" GOTO 331
182 LPRINT "THE REGRESSION FORMULA IS Y = " B " + " M " X"
183 LPRINT CHR$(10)
186 LPRINT CHR$(10)
190 LPRINT "____________________________________________________________________"

200 LPRINT "SAMPLE NUMBER        PEAK HEIGHT (E+"P")         CONCENTRATION (PPM)"
210 LPRINT "____________________________________________________________________"

230 FOR J= 1 TO N
240 PRINT "PLEASE ENTER THE PEAK HEIGHT FOR SAMPLE NUMBER " J
250 INPUT H
251 IF H=0! GOTO 320
252 IF H<B GOTO 297
253 IF H=1 GOTO 380
255 IF I$= "CHLORIDE" GOTO 360
256 IF I$="SULFATE" GOTO 360
257 IF I$="SODIUM" GOTO 375
260 C = (H - B)/ M
270 LPRINT "      "J TAB(22) H TAB(48) C
288 LPRINT "--------------------------------------------------------------------"

290 NEXT J
291 LPRINT CHR$(10)
292 LPRINT CHR$(10)
293 LPRINT CHR$(10)
295 END
297 IF I$= "CHLORIDE" GOTO 360
298 IF I$="SULFATE" GOTO 360
299 IF I$="SODIUM" GOTO 375
300 LPRINT "      "J TAB(22) H TAB(48) "NO DETECTION"
310 GOTO 288
320 LPRINT "      "J"            0.0000                      NO DETECTION"
330 GOTO 288
331 LPRINT "CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMP
LE DILUTION BY A FACTOR OF 4"
332 LPRINT CHR$(10)
335 GOTO 182
340 LPRINT "CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMP
LE DILUTION BY A FACTOR OF 20 (INDICATED BY *) OR 10"
345 LPRINT CHR$(10)
350 GOTO 182
360 C= 10*(H-B)/M
370 GOTO 270
375 C= 4*(H-B)/M
376 GOTO 270
380 LPRINT "      "J" *"
382 LPRINT "-------------------------------------------------------------------"
383 GOTO 290
```

Appendix C: Modified BASIC program for the calculation of ion concentrations with 20 X dilution of samples.

```
100 REM THIS PROGRAM DETERMINES CONCENTRATIONS IN PPM OF SAMPLES USING THE REGR
     ESSION FORMULA OF THE STANDARD CURVE
105 PRINT "PLEASE ENTER THE NAME OF THE ION"
106 INPUT I$
107 PRINT "PLEASE ENTER THE DATE OF THE SAMPLES"
108 INPUT D$
110 PRINT "PLEASE ENTER THE NUMBER OF SAMPLES"
120 INPUT N
130 PRINT "PLEASE ENTER THE Y INTERCEPT"
140 INPUT B
150 PRINT "PLEASE ENTER THE SLOPE VALUES"
160 INPUT R,S
170 M=R/S
175 PRINT "PLEASE ENTER THE EXPONENT FOR PEAK HEIGHT"
176 INPUT P
177 LPRINT "CONCENTRATIONS OF "I$" FOR "D$" SAMPLES DETERMINED BY ION CHROMATOGR
APHY
178 LPRINT CHR$(10)
179 IF I$= "CHLORIDE" GOTO 340
180 IF I$= "SULFATE" GOTO 340
181 IF I$="SODIUM" GOTO 331
182 LPRINT "THE REGRESSION FORMULA IS Y = " B " + " M " X"
183 LPRINT CHR$(10)
186 LPRINT CHR$(10)
190 LPRINT "_______________________________________________________________________"

200 LPRINT "SAMPLE NUMBER        PEAK HEIGHT (E+"P")        CONCENTRATION (PPM)"
210 LPRINT "_______________________________________________________________________"

230 FOR J= 1 TO N
240 PRINT "PLEASE ENTER THE PEAK HEIGHT FOR SAMPLE NUMBER " J
250 INPUT H
251 IF H=0! GOTO 320
252 IF H<B GOTO 297
255 IF I$= "CHLORIDE" GOTO 360
256 IF I$="SULFATE" GOTO 360
257 IF I$="SODIUM" GOTO 375
260 C = (H - B)/ M
270 LPRINT "     "J TAB(22) H TAB(48) C
288 LPRINT "-----------------------------------------------------------------------"

290 NEXT J
291 LPRINT CHR$(10)
292 LPRINT CHR$(10)
293 LPRINT CHR$(10)
295 END
297 IF I$= "CHLORIDE" GOTO 360
298 IF I$="SULFATE" GOTO 360
299 IF I$="SODIUM" GOTO 375
300 LPRINT "     "J TAB(22) H TAB(48) "NO DETECTION"
310 GOTO 288
320 LPRINT "     "J"              0.0000                  NO DETECTION"
330 GOTO 288
331 LPRINT "CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMP
LE DILUTION BY A FACTOR OF 4"
332 LPRINT CHR$(10)
335 GOTO 182
340 LPRINT "CONCENTRATIONS HAVE BEEN CORRECTED FOR AND PEAK HEIGHTS REFLECT SAMP
LE DILUTION BY A FACTOR OF 20"
345 LPRINT CHR$(10)
350 GOTO 182
360 C= 20*(H-B)/M
370 GOTO 270
375 C= 4*(H-B)/M
376 GOTO 270
```

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