

AUTOMATED DATA ACQUISITION FOR ANALYSIS OF FLY ASH BY  
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

A THESIS

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Dedicated to  
my mother, Kathleen Dowds

## TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	v
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
ABSTRACT.....	viii
INTRODUCTION.....	2
CHAPTER I. CHISMAN CREEK FLY ASH DISPOSAL SITE.....	10
CHAPTER II. EXPERIMENTAL METHODS.....	17
CHAPTER III. ANALYTICAL METHODS.....	26
CHAPTER IV. RESULTS AND DISCUSSION.....	52
CHAPTER V. SUMMARY AND CONCLUSIONS.....	88
APPENDIX A .....	90
APPENDIX B .....	98
BIBLIOGRAPHY .....	123

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## LIST OF TABLES

Table	Page
1. Average U.S. coal composition by location .....	7
2. Progressive trace element enrichment in a coal-fired power plant .....	8
3. Comparison of element levels in saturation extracts of Mojave fly ash and 68 California soils .....	9
4. Characteristics of pH 3, pH 5, and pH 8 buffers .....	24
5. Trace element analysis results generated by PDP-11 computer .....	48
6. Portion of PE 380 run sheet illustrating vanadium analysis conditions .....	49
7. Equations derived for absorbance calculations .....	50
8. Voltages measured at sample and hold amplifiers in the PE 380 system with corresponding computed absorbances .....	51
9. Concentration of elements in 5N nitric acid leachates of Site 1 and Site 2 fly ash .....	87
A-1. Calculations performed during data acquisition .....	93
B-1. Functions available from post acquisition processing programs .....	102
B-2. Equations for non-linear regression and corrected solution concentration .....	103

## LIST OF FIGURES

Figure	Page
1. Coal-fired power plant using a flue-gas desulfurization sludge system .....	6
2. Chisman Creek study area and VEPCO facility in Grafton, Virginia .....	15
3. Detailed Map of Chisman Creek Study Area .....	16
4. Comparison of flow rates for pH 3, pH 5, and pH 8 Columns .....	25
5. Components of data acquisition system .....	43
6. PE 380 timing diagram .....	44
7. Data acquisition program flow chart .....	45
8. Transients produced during Atomization as recorded by data acquisition system .....	46
9. Scanning electron micrographs of Site 1 and Site 2 fly ash .....	47
10. Comparison of Ba, Ca, and Sr levels in pH 3, pH 5, and pH 8 columns .....	65-68
11. Comparison of Rb, Sr, and Y levels in pH 3 and pH 5 columns .....	69-71
12. Comparison of Al, Ca, Fe, Mn, and Si levels in pH 3, pH 5, and pH 8 columns .....	72-75
13. Comparison of As, Cu, and Fe levels in pH 3, pH 5, and pH 8 columns .....	76-79
14. Comparison of Ca and Cu in pH 3 and pH 8 columns .....	80-81
15. Comparison of Mn, Ni, and Pb levels in pH 3 columns .....	82
16. Comparison of As, Se, and V levels in pH 3, pH 5, and pH 8 columns .....	83-86

## ABSTRACT

Fly ash deposits from a coal-fired electric generating plant were analyzed for seventeen elements present at trace levels. The amounts of these elements were determined using proton-induced X-ray emission (PIXE) and graphite furnace atomic absorption spectroscopy (GFAA). The effects of pH on leach rates from the fly ash for these elements were studied. Interfacing of the GFAA system to an Apple-Isaac computer data system was also developed.

AUTOMATED DATA ACQUISITION FOR ANALYSIS OF FLY ASH BY GFAA

## INTRODUCTION

### Environmental Significance of Fly Ash Disposal

Coal is the nation's seventh largest natural resource. Its combustion produces a tremendous amount of ash. In 1975, over 36 million tons of fly ash were produced in the U.S. (1,2). By the year 2000, particulate emissions may reach five million tons per year. Since the amount of fly ash produced is so great, many practical uses have been suggested for this material. These include: restoration projects, neutralization of acid mine wastes, highway construction, and concrete fabrication (3-6).

To safely utilize this material, it is important to understand the mechanism of metal release from fly ash under natural environmental conditions. The type of coal and area of origin effect levels of elements present. Coal has been categorized into four groups based on appearance and physical properties. The four groups are lignite, subbituminous, bituminous, and anthracite coal (7). The basis for this categorization is primarily carbon content and volatile matter. From these coal compositions, it is evident that combustion of certain coal types could release high levels of potentially toxic elements. These elements include arsenic, selenium, cadmium, molybdenum, vanadium, nickel, boron, and lead. Most of

these elements exist at higher concentrations in coal than in the earth's crust. These elements are further enriched, approximately tenfold, in fly ash due to the loss of organic matter during coal combustion. Levels of major elements (e.g., aluminum, calcium, iron, manganese, and silicon) are high in all coal types, as they are in the earth's crust.

Geographically, element profiles vary as the type of coal present in a region varies. Table 1 shows concentrations of major, minor, and trace elements by location. Generally, coals from the Western U.S. contain lower trace element and sulphur levels (7,9,10). Supporting this, note that arsenic, cadmium, mercury, and molybdenum concentrations are lowest in the Rocky Mountain coal shown in Table 1. In contrast, arsenic, cadmium, boron, lead, selenium, and molybdenum concentrations are high in the Interior Province coal. When coal combustion takes place, elements incapable of escaping as a gas remain behind in various types of ash. The behavior of an individual element is dependent on both the temperature reached during coal combustion and the compound the element is present in. Most arsenic, cadmium, lead, and selenium species listed would volatilize below 1550 degrees Celsius. Under the right set of conditions in a furnace, these elements could escape as a gas and not be present in any residual ash. The presence of emission control devices in the furnace stack partly determines whether volatile elements are present in ash. Figure 1 illustrates the general configuration and flow in a coal-fired power plant.

Various stages of ash production are shown along with the stages of processing. Fly ash is a type of fine residual ash captured in emission control devices. As the name implies, this type of ash is airborne and can escape into the atmosphere if not caught by electrostatic precipitators. Bottom ash is another type of residual ash that remains in the furnace after coal combustion occurs. Bottom slag, or boiler slag, is produced when bottom ash is melted down. The amount of each ash produced is dependent on the type of furnace used.

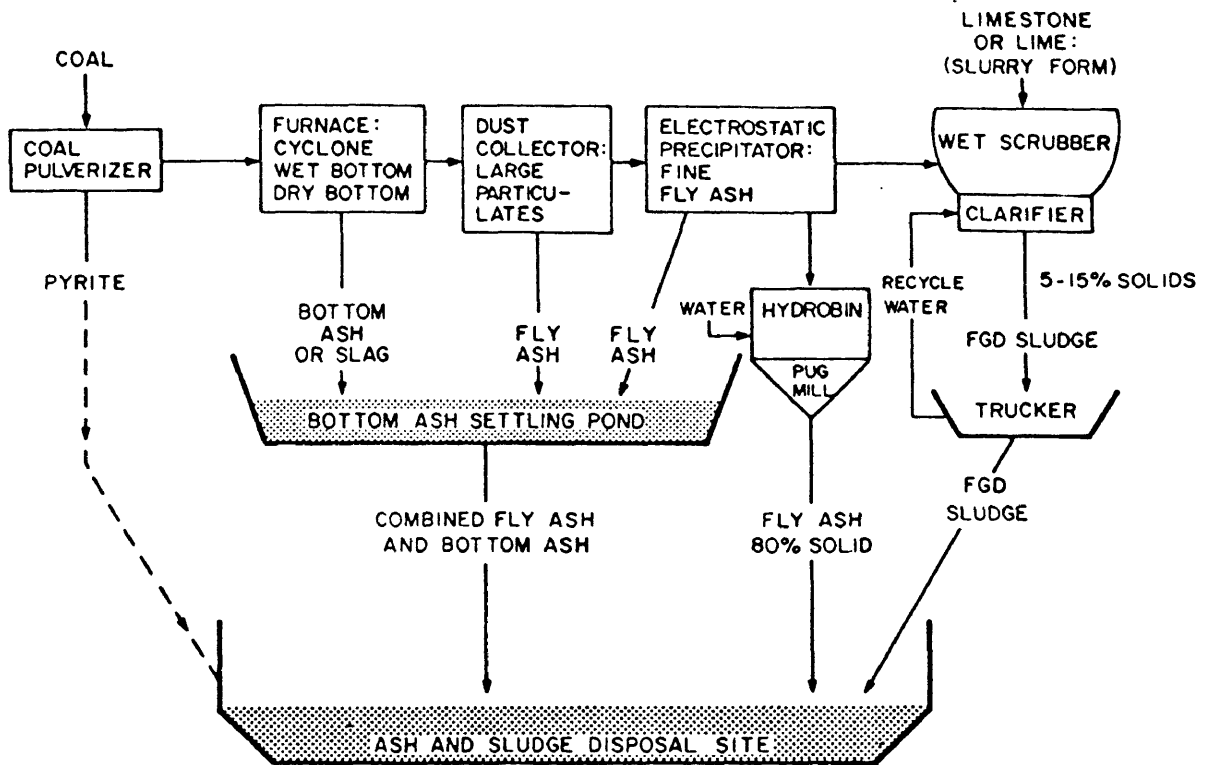
Table 2 contrasts concentrations of some potentially toxic elements by type of ash and coal. Clearly, elements are enriched in all types of ash compared to coal, due to loss of organic matter and mass during the combustion process. The difference in element concentration for each ash type can be explained by differences in ash particle size and temperature/processing at various areas in the power plant. Fly ash is primarily composed of the smallest ash particles. Volatile elements condense on fly ash particles before they leave the furnace stack as a gas. From the data in Table 2, it appears that lead, molybdenum, and arsenic display this type of behavior to a great degree. Elements not volatilizing under furnace temperatures are found in uniform concentrations in both bottom slag and fly ash. Metals displaying this behavior are called matrix elements and include iron, aluminum, silicon, and calcium (13). Aluminum has been used as a reference element to compute enrichment factors for other elements since its concentration neither varies much within the fly ash particle nor

from fly ash to slag (12).

Release of trace elements from fly ash is more pronounced when in contact with fluids, where the metals are more mobile and soluble. Since fly ash is often disposed in pits open to environmental conditions, rainfall can start the leaching process. The solubility of each element is pH dependent. Table 3 contrasts metal concentrations in solutions leached from both Mojave fly ash and soil. Note the dramatic increase in solubility of certain fly ash elements as the pH was adjusted from 12.5 to 6.5. As these elements become soluble and escape from the original disposal site, groundwater quality can be adversely effected. Runoff from the fly ash site could contaminate nearby well water, soil, and vegetation.

Figure 1 \*

Coal-fired power plant using a flue-gas desulfurization sludge system



\* Source: ref. 7,11

Table 1\*  
Average U.S. coal composition by location

Element	Appalachian Region	Interior Province	Gulf Province	Northern Great Plains Province	Rocky Mountain Province	Alaska
Major elements (percent)						
Sulfur, total	2.3	3.9	1.9	1.2	0.6	0.2
Sulfur, sulfate	0.09	0.27	0.33	0.03	0.05	0.01
Sulfur, pyritic	1.56	2.37	0.59	0.76	0.19	0.07
Sulfur, organic	0.74	1.25	0.96	0.37	0.32	0.12
Nitrogen	1.3	1.2	0.4	0.9	1.2	0.7
Silicon	2.7	2	6.6	1.4	2.5	2.9
Aluminum	1.6	0.97	2.1	0.69	1.2	1.5
Calcium	0.12	1.2	1.2	0.97	0.59	1
Magnesium	0.068	0.089	0.291	0.255	0.104	2.5
Sodium	0.032	0.035	0.732	0.182	0.102	0.018
Potassium	0.23	0.16	0.3	0.04	0.076	0.12
Iron	1.9	3.3	2.2	0.75	0.45	0.38
Manganese	0.062	0.014	0.024	0.0051	0.0036	0.0061
Titanium	0.09	0.052	0.16	0.042	0.061	0.077
Minor and trace elements (ppm)						
Antimony	1.2	1.7	0.9	0.6	0.4	2.7
Arsenic	27	21	6	3	2	3
Barium	100	70	200	500	200	700
Beryllium	2	3	2	0.5	0.7	0.7
Boron	30	100	100	70	70	70
Cadmium	0.7	7.1	1.3	0.2	<0.1	<0.2
Chromium	20	15	20	5	5	15
Cobalt	7	7	7	2	2	5
Copper	24	20.2	28	8.3	9.1	16.8
Fluorine	80	71	124	45	70	90
Gallium	7	5	10	3	3	5
Lead	15.3	55	20	5.3	5.5	5.9
Lithium	27.6	11	28	6.0	9.2	10.1
Mercury	0.24	0.14	0.18	0.09	0.06	4.4
Molybdenum	3	5	3	2	1.5	1.5
Nickel	15	30	20	3	30	10
Niobium	5	1.5	7	5	1	3
Scandium	5	3	7	2	2	5
Selenium	4.7	4.6	7	1.0	1.6	2
Strontium	100	50	200	150	100	100
Thallium	4.9	5.2	8.3	2.7	3.6	4.4
Uranium	1.4	3.3	3.2	0.9	1.6	1.2
Vanadium	20	20	50	10	15	30
Ytterbium	1	0.7	2	0.3	0.5	1
Yttrium	10	10	20	5	5	10
Zinc	20	373	40	25.6	9.9	24
Zirconium	50	15	70	15	20	20

\* Source: ref. 7,8

Table 2 \*

Progressive trace element enrichment in a coal-fired power plant

(ppm)

Sample	Cu	Zn	As	Mo	Sb	Pb	Se	Hg
Coal	9.6	7.3	—	0.99	—	—	1.9	0.070
Bottom ash	82	58	15	3.50	2.8	<5	7.7	0.140
Precipitator ash (inlet)	230	250	120	41.00	14.0	66	27	0.310
Precipitator ash (outlet)	320	370	150	60.00	18.0	130	62	—

\* Source: ref. 7,12

Table 3 \*

Comparison of element levels in saturation extracts  
of Mojave fly ash and 68 California soils

Element	Fly Ash ( $\mu\text{g/ml}$ )		Concentration in Soil Saturation Extracts ( $\mu\text{g/ml}$ )	
	Water Soluble Before pH Adjust- ment (pH 12.5)	Water Soluble After pH Adjust- ment (pH 6.5)	Mean	Median
Ca	476	38,234	128	60.0
Mg	<1	849	38	12.4
Na	287	900	524	45.0
K	<100	<100	20	10.0
Si	<0.6	<0.6	3.1	5.0
B	<0.6	65	3.1	<0.1
Ba	50	15	0.26	0.10
Sr	61	333	0.93	0.18
Al	<2	<2	0.40	<0.01
Cr	<1	<1	0.01	<0.01
Fe	0.01	0.11	0.05	0.03
Mn	<0.01	1.3	0.17	<0.01
Cu	0.01	0.02	0.04	0.03
Zn	0.02	0.08	0.07	0.04
Mo	0.12	1.11	0.73	<0.01
Ni	0.01	0.13	0.02	<0.01
Co	<0.01	0.09	0.06	<0.01
V	<0.01	0.02	0.07	0.01
Pb	<0.02	<0.02	0.05	<0.01
Cd	<0.01	0.03	-	-
Ag	<0.001	<0.001	-	-

\* Source: ref. 7,14,15

## CHAPTER I

### CHISMAN CREEK FLY ASH DISPOSAL SITE

The area examined during the current study was a fly ash disposal site located in Yorktown, Virginia. Fly ash was last deposited at this site in the mid-1970s by the Virginia Electric and Power Company (VEPCO). Figure 2 contains a map of the area under study.

Fly ash was produced from 1957 to 1973 when the plant stopped using coal and refinery coke and began using fuel oil. The refinery coke was obtained from the nearby AMOCO refinery. Refinery coke is derived from crude oil; therefore, certain elements, such as vanadium and nickel, are present in especially high concentrations. When the VEPCO plant was in full operation, one thousand tons of fly ash and two hundred fifty tons of bottom ash were produced each week (16,17). This ash was deposited into three separate fly ash pits. Figure 3 displays the location of the fly ash pits in the study area.

Although fly ash had been deposited in the Chisman Creek watershed for several years, environmental effects went unnoticed during that time. However, in the early 1980s, several nearby residential wells were reported to contain green-colored water. The incident prompted the

State Board of Health and the State Water Control Board to undertake a testing program in the immediate area. Several residential wells were tested and found to contain high levels of vanadium. Vanadium and selenium were also present at higher than expected levels in Chisman Creek groundwater (18,19). The groundwater was probably contaminated by vertical and horizontal migration of fly ash. Later collaborative studies by the Virginia Institute of Marine Science and the Virginia Associated Research Campus provided more detailed information on the extent of trace metal contaminants. This work involved an extensive program of analyzing groundwater, stream water, fly ash, sediments, vegetation, and shellfish to understand the dynamics of trace metal mobility. The sampling program primarily involved pit C and the surrounding area, as shown in Figure 3.

The geography and geology of the Chisman Creek watershed are important in understanding the possible effects of drainage from the fly ash pits. The Chisman Creek watershed is located on the Virginia Peninsula, directly south of the VEPCO facility. The watershed encompasses about 4200 acres (16). The tidal creek is approximately 550 acres in area, 3.75 miles in length (in an east/west direction), .5 mile in width and 12 feet in average depth (16). Drainage from the tidal creek is directed into Chesapeake Bay. The fly ash pits are located on a 520 acre area of the watershed (16).

The geology of the area determines the flow of water as it emerges from the fly ash pits. The fly ash pits are located in

an area composed of two layers. The upper layer, known as the Tabb formation, is quite sandy and considered to be moderately permeable (16). This layer extends from the surface to an approximate depth of 20 feet (16).

The second layer, the Yorktown formation, is denser, less permeable, and composed of a fine clayish material (16). To excavate for the fly ash pits, material was only removed from the Tabb formation. Data from previous studies suggested that when drainage reached the Tabb/Yorktown border, it would flow laterally until reaching some surface stream (18,19). This phenomenon may limit contamination of areas beyond where the groundwater surfaced. The VIMS/VARC study indicated that only areas located downhill between an ash deposit and a major surface stream would be effected by this lateral flow.

This information was determined from groundwater samples taken through wells installed in pit C during the VIMS/VARC study and wells previously installed by the the State Board of Health and the State Water Control Board. Water samples contained many elements, including nickel and vanadium which were above background levels. The residential wells examined by the State Board of Health were located in an area subject to this drainage and were proven to be contaminated.

Another important mechanism for trace metal contamination was believed to be erosion and transport of fly ash into streams during storm activity (16). Since runoff from the fly ash pits during storm activity could be quite high, large amounts of particulate matter could be deposited in bottom

layers of nearby streams and made available to vegetation and other living organisms. Samples of stream water and surface particulates were taken and found to contain higher element levels during storm activity, which were correlated with more acidic conditions. The elements found at higher levels included nickel and vanadium. In addition, certain samples also contained higher levels of arsenic and manganese.

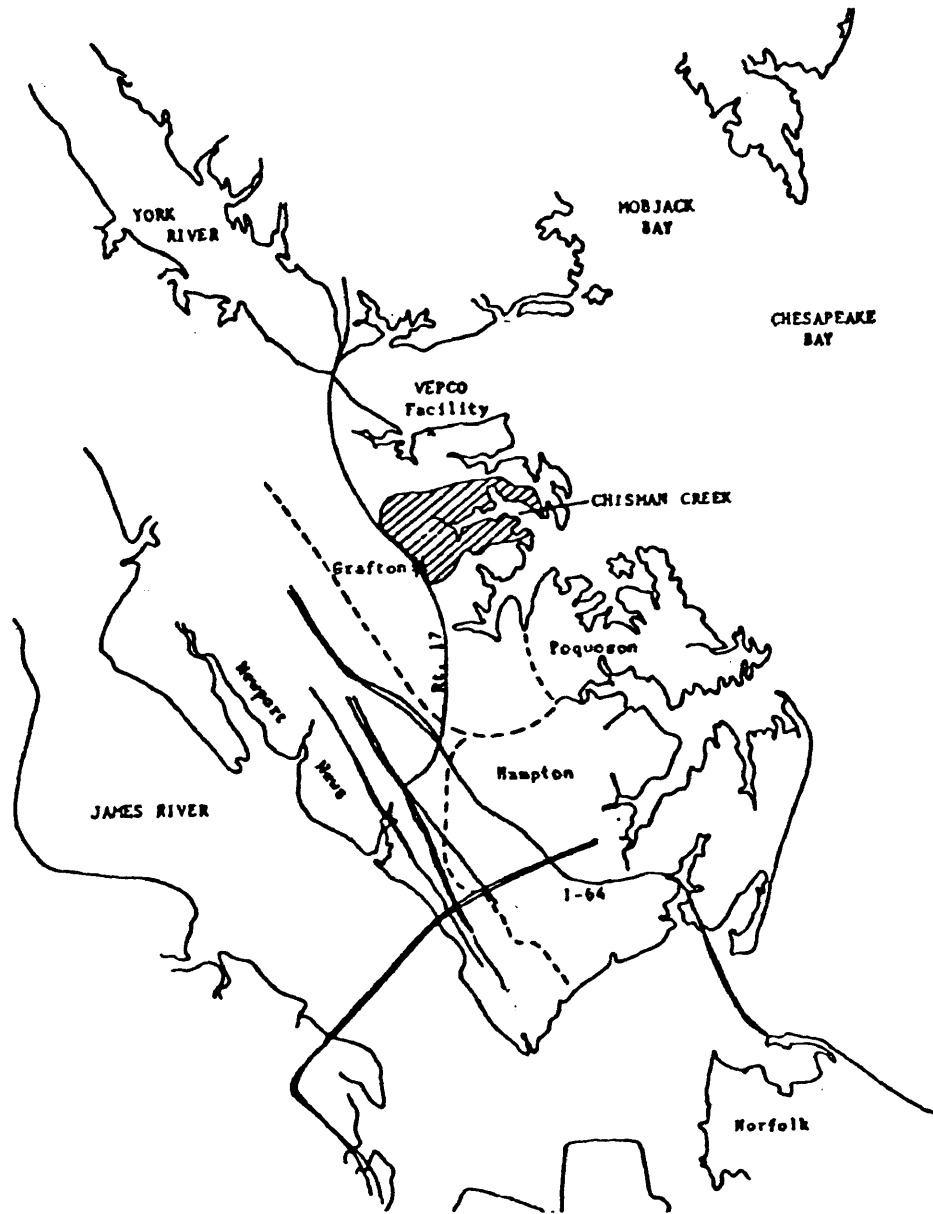
Surface sediments and sediment core samples were also analyzed. High levels of vanadium, nickel, arsenic, and copper were found in both samples types. The element levels in the surface sediment samples were found to decrease with distance downstream from the fly ash pits. This phenomenon was probably due to dilution, changes in sediment particle size, and particulate matter settling out (16). Oysters were also analyzed to determine the extent of element bioaccumulation. The samples were found to contain vanadium, up to 3.6 ppm (16). Since vanadium existed at relatively high levels in all samples analyzed in this study, a more in-depth future study of vanadium and its patterns seemed appropriate. Rather than taking samples from materials contaminated within Chisman Creek, fly ash would be taken back to the laboratory and subject to controlled conditions. The intent of the current study was to determine vanadium availability from fly ash under varying conditions, including changes in pH and ionic strength, which would affect vanadium solubility. The profile of other major, minor, and trace elements would be examined and compared to vanadium levels.

In order to improve analysis for vanadium during the course of the new study, existing instrumentation was modified and enhanced. A Perkin-Elmer graphite furnace atomic absorption spectrophotometer (Model 380) was interfaced with an Apple II+ microcomputer through an ISAAC (Instrumentation System for Acquisition and Control) analog-to-digital converter. Control software for the Apple II+ computer was written in both Assembler and BASIC. This software controlled both the data acquisition and data reduction phase of vanadium analysis on the atomic absorption spectrophotometer.

Two modes of data acquisition were implemented. The first method involved sampling the analog signal from the recorder output. This method was a relatively slow form of data acquisition with the instrument providing a background-corrected signal. The second method involved making hardware modifications to the instrument so that components of signals available from method one became accessible. The second method required a fast algorithm for data acquisition; thus, Assembler routines became necessary. Since method two permitted the separation and display of both background and analyte element signals, chemical interferences became better recognized and understood.

Figure 2\*

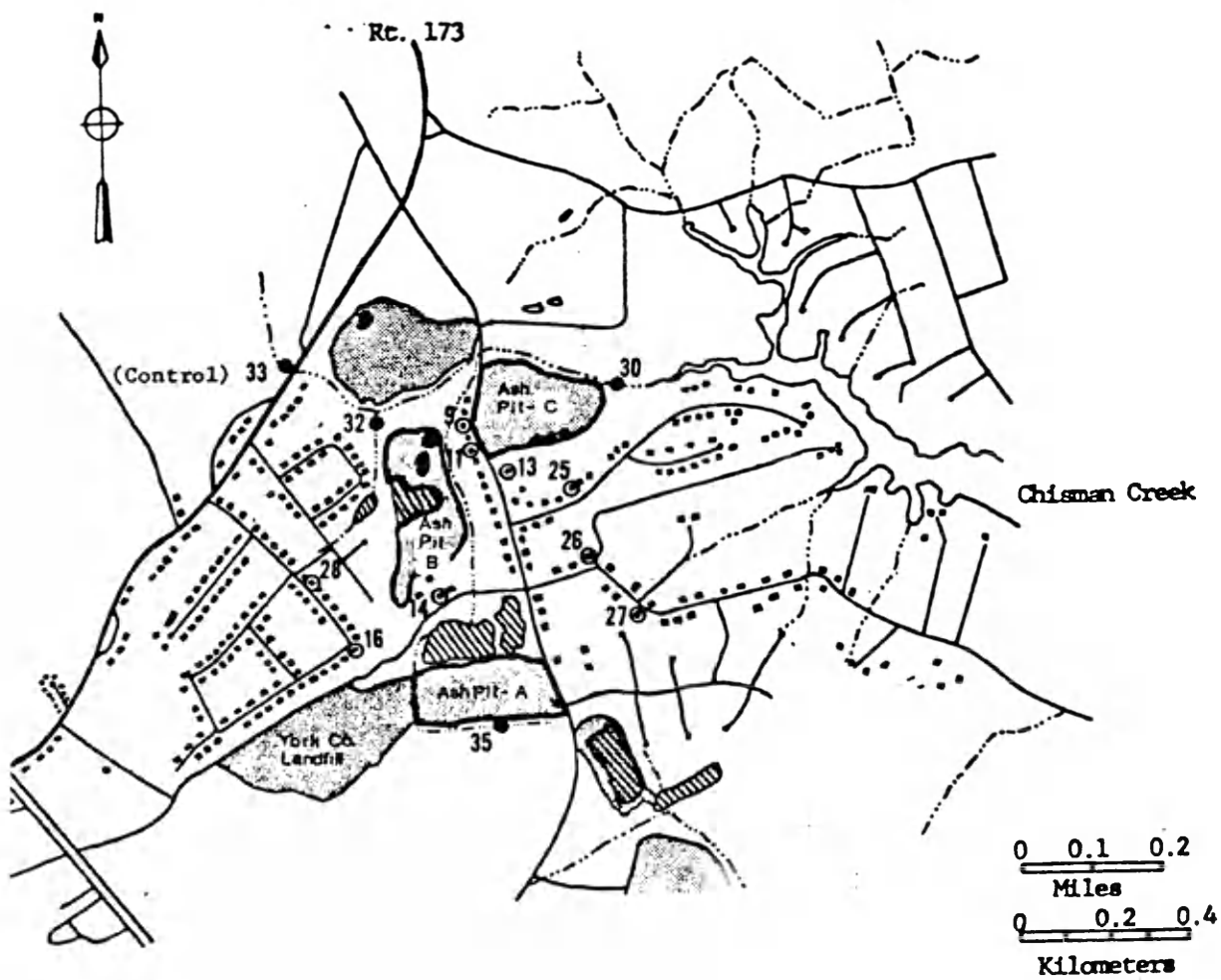
Chisman Creek study area and VEPCO facility in Grafton, Virginia



\* Source: ref. 16

Figure 3 \*

Detailed map of Chisman Creek study area



\* Source: ref. 16

## CHAPTER II

### EXPERIMENTAL METHODS

#### Fly Ash Collection and Processing

During the current study, two sampling sites were selected from fly ash pit A (see Figure 3 for a map of the local area with locations of the three fly ash pits). Site 1 was located approximately one-quarter mile from Wolftrap Road adjacent to a pond and vegetation. Site 2 was located near a county landfill and probably received some landfill drainage due to the site's lower elevation.

At each sampling location, two sets of samples were taken. This included a shallow set from a depth of two to eleven inches, and a deeper sample from a depth of eleven to eighteen inches. Although procedures were used to limit contamination during sampling, the surface fly ash composition had been altered by environmental conditions since it was first deposited. Any sampling site could be composed of several types of ash and soil from the surrounding area. Consequently, metal concentrations varied considerably in this material.

The collected samples were stored in clean polyvinyl chloride (PVC) bags for transport back to the laboratory. All material from the same site was homogenized and sieved through acid-washed

polypropylene 2 mm screens. This removed most of the large material such as rocks, grass, and insects. The remaining material was placed on a double set of acid-washed polypropylene screens, 60 mesh on the upper tier and 120 mesh on the lower tier. This ash was then placed in an oven at 60 degrees Celsius to dry. The ash was gently sifted during the drying process so the sub-120 mesh particles could be collected in the lower tub. Although the sieved material reduced to a fine powder for both sites, the site 2 ash was noticeably darker and coarser than site 1. The shallow and deep samples were pooled from each site and set aside in a desiccator.

#### Chemical Reagents and Buffers

Chloroacetic acid and sodium chloroacetate were chosen for the pH 3 buffer (pKa of chloroacetic acid = 2.85). Part a of Table 4 lists the concentrations of components used for the pH 3, pH 5, and pH 8 buffers. The chloroacetic acid received was analyzed by proton-induced X-ray emission (PIXE) and shown to contain lead, iron, nickel and other elements (see part b of Table 4 for contaminants in each buffer component). The chloroacetic acid was sublimed once prior to use in the pH 3 buffer. After each sublimation, the crystals were reanalyzed by PIXE and shown to be free from detectable contamination. Once a 'clean' set of chloroacetic acid crystal was collected, it was used to produce sodium chloroacetate. The sodium carbonate required for this procedure was also analyzed and

found to be free of metal contamination. Sodium hydroxide was deliberately not used to produce sodium chloroacetate because of contamination with high concentrations of several elements.

For the pH 5 buffer, acetic acid and sodium acetate were chosen (pKa of acetic acid = 4.75). The acetic acid underwent two sub-boiling distillations prior to use. Both acetic acid and sodium acetate were analyzed by PIXE and found to be free from metal contamination. Several components were investigated for use in the pH 8 buffer. Among the most readily available and possessing a suitable pKb was tris(hydroxymethyl) aminomethane (THAM; pKb of THAM = 7.903). The protonated form of THAM was easily synthesized by combining concentrated nitric acid with THAM. THAM was also analyzed by PIXE and shown to be free from metal contamination. Any nitric acid used was distilled twice before use. The nitric acid was also used for cleaning laboratory glassware and utensils to prevent sample contamination.

The pH 3, pH 5, and pH 8 buffers were made up in the appropriate concentrations to result in a .01 ionic strength solution. The pH 5 buffer was also made up at .10 ionic strength to investigate the effect of differing ionic strengths on the dissolution of compounds in the fly ash. The site 2 fly ash required the higher ionic strength buffer to maintain the leachates at pH 5. The lower ionic strength buffer was sufficient to maintain the site 1 column effluents at pH 5. The columns were easy to maintain at pH 8 due to the natural

alkalinity of the fly ash.

#### Preparation of Leachates

Fly ash-filled chromatography columns were set up to simulate the natural leaching process occurring in the fly ash. A fly ash slurry was used to fill 50 ml glass burets equipped with Nucleopore polycarbonate filters. The filters (.40  $\mu\text{m}$  pore size) prevented the escape of ash, while mobile phase flowed through the columns. The polycarbonate filters were held in place by a fine nylon mesh. Several types of mobile phases were chosen, based on properties such as pH and ionic strength. These properties had to be similar to those possessed by liquids presently leaching the fly ash in the disposal site. The columns were constantly replenished with these solutions, which were supplied as the columns drained at their own natural rate. The flow rate was determined by the origin of the ash (site 1 versus site 2), as well as the packing and settling of the columns. All site 2 columns drained more slowly than site 1, possibly due to the abundance of the dark coarse material which settled to the bottom of the columns. Experiments were conducted to determine the best ratio of ash to mobile phase that would give an acceptable flow rate and yield leachates with detectable metal concentrations. A ratio of 20 grams of fly ash to 20 mls of mobile phase was selected. The fly ash slurry produced by this ratio could be easily poured into the burets. Extra mobile phase was used to

rinse all remaining ash into the burets and bring the final volume up to the same location in each buret. The column flow rates continued to vary and decrease until the ash reached a final stage of settling. This occurred about 120 hours after the columns were started. See Figure 4 for plots of flow rate versus volume eluted from each column.

A total of eight columns were leached to simulate a variety of conditions occurring in the fly ash disposal site. Three buffer solutions with pH 3, pH 5, and pH 8 were selected. The buffer solutions were produced with a low ionic strength so they would not interfere with the natural dissociation processes occurring in the ash. These buffers had to have a buffer capacity large enough to maintain the pH of the column effluents to within a few tenths of the intended value despite their low ionic strengths. Buffer components were chosen on the basis of their pKa/pKb values, freedom from metal contamination, availability, and concentrations required to maintain the desired pH. Where circumstances allowed, buffers components were synthesized from compounds already present in the laboratory. These compounds were analyzed and found to be free from metal contamination.

The eight columns will be referred to as column 31 (pH 3, site 1), column 32 (pH 3, site 2), column 510 (pH 5, site 1, ionic strength .01), column 511 (pH 5, site 1, ionic strength .10), column 520 (pH 5, site 2, ionic strength .01), column 521 (pH 5, site 2, ionic strength .10), column 81 (pH8, site 1), and column 82 (pH 8, site 2).

The buffers were made up in large quantities and supplied to the columns by gravity as the liquid levels dropped in the burets. This was accomplished by inverting a volumetric flask over the buret and allowing the buffer to flow from a connecting tube. The rate at which liquid was supplied was dependent on the flow rate of buffer solution through the ash in an individual column. The leaching of metals was dependent on the pH and flow rate of a column. The columns with lower flow rates could exhibit higher metal concentrations due to the extended period of time the ash remained in contact with the buffer. For most of the experiment, the leachates were collected every eight hours in 15 ml acid-washed preweighed polystyrene tubes. This procedure lasted approximately twelve weeks, until changes in metal concentrations levelled off for each column.

Almost all leachates collected during the first several days were analyzed by GFAA and PIXE. As changes in metal concentrations became more gradual, fewer samples had to be analyzed to obtain column profiles. By the time the columns were stopped, a total of 2010 mls had been collected from column 31 over 1710 hours, 2890 mls from column 32 over 1710 hours, 2040 mls from column 510 over 1750 hours, 2290 mls from column 511 over 1750 hours, 1860 mls from column 520 over 1750 hours, 2560 mls from column 521 over 1990 hours, 1640 mls from column 81 over 2310 hours, and 1170 mls had been collected from column 82 over 2230 hours.

Generally, at least 5 mls of leachate had to be available for

various analyses. For the leachates requiring filtration, due to presence of small fly ash particles, a larger volume had to be collected. Immediately after collection, the tubes were weighed. If filtration was required, it was performed before weighing. The samples were then preserved by addition of concentrated nitric acid until a pH of 2 or less was obtained.

All samples to undergo PIXE analysis were doped with Indium to produce a concentration of about 45 ppm of Indium. Samples to undergo atomic absorption analysis required no further preparation, other than dilution which varied from sample to sample.

Table 4

Characteristics of pH 3, pH 5, and pH 8 buffers

## a) Composition of pH 3, pH 5, and pH 8 Solutions

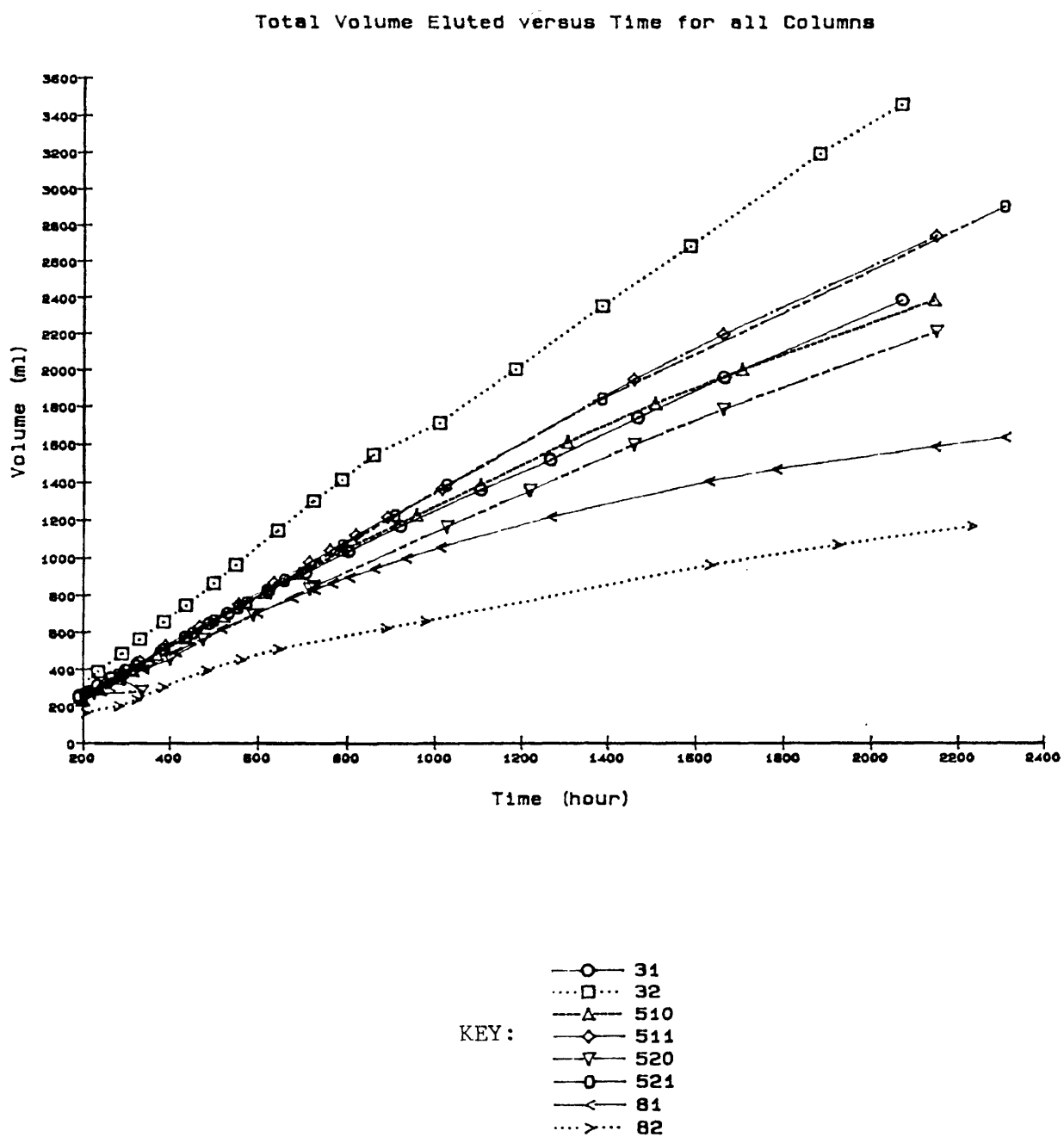
pH	Ionic Strength	Conjugate Base/Acid	Molarity	Acid/Base	Molarity
pH 3	0.10	$\text{ClCH}_2\text{COO}^-\text{Na}^+$	0.0960	$\text{ClCH}_2\text{COOH}$	0.0680
pH 5	0.01	$\text{CH}_3\text{COO}^-\text{Na}^+$	0.0096	$\text{CH}_3\text{COOH}$	0.0054
pH 5	0.10	$\text{CH}_3\text{COO}^-\text{Na}^+$	0.0960	$\text{CH}_3\text{COOH}$	0.0540
pH 8	0.01	$(\text{CH}_2\text{OH})_3\text{CNH}_2(\text{H})^+$	0.0096	$(\text{CH}_2\text{OH})_3\text{CNH}_2$	0.0120

## b) Concentration of Trace Metal Contaminants in pH 3, pH 5 and pH 8 Buffers (concentration in ug/g)

	Fe	Ni	Zn	Pb	Ag	Sr
Concentrated pH 3 buffer 0.9600 M $\text{ClCH}_2\text{COO}^-\text{Na}^+$ 0.6800 M $\text{ClCH}_2\text{COOH}$	3.5	2.1	<1.1	52.0	2.2	5.1
Concentrated sodium carbonate solution 0.4850 M $\text{Na}_2\text{CO}_3$	<0.20	<0.08	<0.04	<0.07	<0.40	<0.04
Concentrated sodium acetate solution 0.8270 M $\text{CH}_3\text{COO}^-\text{Na}^+$	<0.13	<0.05	<0.04	<0.07	<0.30	<0.07
Regular pH 8 buffer 0.0096 M $(\text{CH}_2\text{OH})_3\text{CNH}_2(\text{H})^+$ 0.0120 M $(\text{CH}_2\text{OH})_3\text{CNH}_2$	<0.06	<0.30	0.027	<0.02	<0.06	0.016
THAM solid sample 0.00874 g $(\text{CH}_2\text{OH})_3\text{CNH}_2$	2.0	<0.40	<3.6	<0.30	<0.60	<0.13

Figure 4

Comparison of flow rates for pH 3, pH 5, and pH 8 columns



## CHAPTER III

### ANALYTICAL METHODS

Both graphite furnace atomic absorption spectrophotometry (GFAA) and proton-induced X-ray emission (PIXE) were used for analysis of leachates obtained from all columns. Vanadium was determined by GFAA. All additional elements were determined by PIXE. The concentration of forty elements, from silicon to uranium, can be determined simultaneously with PIXE. In addition to chemical analyses performed on fly ash samples, the material was also analyzed via scanning electron microscopy (SEM). This analysis provided qualitative information on the fly ash, which was useful in comparing the current samples with materials reviewed in the literature.

#### Scanning Electron Microscopy

Both site 1 and site 2 samples were analyzed by SEM at the Virginia Institute of Marine Science. The fly ash samples were mounted on aluminum stubs with carbon paint. The samples were then coated with a Au-Pd layer of 150 Å in thickness to enhance conductivity of the electron beam. The coating process occurred in a vacuum evaporator taken down to a pressure of  $5 \times 10^{-7}$  torr. SEM micrographs were taken with an AMR 1000

scanning electron microscope operated at an accelerating voltage of 20 kV. Micrographs were taken at several magnifications from 6X to 5200X. The most useful micrographs produced were taken between 230X and 700X magnification. Two micrographs of the site 1 and site 2 fly ash are shown in Figure 9.

#### Proton-Induced X-ray Emission

Samples were doped with a known amount of the internal standard indium. Indium was selected as the internal standard since it was unlikely to exist naturally in the samples and it did not interfere with the analysis of other elements. Liquid samples, like the leachates, were 'spotted' as a thin film ( $0.5 \text{ mg/cm}^2$ ) on a graphite-impregnated polycarbonate target that is subject to a beam of high energy protons. Each element then produces a characteristic X-ray spectrum that contributes to the total X-ray spectrum emitted by the sample. There is an attenuation of X-rays that occurs for each element based on the amount of sample on the target. This prevents light elements (low atomic number) from being analyzed accurately. In order to separate each elements' spectrum to determine concentration, a least squares analysis is used to obtain a theoretical set of amplitudes that is compared to the spectrum of the composite sample (20). The isolated amplitudes for each element can be converted to a concentration for that element based on the concentration of the dopant, indium. Accuracy is checked by routinely analyzing check standards that contain a known amount of several elements.

## Graphite Furnace Atomic Absorption Spectrophotometry

### Native Perkin-Elmer GFAA Mode

Vanadium analysis was accomplished through graphite furnace (electrothermal) atomization of samples on the Perkin-Elmer 380 atomic absorption spectrophotometer (which will be referred to as the PE 380 system). The standard Perkin-Elmer system provided for deuterium background correction required on the samples, which contained a high concentration of salts due to presence of acids and buffers in the leachates. The HGA 400 furnace could be programmed for the temperature and times required in the dry, char, and atomize cycles. The system also possessed an AS 40 autosampler that allowed for sample injection replication and calibration/recalibration of standards as needed.

A recorder was present on the Perkin-Elmer system, which could only display corrected samples absorbances. Peak heights or peak areas could be seen on the instrument's LED digital display and reported on a PRS 10 printer. During native operation, the instrument microprocessor could perform internal calibration with up to three standards. However, the 380 microprocessor only used a single atomization transient for recalibration and the original data was erased. This may be acceptable for flame atomization but it is not compatible with the poorer precision often found with furnace atomization.

To gain flexibility and accuracy, data analysis was performed on a DEC PDP-11 computer after completion of a run. The PDP-11

software better compensated for more stringent calibration requirements, especially where more than three standards were required. The ability to use several standards was important in defining calibration curves that were frequently non-linear at higher concentrations. All sample and baseline readings, available on paper tapes generated by the atomic absorption spectrophotometer, were manually entered into data tables on the PDP-11 computer. Average baseline readings were then subtracted from all sample absorbances. The resultant absorbances were used for all further calculations. A data summary report generated by the PDP-11 computer program (21) is included in Table 5.

Each run included the analysis of several blocks of standards to obtain a calibration curve. Generally, five different concentrations of standard solutions were analyzed in triplicate. Replicate absorbances for each standard were averaged before entry into a second order non-linear regression algorithm. If the relative standard deviation for any standard's absorbances rose above about 3.0%, the average absorbance was not used to produce the calibration curve (see column 9 in Table 5). In Table 5, note that the standard labelled '31 77 5' failed this requirement. As a result, the notation '\*' appears in the right column, which means the results were not stored. Before installation of the data acquisition system, the RSDs had to be manually monitored, since an entire run could be lost if the standards had poor reproducibility. Normally, this information was not available until the final report was

generated on the PDP-11. The advantage of a real-time data acquisition system was that poor RSD values could be flagged immediately after a standard's final replicate was analyzed. The PDP-11 summary report also included other quality control parameters, such as the RSD for computed standard concentrations, as determined from the calibration curve. The computed standard concentrations are in column 6 and the RSD values are located in column 7 of Table 5. The ratios of computed standard concentration to solution concentration are located in column 11. These ratios ranged from about 95% to 105%. Values from 98% to 102% were considered acceptable.

#### The Apple II+/ISAAC Data Acquisition Hardware

The major drawback of the PDP-11 was that it was an off-line system. It could not display real-time absorbances which occurred during the char and atomization cycles. For this reason, a data acquisition system was highly desirable. This acquisition system would be required to display both the element plus background and background peaks during atomization. These peaks would aid in showing the sample matrix subtraction process and the effect of this matrix on the graphite tube. The data acquisition system would still have to provide the analysis capabilities previously available with the PDP-11 software. The first step in selecting a data acquisition system was to pick an analog-to-digital converter capable of sampling instrument signals at a 60 Hz frequency.

Slower sampling rates, as those used in liquid chromatography automation, were not sufficient to measure changes that occurred during atomization since an entire peak could be generated in two seconds. The A/D converter had to operate with an Apple II+ microcomputer, which had already been purchased by the laboratory. The ability to read autosampler tray position and other logic signals was also a high priority.

A data acquisition system manufactured by Cyborg Corporation (55 Chapel St., Newton, MA.), the ISAAC Model 91A, was selected. ISAAC used a 12-bit successive approximation analog-to-digital conversion technique to produce the digitized values. The ISAAC system includes sixteen single-ended analog inputs (or eight differential analog inputs), sixteen binary inputs, four Schmitt triggers, a clock, a timer, a counter, and a buzzer/beeper. Software for data acquisition was provided in both BASIC and assembler. The BASIC software provided, LabSoft, loaded into a 12K memory extender card on the Apple II+. The A/D converter was connected to slot number three on the interface board of the Apple II+ computer (see Figure 5 for a block diagram of the configuration).

#### Recorder Mode Data Acquisition

Initially, only the instrument recorder signal was interfaced to ISAAC. For each sample injected into the instrument, analog signals were collected for two time periods. The baseline

absorbance was measured at the end of the instrument char cycle. The background-corrected vanadium peak was sampled during the atomization cycle. This is illustrated by Table 6, which displays the programmed furnace temperatures for each injection. Steps 1-4 represent the dry, char, atomize, and clean-out cycles, respectively. The temperature row represents the maximum temperature reached during the corresponding cycle. The ramp time is the number of seconds required to reach maximum temperature while the hold time is the number of seconds the maximum temperature is to be maintained. The recorder was activated 24 seconds into the char cycle and remained on until the end of the atomize cycle. The 'read' row in Table 6 indicates the relative time each absorbance signal was measured. Note that the gas flow was reduced during the atomize cycle, as indicated by the mini-flow selection, to enhance the absorbance signal. The parameters on the right of Table 6 include the analyst ID, run number, sample description, analysis date, element, and absorbance versus concentration selection. The wavelength of the lamp output was also reported with the filter position, slit width, deuterium lamp selection (ON/OFF), lamp energy, peak versus area analysis selection, and sample injection volume. The remaining parameters were only required for special analysis types (e.g., standard additions).

The software that collected the recorder signals was written in BASIC and LabSoft. Recorder peaks were sampled at a rate determined by the execution time of the

LabSoft commands. Testing was performed to determine the length of time required to execute commands for reading a single analog input channel.

Under these conditions, the sampling rate was a limited 35 msec per point because LabSoft commands had to be 'interpreted' first before execution. Commands preceded by an ampersand sign (&) directed program execution to Assembler routines located in the 12K memory extender card, where LabSoft resided. Considering the number of points obtained per injection, data from approximately 60 samples could be stored on a single side of a floppy disk. The principal benefits of the data acquisition system were the acquisition and storage of complete transients and the elimination of manual data entry. In addition to obtaining the recorder signal, the position of each sample was automatically read from the autosampler tray as a binary-coded decimal number. A total of six signals were read into the binary-coded decimal inputs of ISAAC and translated to tray positions one through 39.

Although the 'recorder mode' of data acquisition was easy to implement, the analytical capabilities of the Perkin-Elmer graphite furnace system were not affected. The principal benefits were the acquisition and storage of complete transients and the elimination of manual data entry.

#### Enhanced Data Acquisition and Hardware Modifications

The primary purpose for implementing the more complex 'enhanced

mode' of data acquisition was the acquisition and display of the background correction signal. Direct measurement of the background correction signal was not possible with the instrument operating as received. However, display of background information is very useful in method development and detection of problem samples (high dissolved solids). Thus, the enhancements improve accuracy and facilitate method development. All hardware modifications were performed so that original instrument performance was unaffected. In the event the computer or ISAAC malfunctioned, the instrument could still be used in its native mode.

The second method for acquiring instrument signals required making additional connections to several sample and hold amplifiers on the analog and background correction boards of the Perkin-Elmer 380 instrument. The amplifiers were interfaced with shielded cables and connected to the first four analog inputs on the ISAAC A/D converter. The signals corresponded to the deuterium and hollow cathode lamp signals from the sample and reference beams. These signals will be referred to as BG (background signal - sample beam), I (hollow cathode signal - sample beam), BGO (background signal - reference beam), and IO (hollow cathode signal - reference beam). Each set of signals was acquired every 16.67 msec (60 times per second). ISAAC was programmed to wait for a 12 volt timing pulse before the four channels of data were acquired from the instrument (see Figure 6 for timing diagrams of these signals). The PE 380 timing diagram was measured with a

Tektronix 564 oscilloscope. The voltage corresponding to each signal was available to ISAAC at any time after the gating interval shown in the timing diagram.

Equations used for absorbance calculations and instrument electronic experiments are given in Tables 7 and 8. A correction was applied to the rapidly changing background signals since they were not sampled at the same time as the hollow cathode signals. To compensate for this time difference, contributions of signal values from the current and next sampling period had to be applied to the signal currently being collected. The time at which the hollow cathode sample beam signal was collected was selected to be 'time zero'. For example, the BG signal was actually obtained by ISAAC 13.77 msec after the instrument had updated the hollow cathode sample beam signal (I) and 2.90 msec before the hollow cathode signal would be updated again. In order to calculate a corrected BG value, 82.6% of the current signal value had to be added to 17.4% of the signal value from the next sampling period (details are given in Appendix A). This correction was only necessary for the BG signal. The reference beam signals, BG0 and I0, remained at a nearly constant level during the char and atomize cycles.

The experiments used to determine appropriate equations for calculating absorbance are summarized in Table 8. These experiments involved using fine wire mesh screens (0.35 and 0.80 absorbance units) to block both copper lamp radiation and deuterium (background) radiation. During this process, a digital voltmeter was used to measure voltages at

the four sample and hold amplifiers where the BG, I, BG0, and I0 signals were available. The lamp current was varied from nine ma through 12 ma to demonstrate compensation features of the instrument. In Table 8, note the instrument will always maintain the same voltage level for the hollow cathode reference beam signal (I0), even when the energy of the deuterium lamp changes (BG0). When the energy output of the hollow cathode lamp drifts, the auto gain circuit for the PMT will adjust to compensate for the drift. Thus, the hollow cathode signal in the reference beam is maintained at 2.48 volts, independent of the lamp current. Note that the reference and sample signals are not equal, even under balance conditions when there is no actual sample absorbance. Also note the voltages of BG0 and I0 remain at the same level (at constant hollow cathode lamp energy), although the conditions ranged from zero absorbance (balance) to 0.80 absorbance. This fact permits use of I' and BG' in the computation of hollow cathode and deuterium sample beam absorbances. The absorbance of radiation from the hollow cathode lamp can be defined using expressions for sample and reference beam signals that exist during the atomization process (see Table 7).  $\log I_0/I$ ,  $A(t)$ , represents the absorbance of radiation from the hollow cathode lamp; I0 and I are the lamp intensities after passing through the reference and sample paths, respectively. Average values of I0 and I, obtained and computed during the char cycle, can be used to compute the hollow cathode lamp absorbance during atomization. A' is used to denote

the absorbance under balance or 'no sample' conditions. The corresponding components are denoted as  $I_0'$  and  $I'$ . Since instrument electronics force  $A'$  to a non-zero value, it must be subtracted from the total absorbance to obtain the true absorbance.

The absorbance expression in equation F simplifies to  $\log I'/I$ , since  $I_0'$  and  $I_0$  should be equal. This principle applies to calculating the deuterium lamp absorbance,  $A(BG)$  in equation G. The final corrected absorbance,  $A_{corr}$  in equation I, is the difference between the hollow cathode,  $A$ , and deuterium absorbance,  $A(BG)$ .  $A(t) - A'$  is the quantity of radiation reaching the photomultiplier tube (PMT) that has been reduced by atomic absorption (monochromatic absorption), molecular absorption, and scattering of light by particles. The amount of light reduced by other than monochromatic absorption can be determined and compensated for by quantifying the amount of deuterium lamp radiation absorbed.

#### Atomic Absorption Application Software

Machine language software was required to obtain the  $BG_0$ ,  $I_0$ ,  $BG$ , and  $I$  signals from the instrument. Related software was available from Cyborg. However, to accommodate the speed at which data was updated on the instrument (every 16.67 msec), additional machine language programming was necessary to overcome delays in BASIC and LabSoft. The BASIC section of the program was designed to call a machine

language subroutine when ISAAC received a 'start acquire' signal from the instrument. This signal was a 12 volt timing pulse present on the analog board of the instrument. As this signal reached its appropriate 'high' state, which occurred every 16.67 msecs, four analog signals were collected and digitized. The data was collected in the following order: BG, I, BG0, and IO. To preserve the data for later calculations, the individual digitized values were saved from each sampling period. Generally, for each sample injected, 300 sets of BG0, IO, BG, and I signals were collected over a five second period at the end of the char cycle. Acquisition during the char cycle was triggered by the recorder signal dropping to zero volts. Another 300 data sets were collected during the atomization cycle; that is, the collection was triggered by the atomize signal dropping from five to zero volts. The 600 sets of data were saved to disk between sample injections.

Within-run Calculations: Figure 7 is a flow chart illustrating the order of events during data acquisition and various calculations performed. Most of these computations were executed between sample injections, since there was approximately two minutes during this period. The actual computations performed in these equations are shown in Appendix A. Referring to the flow chart, the first set of signals to be collected was the hollow cathode/deuterium sample and reference beam signals occurring during the instrument char cycle. Next, these hollow cathode and deuterium sample beam signals were averaged and displayed on the monitor for the operator to view for each sample. Once the

atomization cycle started, sets of these four signals were again collected. At this point, before any further calculations were performed, the operator was given the opportunity to ignore data for the current sample and go onto the next sample. If no intervention occurred, the timing corrections previously discussed were immediately applied to the deuterium sample beam signals collected during the atomize cycle.

All time-corrected signals were then used to compute the deuterium and hollow cathode lamp absorbance during the atomization cycle. The final corrected solution absorbance was then computed from these signals. Values for average deuterium and hollow cathode lamp drift were also computed between samples. The background and corrected solution absorbances were plotted on a monitor during the atomization cycle. This technique was very useful in predicting impending graphite tube failure. Frequently, the curve shapes plotted became erratic several injections before complete tube failure occurred. Figure 8 contains a real time plot of the deuterium background absorbance signal (highest signal) and the corrected hollow cathode absorbance signal. The peak height, peak area, and peak position were also reported for the corrected hollow cathode absorbance signal.

Data Storage: The flow chart in Figure 7 illustrates the parameters and values stored to disk for each run. These parameters include: tray position, peak crest, location of peak crest, each corrected absorbance value determined during the atomization cycle, each background absorbance value

computed from the first half of the atomization cycle and every fourth background absorbance value computed from the second half of the atomization cycle. The average hollow cathode and deuterium lamp drift values were also stored. If these values were less than .01 percent, zero was stored instead. Run parameters stored included the total number of injections per run, the element analyzed, and the number of points acquired per peak. The largest runs required three low density floppy disks for storage of both raw data and the computed values described above.

Post-run Calculations: The raw data values stored during the data acquisition were analyzed by secondary programs, which performed a number of calculations and sample labelling functions. A secondary file, or 'calculated' data file, was created by these programs after the raw data was analyzed. The main functions available in these programs are shown in Table B-1 in Appendix B.

The main goal after data acquisition was to compute concentrations for samples, standards, and QA samples. The next step in obtaining concentrations from raw data stored on the Apple II+ was to determine areas for each curve collected during data acquisition (item A for program 1 in Table B-1: area calculations). The difficulties encountered in this process are discussed in Appendix B along with special techniques used.

Once peak areas were computed, average peak height and peak area values had to be determined for each sample along with the relative standard deviation for peak height and area. The BCD

tray position previously stored with the raw data was used to determine replicates for each sample and was also later used in assigning sample identification information, dilution volumes, and adjusted sample weights. The sample labelling option (item C or D for program 1 in Table B-1) was generally selected next after area computation since any further data analysis required these labels. It was not necessary to enter adjusted sample weights if the sample was originally in a liquid state. Adjusted sample weights were only entered if samples were originally solid and underwent acid digestion. Other values entered upon selection of option C or D include label information ('STD' for standard, 'TEG' or 'EPA' for QA samples), dilution factors, and replicate number (the number of times an analysis was repeated on a sample). Data belonging to each sample could be reviewed to optionally flag outlying values if option B was selected in program 1.

After all options in program 1 were completed, the next task was to perform a second order non-linear regression on the data. This was accomplished by selecting options from program 2 listed in Table B-1. The regression was executed twice, once for peak height and once for peak area. Along with executing the non-linear regression, all other calculations necessary to determine final solution concentration, with the appropriate statistics, were also performed by program 2.

The regression was based on the first five standards analyzed during the run. Recalibration occurred every seven to eight samples to determine the direction and amount of any instrument

sensitivity change, which was compensated in calculation of solution concentration. Concentrations were computed for all solutions analyzed in the run, including standards, samples, and QA samples. Since there was no conversion back to a dry weight concentration for the fly ash leachates, the solution concentration was the final concentration reported for these samples. A relative standard deviation was calculated for each sample concentration and standard concentration computed from the regression. Also, a mean relative standard deviation (MRSD) and a relative mean standard deviation (RMSD) was computed for the first group of standards used in the regression. Finally, a third program was available to report the analysis results and raw data belonging to a run. The options for the report program are discussed in Appendix B.

Figure 5  
Components of data acquisition system

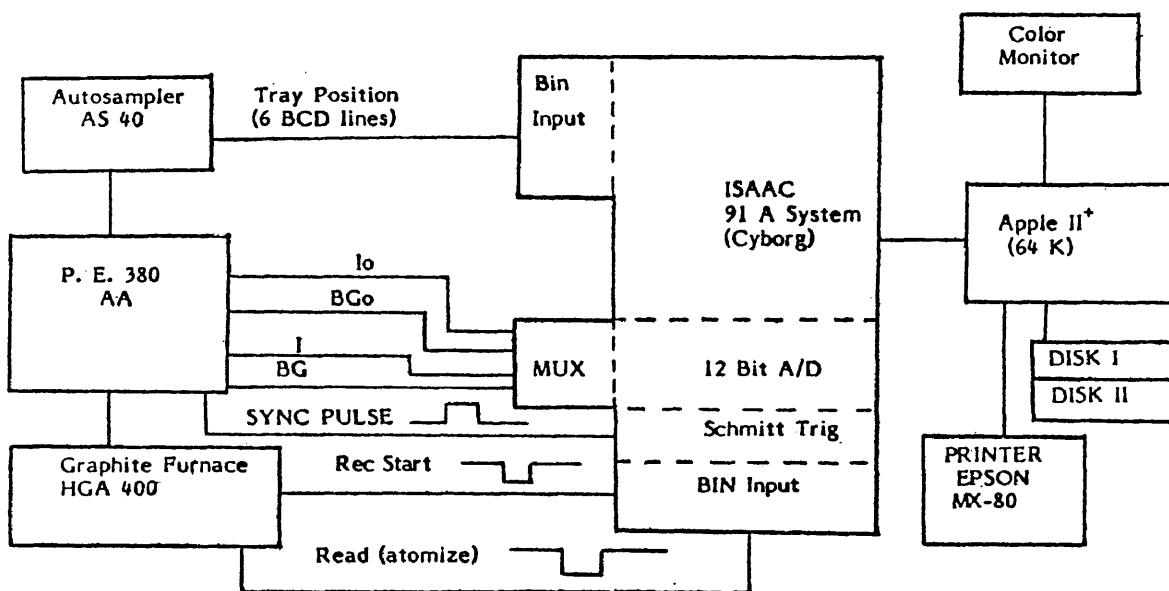


Figure 6

PE 380 timing diagram (60 Hz)

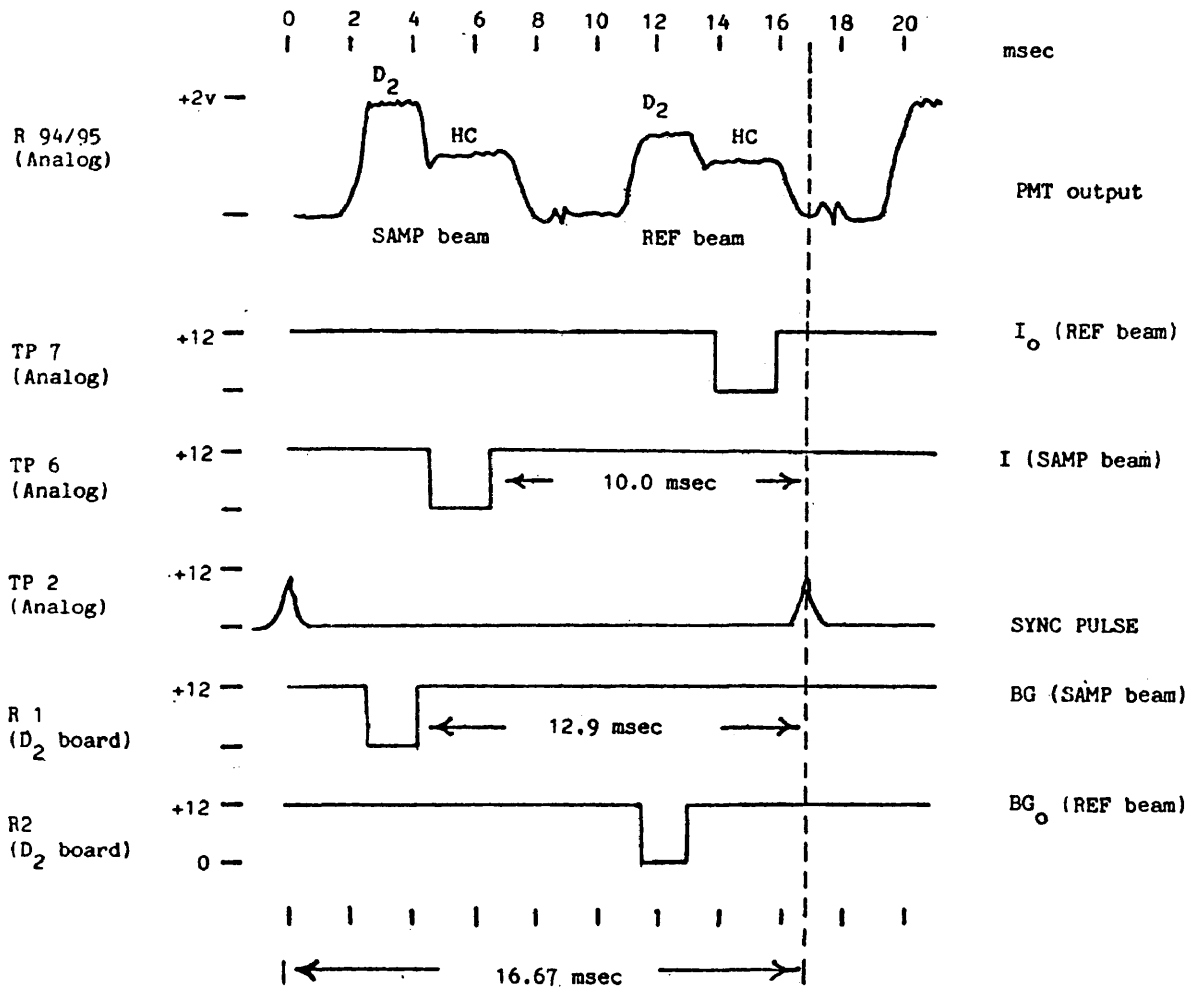


Figure 7

Data acquisition program flow chart

## Apple II DAQ Program

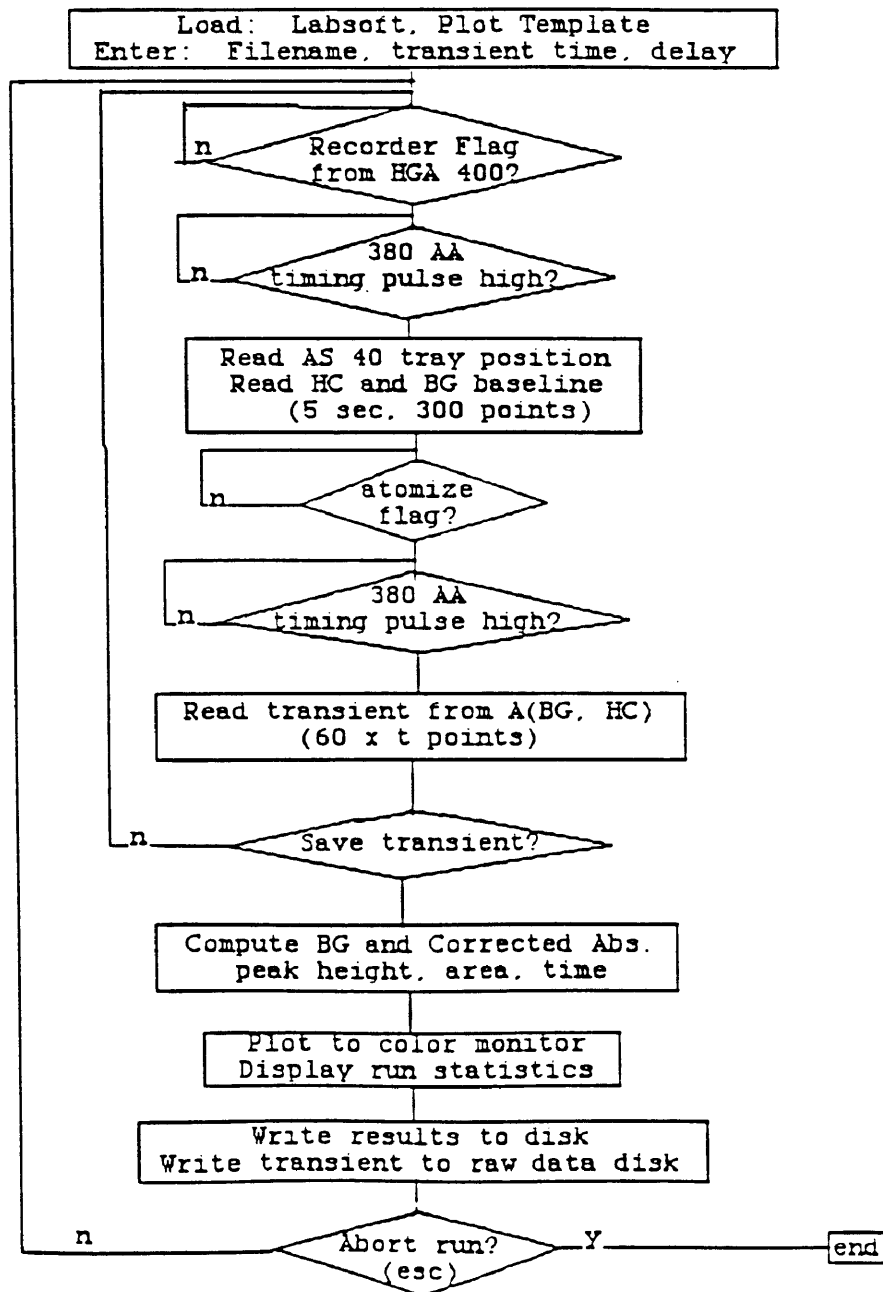


Figure 8

Transients produced during atomization as recorded  
by data acquisition system

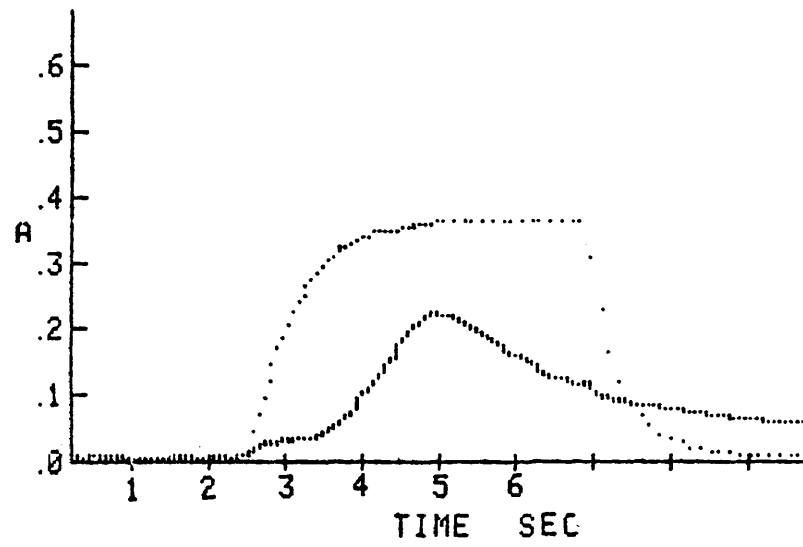
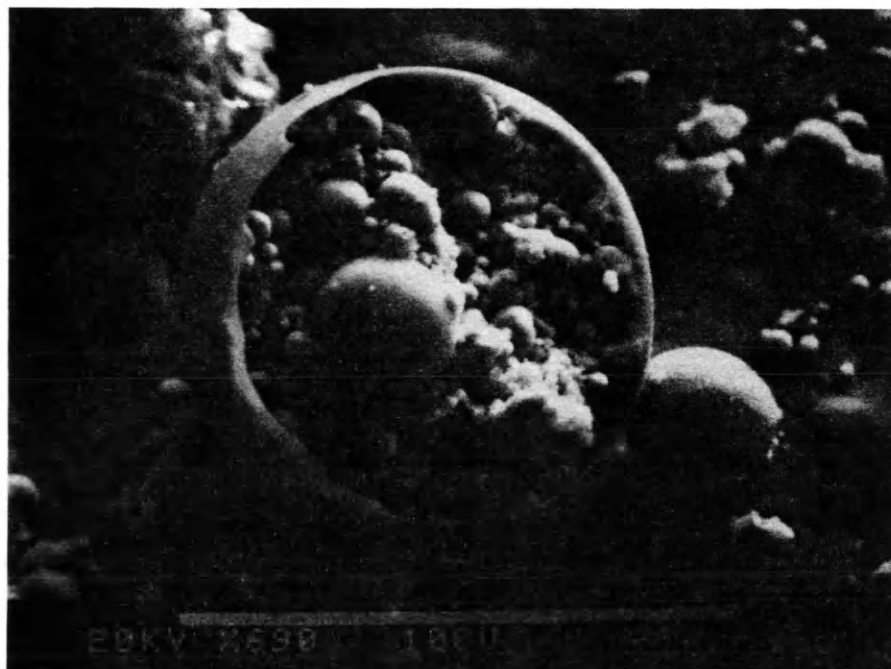


Figure 9

Scanning electron micrographs of Site 1 (a) and Site 2 (b) fly ash

(a)



(b)

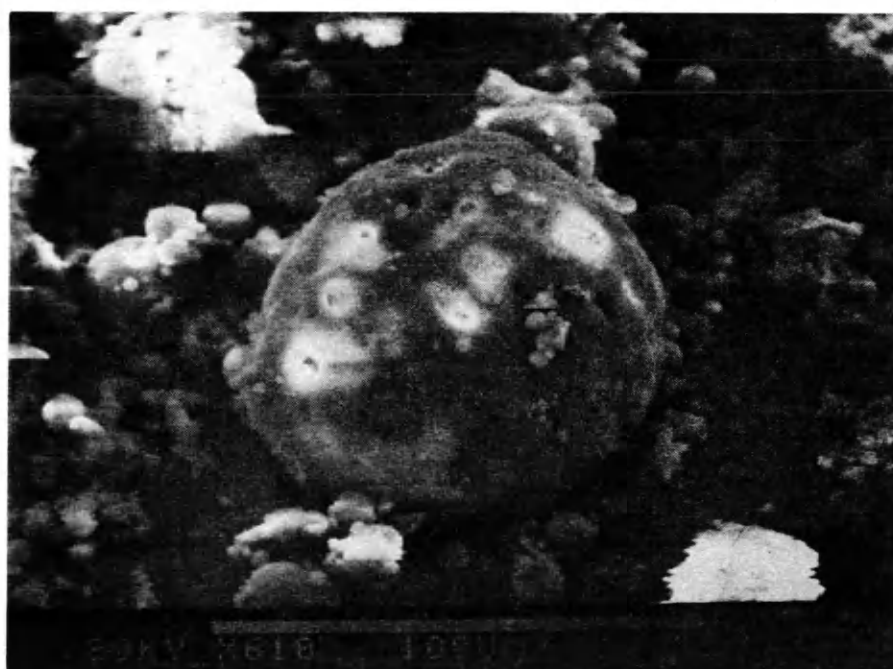


Table 5

Trace element analysis results generated by PDP-11 computer

AA RESULTS FOR V 410-5174 FLYASH LEACHATE ED  
 DATE ANALYZED DIL.VOL.SUR.BG(PPM) ABSORBANCE CORRECTION  
 23-JUN-85 1.000 0 0  
 PO(P ZERO) P1(P ONE) P2(P TWO) RMSD(STANDARDS)  
 7780.7 -.21582 -.0077069 .0050135  
 REGRESSION EQUATION: A/C=PO+P1A+P2\*(A\*\*2)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
---	---	---	---	---	---	---	---	---	----	----	----	----	----	----

SAMPLE ID	DILTN	SULTN	CON.	ABSORBANCE	SAMPLE	DRY.WT.	CONC.							
TYPE BK PG NM REP FACTOR	MEAN#RSD	MEAN#RSD	WEIGHT	MEAN#RSP	***S.D.	LABL								
31 77 2 0 .07611 .07582 2.4	459.2 2.3	0 .9961	2.4	.02373	STD									
31 77 3 0 .05742 .05788 1.0	380.9 .92	0 1.008	1.0	.01056	STD									
31 77 4 0 .03880 .03862 2.0	275.6 1.9	0 .9953	2.0	.01942	STD									
STDD 31 77 5 0 .01937 .01864 3.7	141.6 3.6	0 .01864	3.7	.000681	STDD *									
31 77 6 0.009850.009857 2.3	76.10 2.2	0 1.001	2.3	.02281	STD									
HTX 15130 31 1 1.000.000207 94	1.619 94	1.000	Less Than	.000391	HTX									
TEGC 38904 1 1 9.000.001509 21	11.76 21	0.001509	21.000	.00312	TEGC *									
EPA1 22138 1 1 2.000 .03750 2.3	269.2 2.2	1.000 .07501	2.3	.001699	EPA1									
5102 1510 2 1 1.000 .01971 2.0	149.6 1.4	1.000 .01971	2.0	.000391	5102									
5104 1510 4 1 1.000.000189 180	1.476 180	1.000	Less Than	.000699	5104									
31 77 4 0 .03880 .03932 .64	279.9 .40	0 1.014	.64	.006489	STD									
31 77 5 0 .01937 .01926 1.4	146.0 1.3	0 .9941	1.4	.01404	STD									
5105 1510 5 1 1.000 .02399 2.0	174.0 1.1	1.000 .02399	2.0	.000476	5105									
5106 1510 6 1 1.000-.00017 **	-1.333 .30	1.000	Less Than	.000389	5106									
5108 1510 8 1 1.000 .02665 2.0	191.9 .82	1.000 .02665	2.0	.000529	5108									
5101 1510 10 1 1.000 .01847 2.0	135.8 1.9	1.000 .01847	2.0	.000366	5101									
5107 1510 7 1 1.000 .02012 2.0	147.3 .45	1.000 .02012	2.0	.000399	5107									
5109 1510 9 1 1.000 .01758 3.2	129.5 3.2	1.000 .01758	3.2	.000564	5109									
31 77 4 0 .03880 .03638 .89	261.8 .74	0 .9375	.89	.008342	STD									
31 77 5 0 .01937 .01780 2.8	135.5 2.7	0 .9191	2.8	.02529	STD									
510 1510 11 1 1.000 .01844 2.0	123.5 .81	1.000 .01844	2.0	.000366	510									
510 1510 12 1 1.000 .01652 2.0	111.0 1.0	1.000 .01652	2.0	.000328	510									
510 1510 14 1 1.000 .01698 2.0	114.0 1.5	1.000 .01698	2.0	.000337	510									
510 1510 16 1 1.000 .01350 2.0	91.14 .68	1.000 .01350	2.0	.000268	510									
510 1510 18 1 1.000 .01443 2.3	97.29 2.2	1.000 .01443	2.3	.000326	510									
510 1510 22 1 1.000 .01043 4.0	70.67 4.0	1.000 .01043	4.0	.000417	510									
31 77 4 0 .03880 .03239 .66	236.4 .42	0 .8349	.66	.005476	STD									
31 77 5 0 .01937 .01582 1.9	120.9 1.9	0 .8168	1.9	.01569	STD									
510 1510 26 1 1.000 .01276 4.7	75.76 4.7	1.000 .01276	4.7	.000600	510									
510 1510 27 1 1.000 .01012 2.5	60.24 2.2	1.000 .01012	2.5	.000250	510									
510 1510 32 1 1.000 .009552 2.6	56.90 2.1	1.000 .009552	2.6	.000250	510									
510 1510 36 1 1.000 .008940 2.8	53.29 .27	1.000 .008940	2.8	.000249	510									
510 1510 44 1 1.000 .007405 3.3	44.19 .19	1.000 .007405	3.3	.000247	510									
510 1510 51 1 1.000 .007004 4.0	41.81 4.0	1.000 .007004	4.0	.000281	510									
31 77 4 0 .03880 .02789 .92	206.6 .77	0 .7188	.92	.006609	STD									
31 77 5 0 .01937 .01370 1.1	105.1 1.0	0 .7071	1.1	.008040	STD									
510 1510 61 1 1.000 .008006 3.6	41.24 1.3	1.000 .008006	3.6	.000286	510									
510 1510 72 1 1.000 .006476 4.4	33.38 2.0	1.000 .006476	4.4	.000285	510									
510 1510 81 1 1.000 .004532 6.3	23.38 2.8	1.000 .004532	6.3	.000284	510									
510 1510 94 1 1.000 .005318 5.4	27.43 1.8	1.000 .005318	5.4	.000284	510									
510 1610 12 1 1.000 .002601 11	13.43 9.2	1.000 .002601	11	.000283	510									
510 1610 39 1 1.000 .001282 36	6.619 36	1.000 .001282	36	.000463	510									
EPA1 22138 1 1 2.000 .03726 2.0	185.0 .85	1.000 .07452	2.0	.001480	EPA1									
31 77 4 0 .03880 .02418 1.4	181.0 1.4	0 .6231	1.4	.008995	STD									
31 77 5 0 .01937 .01175 .51	90.43 .10	0 .6064	.51	.003100	STD									

REPLICATES: BK PG NUM REP DRY MEAN S.D. REFS  
 22 138 1 1 .0747641 .00170 2

\*\* DATA STORED \*\*

Table 6

Portion of PE 380 run sheet illustrating vanadium analysis conditions

Graphite Tube Number: 34-124-50

STEP	1	2	3	4	5	Flameless AA	Analyst DowDS
TEMP (°C)	120	1600	2700	2800		Run <sup>410</sup> 5174 - Sample <sup>FLYASH</sup> LEACHATE	Date 6/23/85
RAMP TIME (s)	10	10	0	1		Element <input checked="" type="checkbox"/>	<input checked="" type="radio"/> ABS/ <input type="radio"/> CONC
HOLD TIME (s)	60	20	2	3		Wavelength 318.4nm	Filter: <input type="radio"/> IN/ <input checked="" type="radio"/> OUT
RECORD	24					Slit(ALT) .7 nm	D <sub>2</sub> : <input checked="" type="radio"/> ON/ <input type="radio"/> OFF
READ	24 -5					Lamp 15 ma	MODE: TC INT <input checked="" type="radio"/> PEAK
BASELINE						Samp Volume 50µl	Method # 1
MINI FLOW						Alt volume	STD ADD CONC
ml/min						Alt soln	
STOP FLOW							

Table 7

Equations derived for absorbance calculations

(' values indicate signals measured immediately before atomization)

---

- A)  $A = A(t) - A'$  ( $A' = \log (I_0'/I')$  and  $A(t) = \log (I_0/I)$ )
- B)  $A = \log (I_0/I) - \log (I_0'/I')$
- C)  $A = \log (I_0/I) + \log (I'/I_0')$
- D)  $A = \log (I_0/I * I'/I_0')$
- E)  $A = \log (I'/I * I_0/I_0')$
- F)  $A = \log (I'/I)$  (since  $I_0' = I_0$ , autogain circuit)

Following this approach, equations for background absorbance and corrected absorbance were derived :

- G)  $A(BG) = \log (BG'/BG)$
- H)  $A_{corr} = A - A(BG)$

Table 8

Voltages measured at sample and hold amplifiers in the PE 380 system  
with corresponding computed absorbances

Copper lamp current/ absorbance conditions	BG0	BG	I0	I	<sup>a</sup> A	<sup>b</sup> A(BG)
Cu lamp - 10ma						
Balance*	2.300	1.770	2.480	1.010		
0.35 absorbance	2.300	0.800	2.480	0.458	0.343	0.345
0.80 absorbance	2.270	0.277	2.480	0.160	0.800	0.805
Cu lamp - 12ma						
BGen 26.0**	1.695	1.308	2.480	1.017		
0.35 absorbance	1.693	0.582	2.480	0.455	0.349	0.351
0.80 absorbance	1.693	0.200	2.480	0.160	0.803	0.815
Cu lamp - 9ma						
BGen 44.5	2.590	1.990	2.480	1.013		
BGen 39.5	2.590	1.970	2.480	1.014		
0.35 absorbance	2.590	0.885	2.480	0.453	0.349	0.350
0.80 absorbance	2.590	0.305	2.480	0.161	0.800	0.812

$${}^a A = \log (I'/I) \quad I' \text{ represents balance conditions}$$

$${}^b A(BG) = \log (BG'/BG) \quad BG' \text{ represents balance conditions}$$

\* PE 380 balance conditions from autogain circuitry  
\*\* deuterium lamp energy

## CHAPTER IV

### RESULTS AND DISCUSSION

#### Chemical Availability from Chisman Creek Fly Ash

In this study, several sample types were analyzed for major, minor, and trace metal content by two different methods. Leachates of weathered fly ash were generated from chromatography columns operated at several pHs and ionic strengths. A profile of the leached elements was provided by proton-induced X-ray emission (PIXE) analysis. Since this technique allowed many elements to be analyzed simultaneously, a complex profile of aluminum, silicon, calcium, vanadium, manganese, iron, nickel, copper, gallium, germanium, arsenic, selenium, rubidium, strontium, yttrium, barium, and lead could be efficiently obtained. The leachates were also analyzed for vanadium by atomic absorption spectrophotometry. To provide an estimate of the total 'available' elemental content, other samples were produced by mixing 15.0 grams of fly ash with 20.0 mls of 5N nitric acid at room temperature. This technique was expected to estimate trace elements available under strongly acidic non-oxidizing conditions. These samples were also analyzed by proton-induced X-ray emission.

Table 9 shows the main elements released from a 5N nitric acid leach of both site 1 and site 2. As mentioned previously, the 5N leach more closely simulates natural conditions when evaluating total element availability than the hydrofluoric acid technique commonly used with geological samples. As trace metals are released with hydrofluoric acid, the silicate mineral's crystalline structure is actually dissolved. Although this method releases the greatest level of elements, it does not realistically model natural availability. The addition of fluoride has a further negative effect because of its interference with any subsequent PIXE analysis. Another alternate method, the aqua regia digest, also releases a larger portion of all elements than the 5N leach.

The ash analyzed in the current study had been exposed to the environment for a period of about 7 to 22 years. This weathering undoubtedly reduced the level of various elements found in the fly ash leachates compared to fresh fly ash. On the other hand, leachates analyzed in the present work provide an estimate of future environmental risk, since they measure trace elements currently available from the already weathered fly ash at the site.

In order to understand the trends in metal release from fly ash at various pHs, it is important to understand the structure and formation of fly ash particles. Coal is believed to form molten salt particles under the conditions and temperatures in a combustion furnace. As these particles condense, elements partition themselves into glass, quartz, and

mullite phases (22). During this process, trace elements may be forced out of other phases and into the glass phase; the glass phase forms a 'cement' which holds the quartz and mullite phases together. As this partitioning occurs, certain elements become concentrated on the surface of fly ash particles. Sulfur, molybdenum, arsenic, and other trace elements may be preferentially concentrated at the particle surface because they were last to condense on the fly ash particle core (22). The fly ash 'core' is composed of thermally stable minerals, called aluminosilicates (3,23,24,25). Some elements may undergo a 'diffusion' process from the inner particle to the surface (22). Regardless of what phenomenon is responsible for surface enrichment of elements, the elements in this surface layer should be available first from fresh ash when weathering occurs.

In the present work, the pattern of metal availability from weathered fly ash cannot be expected to follow the same trends displayed by fresh ash. Despite the age of the fly ash used in the current study, patterns for many elements are still evident.

Previous reports show that electron micrographs made of weathered fly ash are noticeably different than those made of fresh fly ash. Micrographs of relatively fresh ash contain spheres of actual fly ash particles that are often covered with a coating of salt crystals deposited on the surface (26,27). The particles are called plerospheres (28) because they contain smaller spheres inside, which is evident when the particle is broken. This structure has been proposed to

occur from the boiling and production of gas in the inner core as the particle enters the high temperature combustion zone (28). Any crystals present on the fly ash particle form slowly after the liquids on the surface crystallize (28). The larger crystals, 20  $\mu\text{m}$  and larger, are composed chiefly of anhydrite ( $\text{CaSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (29,28). Calcium is probably chiefly present from intrusions of  $\text{CaCO}_3$ . The larger crystals contain  $\text{H}_2\text{SO}_4$ , which contribute to leaching of metal oxides producing microcrystals of metal sulfates on the surface (28). Other surface crystals are usually made of high concentrations of sodium, calcium, sulfate, hydroxide, and boron. Micrographs of weathered ash show this surface coating to be flaky in appearance (26).

Electron micrographs of fly ash used in this study are shown in Figure 9. The 'plerosphere' structure discussed above is evident in the site 1 fly ash micrographs. Although several micrographs were taken of site 2 fly ash at the same magnification, this type of structure was not found. The micrograph included for the site 2 fly ash was the only picture taken that included larger particles. The fly ash analyzed in the current study contained high levels of calcium despite its weathered state, yet surface crystals were not present in any of the micrographs. Investigators have proposed that these elements are not just present as discrete salts but as surface adsorbed or admixed salts which cannot be dissolved in a short period of time (1,30).

The buffer compositions were chosen on the basis of recent

groundwater measurements in monitoring wells located in pit C (16). Wells unaffected by fly ash had a pH near 8. Wells within pit C had varying acidities and one well was measured at pH 3.5. Accordingly, pH 3.0 was chosen to represent the most strongly acidic, pH 5.0 represents mildly acidic conditions, and pH 8 represents the usual acidity of groundwater in this area.

Various plots were generated to show trends between concentration and volume eluted from each column under varying conditions, including pH, site, and ionic strength. The following paragraphs will compare and contrast element behavior under the varying conditions used in all columns. In all plots, 'open' symbols (such as circles, triangles, squares, etc.) are used to represent concentrations for the specific elements discussed. In cases where element concentration was less than instrument detection limits, the symbol for that particular concentration value is darkened.

Plots in Figure 10 display calcium, strontium, and barium concentrations during the leaching process for the pH 3, pH 5, and pH 8 columns. The exponential decrease in concentration exhibited in the plots could indicate these elements are present as a type of salt which initially dissolves very quickly. This is most evident for Ca in the 510, 511, and 521 columns, where the concentration dropped approximately 100 ppm during the first 200 mls of leaching. In whatever form Ca may have been present, its solubility is the greatest under pH 3 conditions as indicated by Ca concentrations remaining high throughout the leaching process. The same general trend exists

for Sr, although its soluble levels are about one order of magnitude lower than Ca. Note that there appears to be a pattern between the .01 and .1 ionic strength pH 5 columns. For both Ca and Sr, solubility seems to be hampered under the higher ionic strength conditions, as indicated by low Ca and Sr levels reached quickly. Trends displayed by Ba under pH 3 conditions, which were similar to Ca and Sr, disappeared in the pH 5 columns. In fact, trends for Ba in the 510, 511, and 520 columns show increasing concentration, although average Ba levels are not very different between the two pHs. No data was available for Ba at pH 8.

Sodium trends were not investigated in any of the columns because sodium was present in buffer components used for the pH 3 and pH 5 solutions. However, rubidium trends are shown in Figure 11 along with strontium and yttrium. In the pH 3 columns, both rubidium and yttrium display trends similar to strontium, as shown in Figure 10. Strontium levels are consistently higher than all other elements in any of the columns illustrated in Figure 11. This is consistent with the data in Table 9, showing soluble Sr levels to be about 15 to 40 times higher than either Rb or Y after a 5N nitric acid leach. Yttrium levels fell almost two orders of magnitude as the pH increased from 3 to 5, illustrating yttrium's greater solubility at pH 3. Rubidium levels also fell under pH 5 conditions, but not so dramatically. Fluctuations develop in both yttrium and rubidium patterns as their concentrations drop to near detection limits. No data was available for any of the elements under pH 8

conditions.

Figure 12 includes plots of aluminum, calcium, iron, manganese, and silicon. Typically, concentrations of aluminum, silicon, and iron are high in fly ash, reflecting levels in the type of coal used. Silicon, aluminum, iron, and calcium are the second, third, fourth and fifth most abundant elements in the earth's crust, respectively. Manganese concentrations are lower in magnitude but it can still have an important effect on other elements. This phenomenon will be discussed in more detail in a later section. Note that detectable manganese levels in the pH 3 columns, being most soluble, are two to three orders of magnitude lower than the other elements.

Silicon concentrations remain at a fairly constant level within each column, supporting the theory that silicon is a matrix element. Many researchers believe that under conditions in a combustion furnace, the lighter elements in coal volatilize and eventually condense on the thermally stable aluminosilicate matrix (26,1,23). The matrix compounds include  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{FeO}$ , and  $\text{MnO}$  (13).

Of the matrix compounds, both aluminum and silicon constitute approximately 84% of the fly ash content (31) yet these elements are eluted at low concentrations. About 91% of silicon and 63% of aluminum exist in aluminosilicate 'glass' (31). Elements locked in the aluminosilicate glass are tightly bound; that is, they are only soluble in HF.

Although silicon levels remain fairly steady within each column,

there is a small decrease in solubility when going from pH 3 columns to pH 5 and pH 8 columns. Iron levels fall drastically under the same changes in pH. Iron levels average about 50 ppm at pH 3 and only about .1 ppm at pH 5. This reflects iron's greater solubility at low pHs. Also, iron may be present in several forms of fly ash that explain its very different behavior at pH 5 and pH 8. About 68% of iron is believed to exist in the aluminosilicate 'glass' but it also exists in more soluble forms, such as magnetic spinels existing in fly ash and in sulfate, phosphate, and fluoride salts (31,22). Although aluminum levels were approximately the same as iron, silicon, and calcium in the pH 3 columns, its concentration was not well determined due to the inherent problems in its analysis with PIXE. Even aluminum levels of about 50 ppm were near the detection limits for this element.

The process that occurs when gases condense on the fly ash matrix causes a preferential concentration of certain volatile elements on the shell of the fly ash particle (26). These lighter elements include arsenic, cadmium, molybdenum, antimony, selenium, tungsten, zinc, cobalt, chromium, copper, and vanadium (12,32,33,34). This process becomes more important for smaller fly ash particles because of their larger surface area-to-mass ratio (13). The concentration of certain elements on the surface layer plays a critical role in the element's availability in the presence of leaching agents. The elements comprising the outer core are usually present as surface salts and should be available first when fresh

ash is leached. Eventually, the concentrations of these elements should decrease and the matrix elements (aluminum, iron, silicon, calcium, and manganese) should predominate. The pattern of metal release is more difficult to predict in older ash since the stage of particle dissolution is unknown.

#### Environmental Significance of Trace Element Leachates

Trace elements frequently 'track' the matrix components silicon, aluminum, and manganese. Studies on leaching of matrix components have shown that there is an association between matrix components and certain trace elements (1,35,36). The experiments involved using extraction techniques with ammonium oxalate and hydroxylamine hydrochloride. Ammonium oxalate preferentially extracts aluminum and iron (1,35) while hydroxylamine hydrochloride extracts manganese (1,36). Matrix compounds which contain aluminum, iron, and manganese attract trace metals due to the presence of active sites on their surface. Manganese has a sorptive capacity fifteen to twenty times higher than aluminum or iron (1,37). Consequently, compounds containing manganese are much more active than those containing either iron or aluminum. However, since manganese is often present in much lower concentrations than aluminum or iron, its scavenging effect is usually not as great as these elements. Surface area and dielectric are the physical properties which cause trace element

attraction to iron, aluminum, and manganese compounds (1,29). The charged surfaces on these compounds change with pH. This phenomenon causes metallic cations, or any charged species, to be attracted to the compound's surface. Manganese may have a greater available surface area than either aluminum or iron, thus explaining its greater sorptive capacity (1,29).

Studies of arsenic illustrate trace metal attraction to matrix compounds containing iron. Normally arsenic exists as oxyanions and oxyacids from pH 4 to pH 12 (30,38). The absence of arsenic oxyanions can be explained by an active iron surface scavenging this ion. Iron probably exists as amorphous iron oxyhydroxide, which is commonly present in fly ash (30). The isoelectric point of this compound occurs at high pHs so the surface retains a positive charge throughout most of the pH range (30,39). The charged surface probably attracts the negatively charged arsenic oxyanion, thus reducing its 'free' concentration. This process may also act on the uncharged arsenious acid.

To understand the association of matrix elements with other trace elements, it is important to understand both the mineralogy of coal and conditions present inside the coal furnace. Several studies have associated the matrix element iron with arsenic, chromium, cobalt, and zinc (29,1). Sulfides of iron and arsenic are volatile and may condense at the same temperature, further explaining the association of the two elements (1). Figure 13 contains plots of iron, arsenic, and copper. The iron and arsenic data show many similarities in the

pH 3 site 1 column. Trends are also evident in the pH 3 site 2 data. Some trends are present in the pH 5 columns, although both elements' concentrations are closer to detection limits which makes real similarities difficult to observe. Data was not available for either chromium or cobalt; therefore, these elements were not included in the plots. Zinc data was not included because it was not known what percentage of its concentration was due to contamination. Zinc is a common contaminant in the laboratory and, therefore, difficult to analyze properly. Copper was substituted for zinc due to its proximity to zinc on the periodic chart. The copper data followed a more exponential decrease in the pH 3 columns, which is quite different from iron's trend. Although no previous information was available about calcium and its behavior as a matrix 'scavenger', its pattern follows quite closely with copper (see Figure 14). The similarity may also be due to copper's, and other cationic metals, association with anionic salts, such as phosphate, and calcium's presence as apatite ( $\text{Ca}_3(\text{PO}_4)_2$ ) (31). This similarity is most noticeable in the pH 3 experiments but also present at pH 8 and in some of the pH 5 columns. The concentrations are closer to detection limits in the pH 5 experiments as noted by the irregular patterns. The matrix element manganese has been associated with cadmium, lead, and nickel (1). Previous studies have shown that about 24% of manganese is found on the surface of the fly ash particle, which is consistent with patterns for lead, cadmium, and nickel (1,40). Some researchers have proposed that these

elements had prior geological association with manganese, which could explain an association between these elements. Cadmium was not included in any of the plots since it could not be detected in any of the samples. It is difficult to see any trends with manganese in the pH 3 data although the other elements are detected (see Figure 15). The pH 5 data for manganese, nickel, and lead are too close to detection limits to make any judgements. No data was available for any of these elements in the pH 8 experiments. Nickel concentrations are too close to detection limits in the remainder of the columns for any similarities to be seen.

It becomes more difficult to predict trends when attempting to leach trace elements from the matrix compounds. The processes controlling trace metal release are probably solubility dependent. The solubility of the matrix 'scavenger' may dictate the release of the associated trace metal (1). This process can be quite complex. Some trace elements display concentration patterns which cannot be explained by solubility of the matrix compound associated with it.

Other processes, which are pH dependent, also play an important role. Previous studies have determined the percentage of several elements that should be leachable under strongly acidic (pH = .5) or strongly basic (pH = 11.9) conditions (41). Data from this study illustrates that more than 30% of the total amount of arsenic, boron, cadmium, fluorine, molybdenum, and selenium should be available under acidic conditions. Between 10-30% of chromium and vanadium and between

1-10% of beryllium, copper, and zinc should be available under strongly acidic conditions. More than 30% of molybdenum should be available under strongly basic conditions. Between 1-10% of boron, fluorine, and selenium and between .1-1.0% of arsenic and chromium should be available under these conditions. Less than .1% of beryllium, cadmium, copper, vanadium, and zinc should be available at strongly basic pHs.

It is a well-known fact that many transition elements are more soluble at acidic pHs than neutral pHs (41,42). Transition metal behavior is unpredictable at high pHs due to the possible formation of anions. These anions are soluble at high pHs when the corresponding metallic cation would precipitate from solution (41,42). The formation of molybdate, borate, fluoride, selenate, arsenate, chromate, and vanadate are examples of this behavior (41).

Plots of arsenic shown in Figure 16 clearly display this dual trend at pH 3 and pH 8. Selenium displays greater solubility at pH 8 than at pH 3 in Figure 16, although the pH 3 site 1 levels are relatively high. Vanadium, on the other hand, clearly displays a higher solubility at pH 3. Refer to Table 9 for total 'available' levels of these elements as determined by the 5N nitric acid leach technique. Reliable data was not available for beryllium, zinc, fluorine, chromium, and cadmium to make any conclusions about their behavior.

Figure 10a

Comparison of Ba, Ca, and Sr levels in pH 3, pH 5, and pH 8 columns

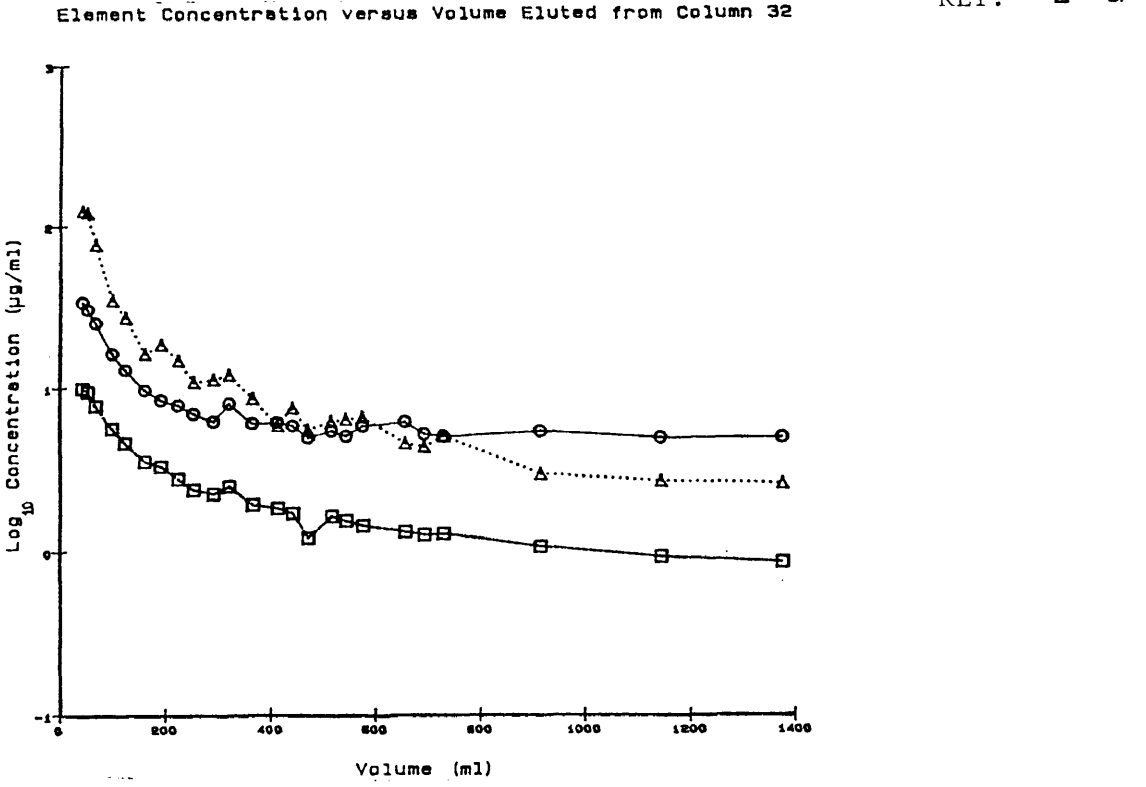
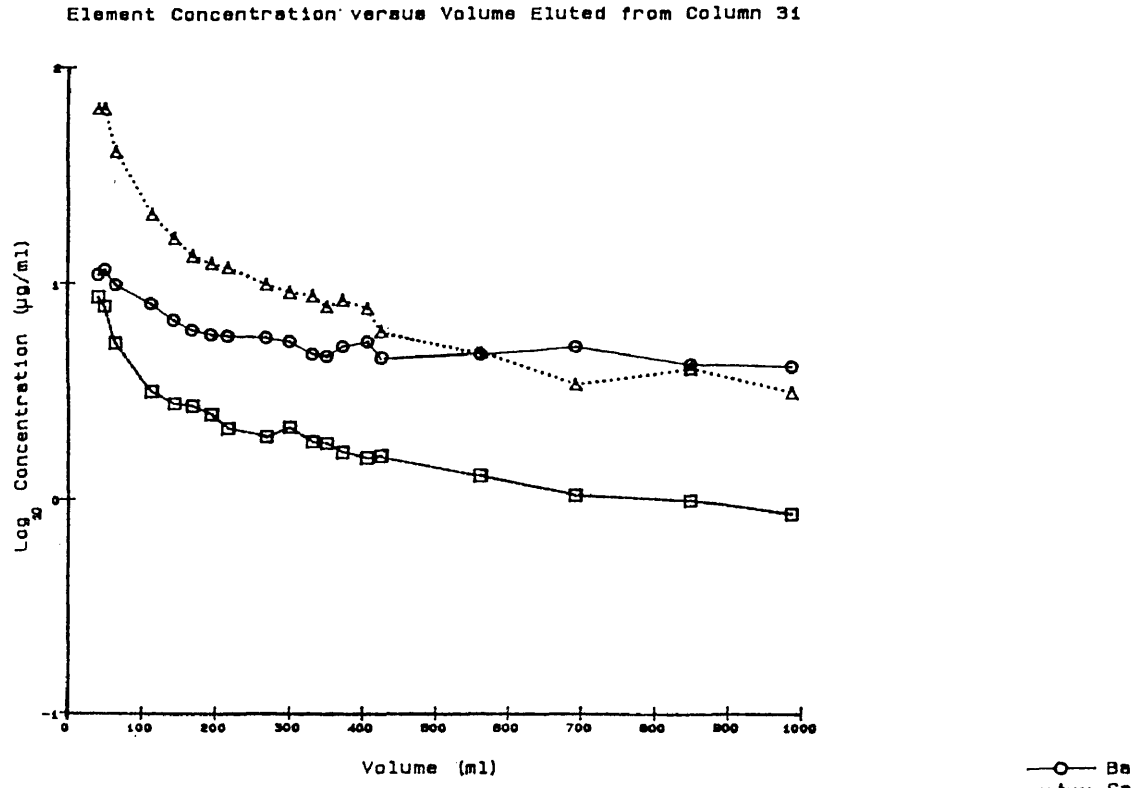
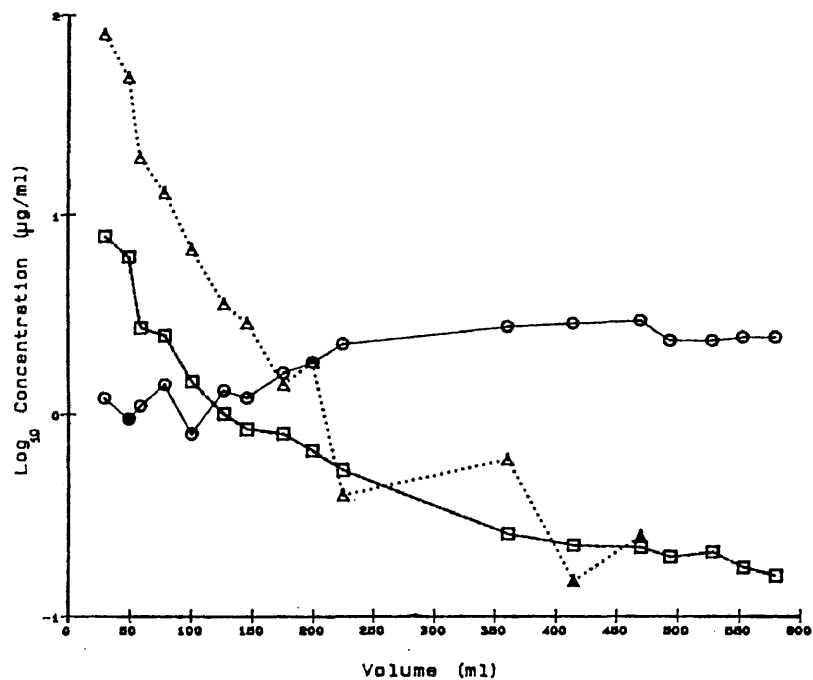


Figure 10b

Comparison of Ba, Ca, and Sr levels in pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 510



KEY:  
 ○ Ba  
 △ Ca  
 □ Sr

Element Concentration versus Volume Eluted from Column 511

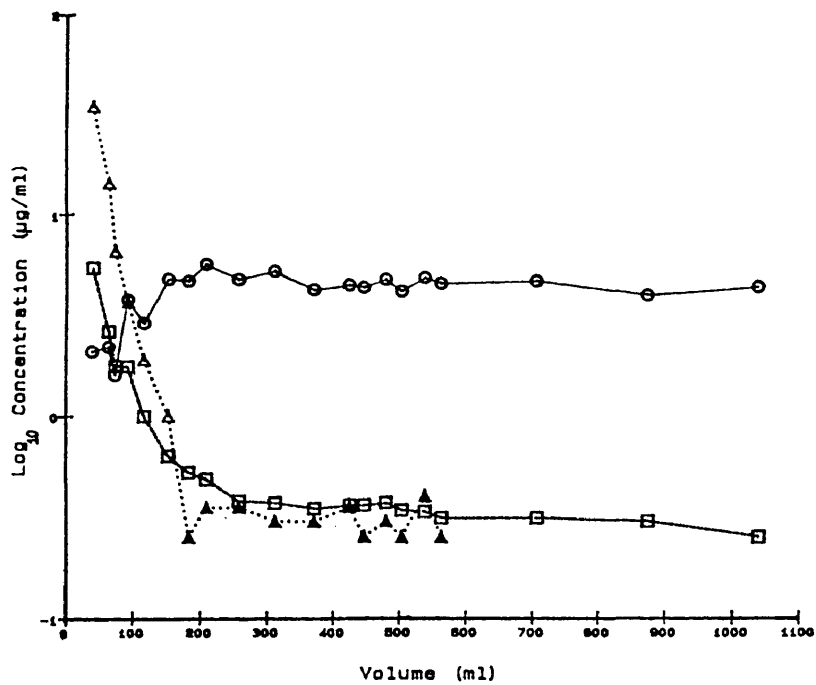


Figure 10c

Comparison of Ba, Ca, and Sr levels in pH 3, pH 5, and pH 8 columns

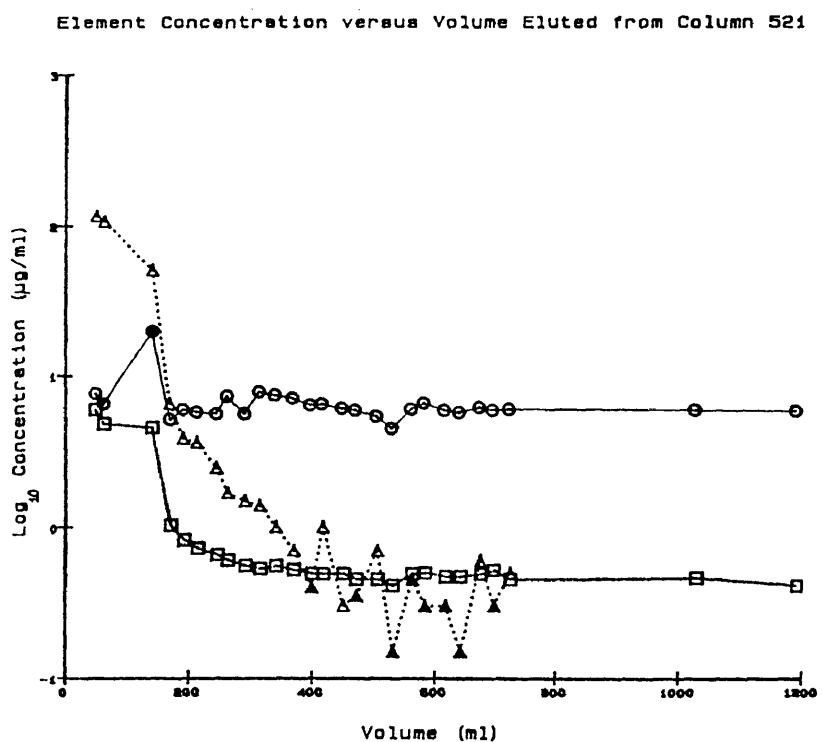
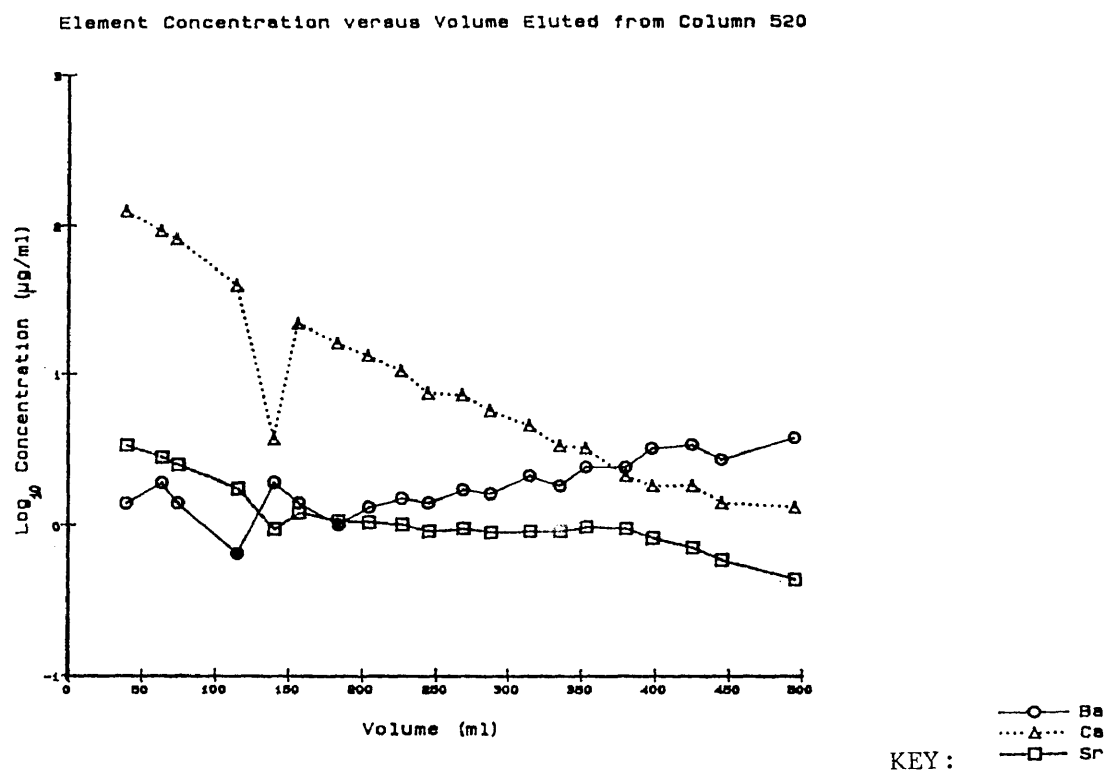
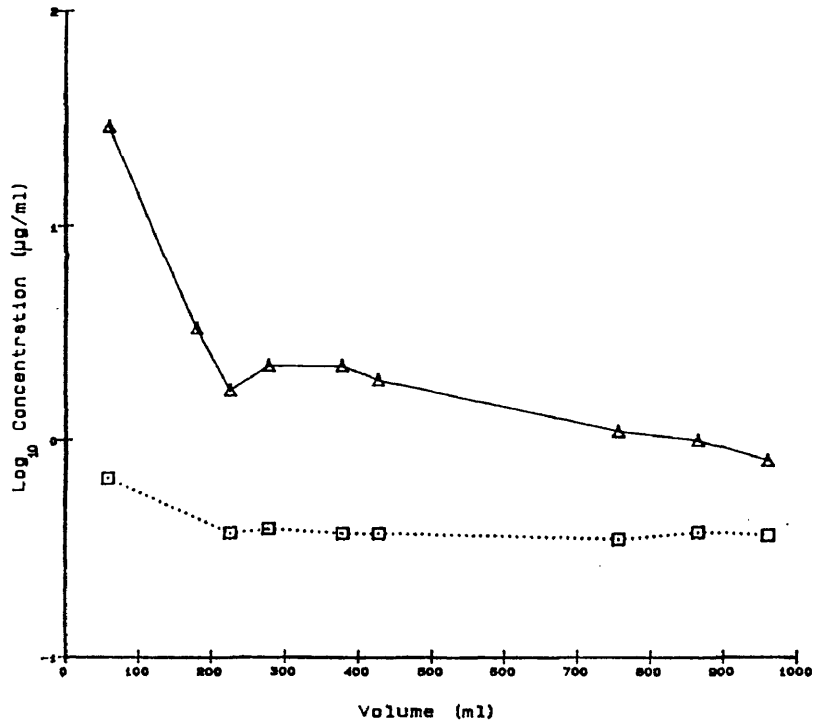


Figure 10d

Comparison of Ba, Ca, and Sr levels in pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column B1



KEY: —△— Ca  
 .....□..... Sr

Element Concentration versus Volume Eluted from Column B2

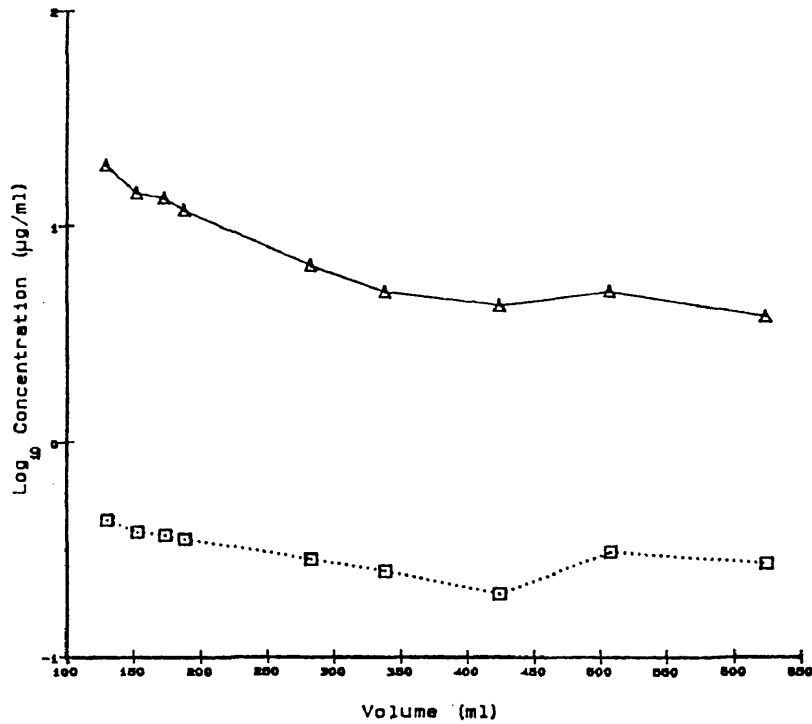
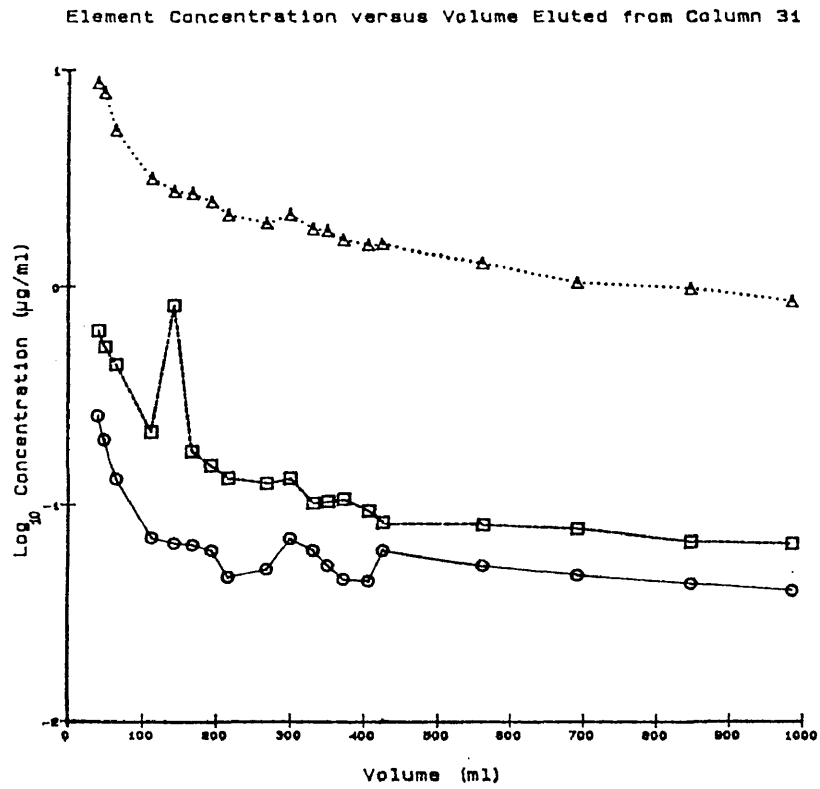


Figure 11a

Comparison of Rb, Sr and Y levels in pH 3, and pH 5 columns



KEY: ○ Rb  
△ Sr  
□ Y

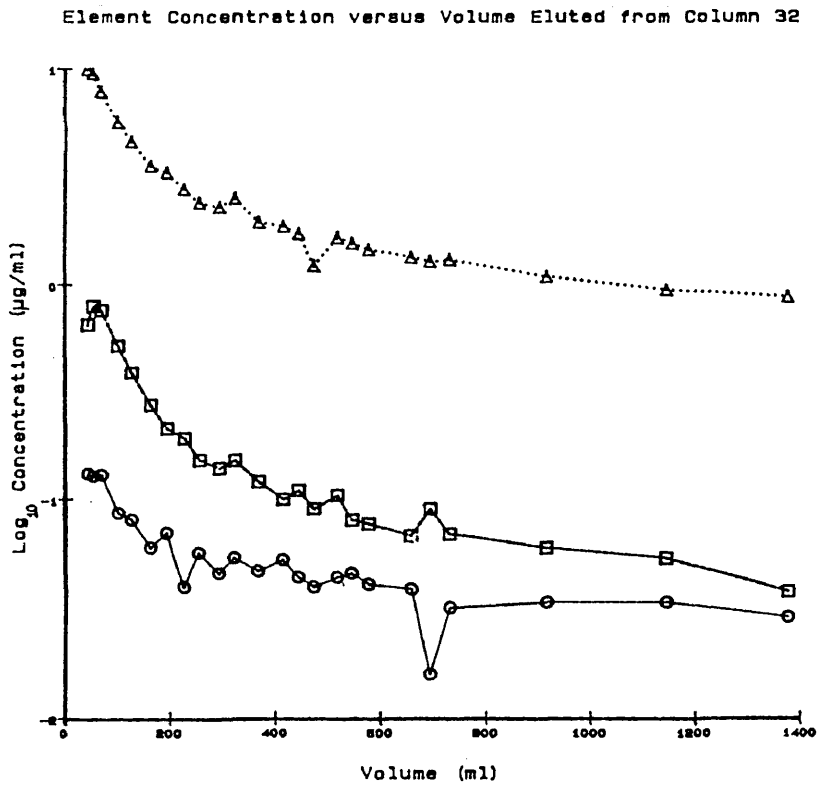


Figure 11b

Comparison of Rb, Sr, and Y levels in pH 3, and pH 5 columns

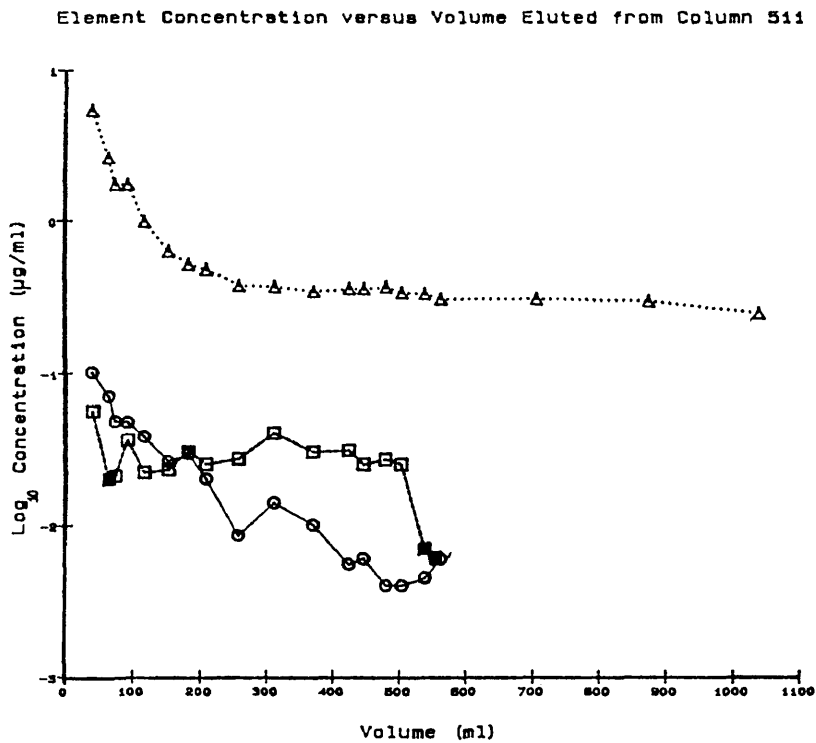
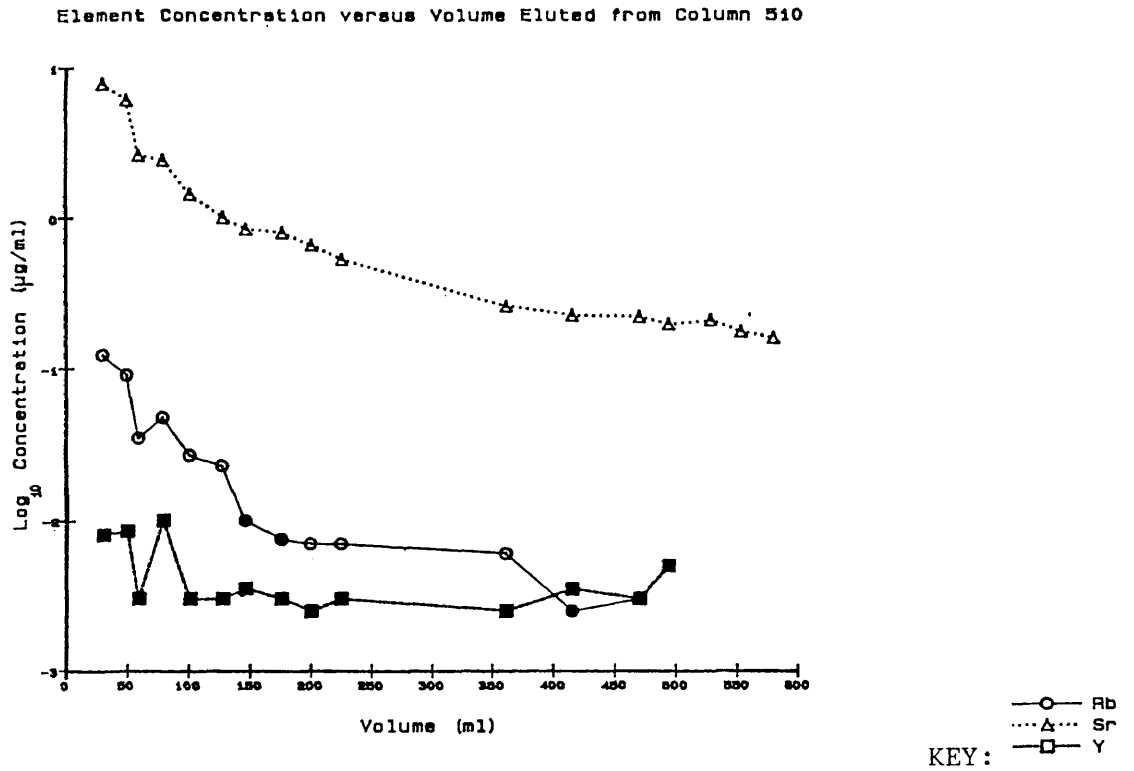


Figure 11c

Comparison of Rb, Sr, and Y levels in pH 3, and pH 5 columns

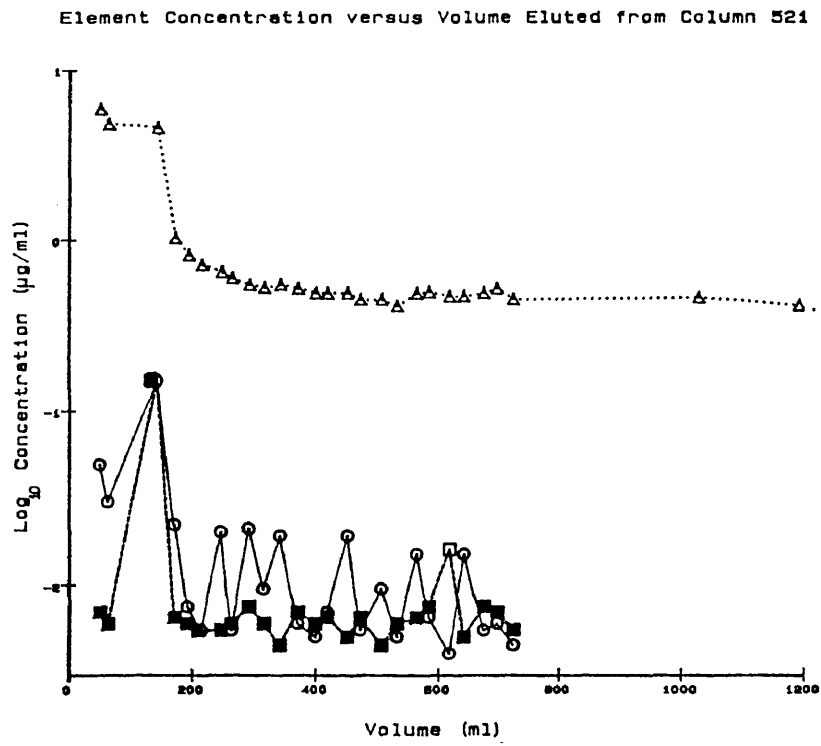
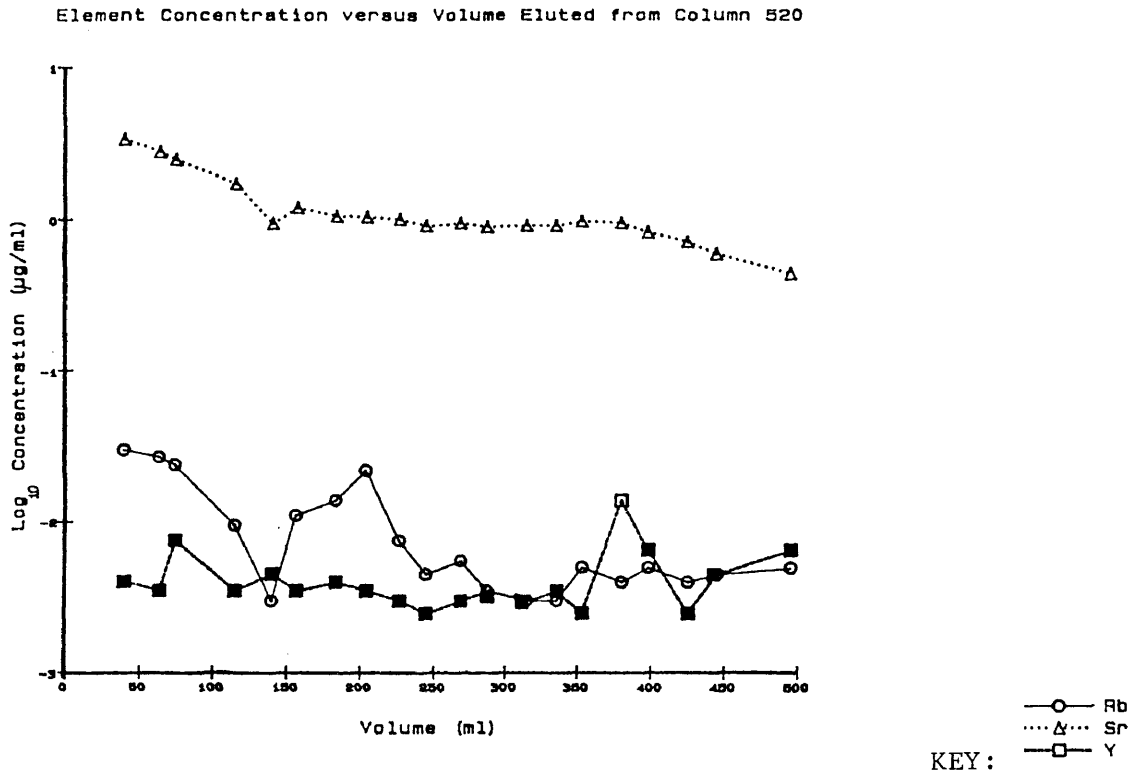
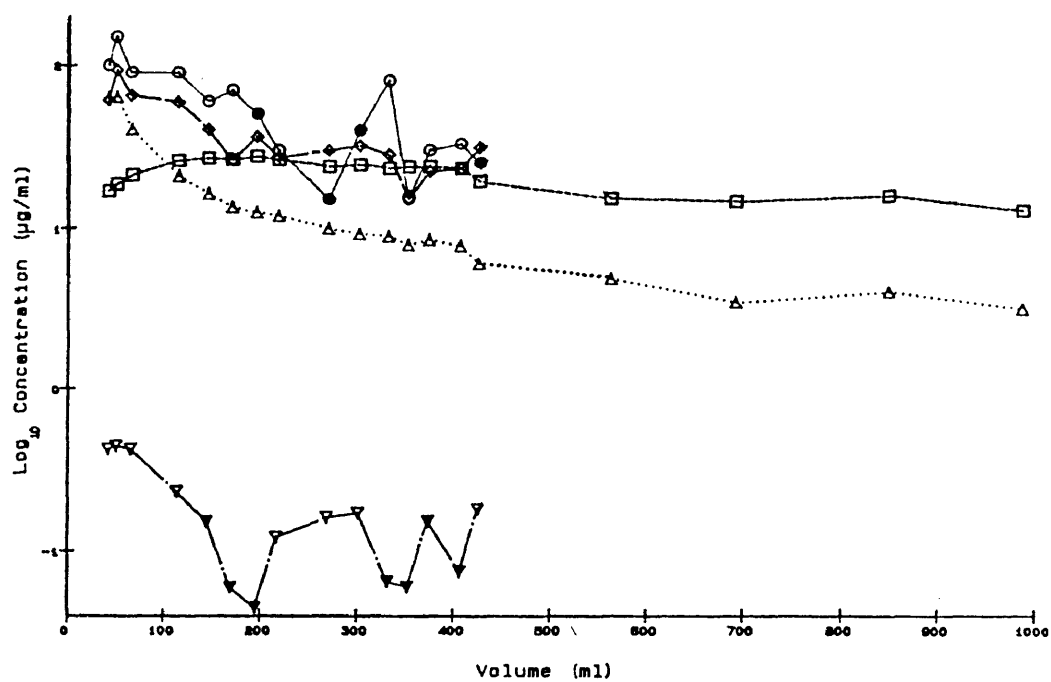


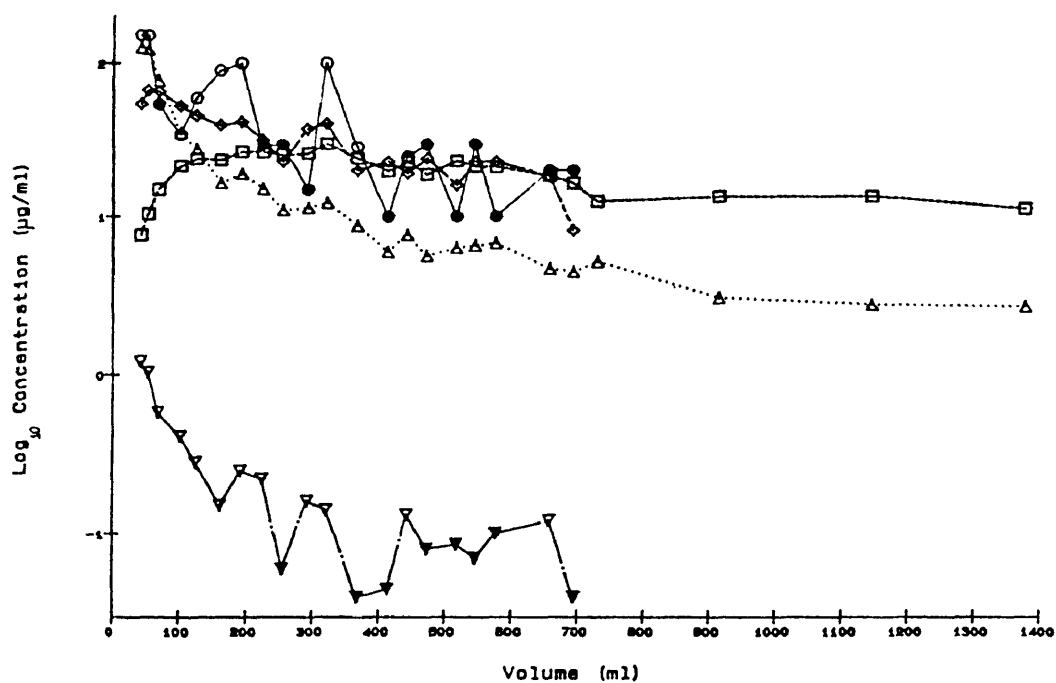
Figure 12a

Comparison of Al, Ca, Fe, Mn, and Si levels in  
pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 31



Element Concentration versus Volume Eluted from Column 32



KEY

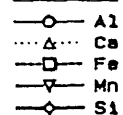


Figure 12b

Comparison of Al, Ca, Fe, Mn, and Si levels in  
pH 3, pH 5, and pH 8 columns

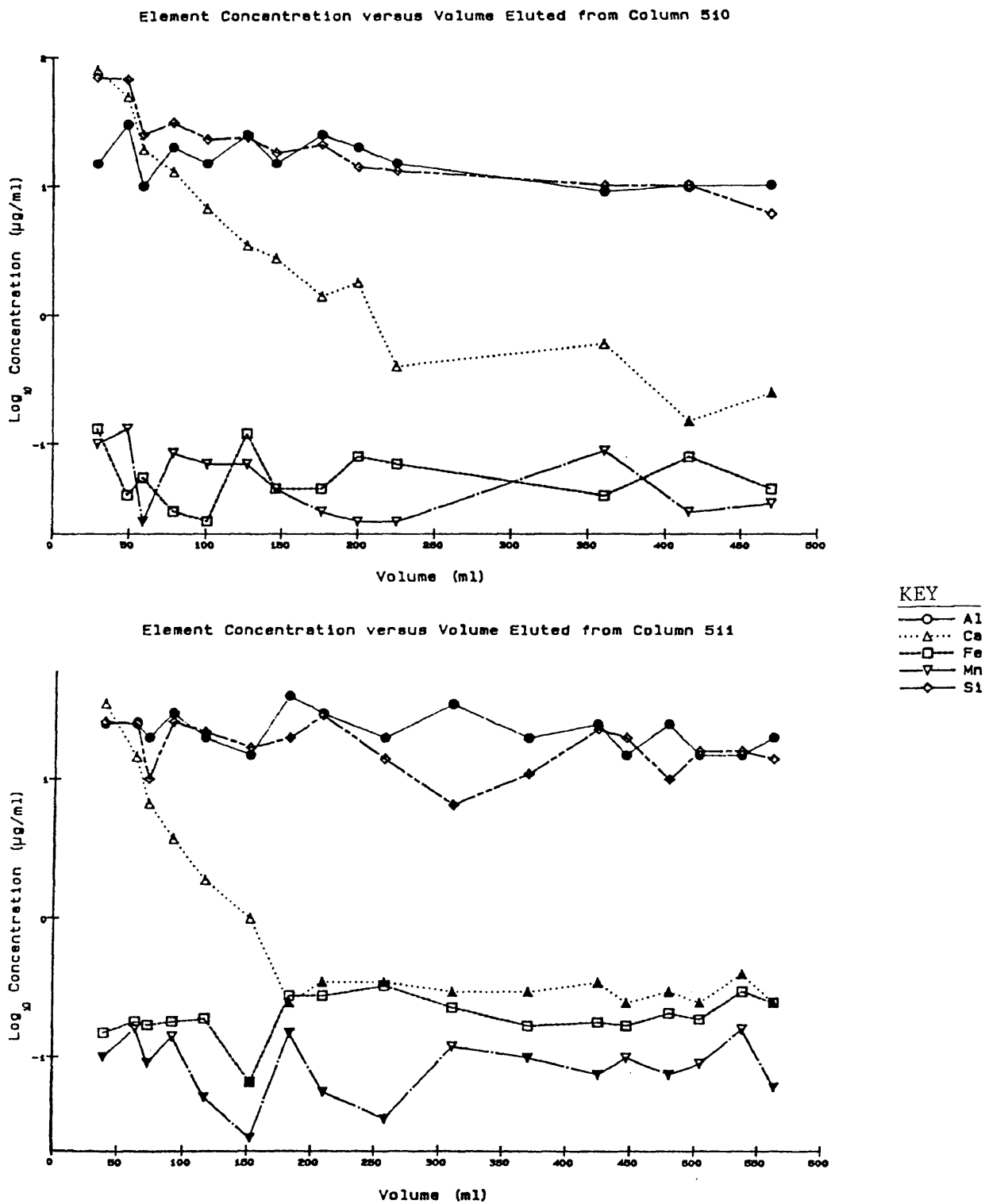


Figure 12c

Comparison of Al, Ca, Fe, Mn, and Si levels in  
pH 3, pH 5, and pH 8 columns

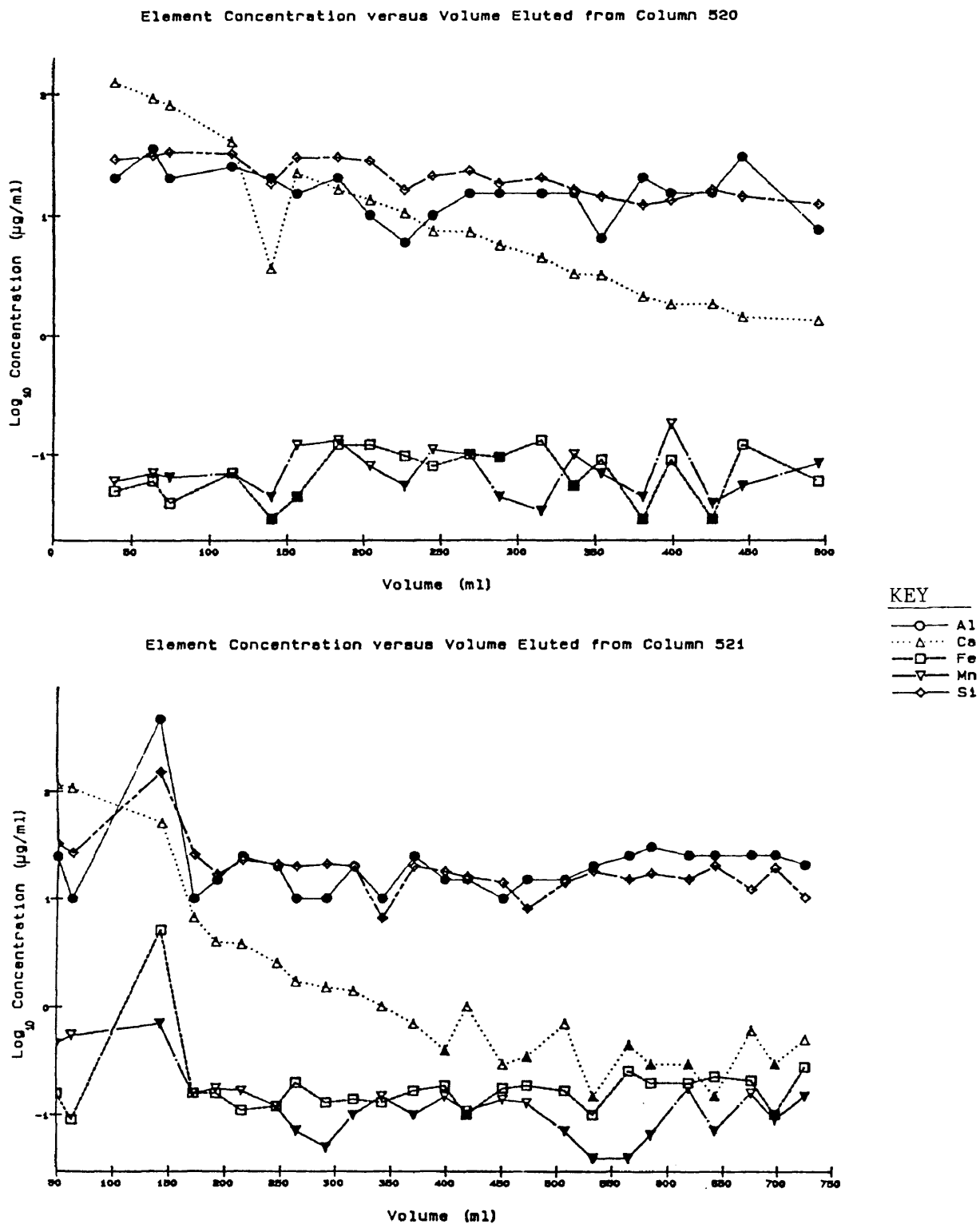
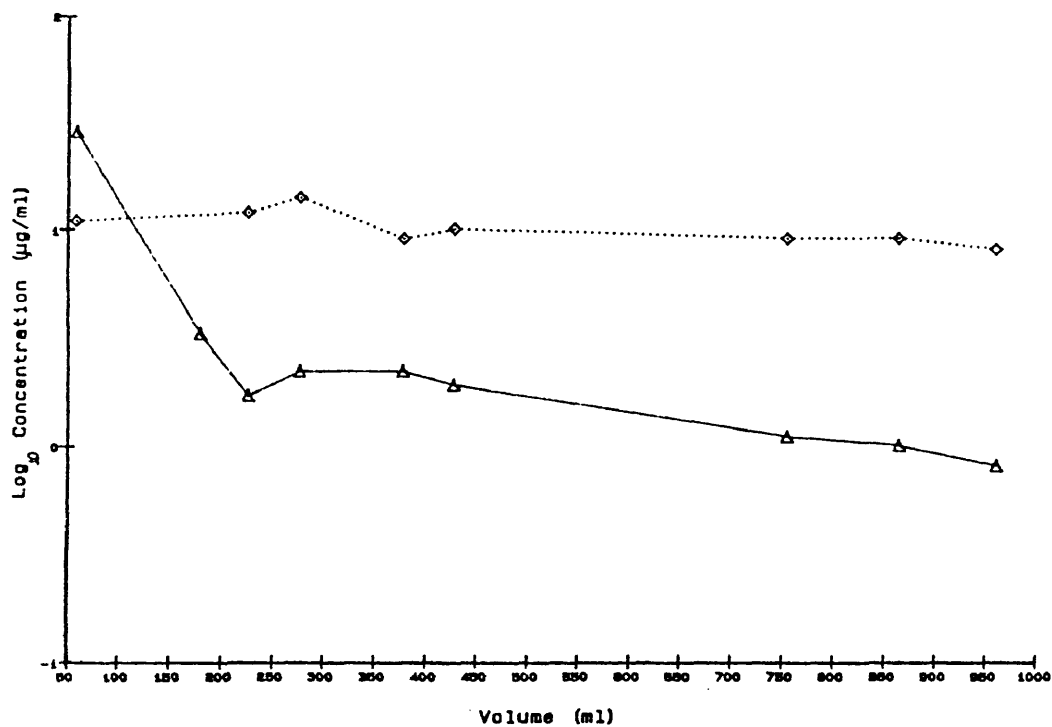


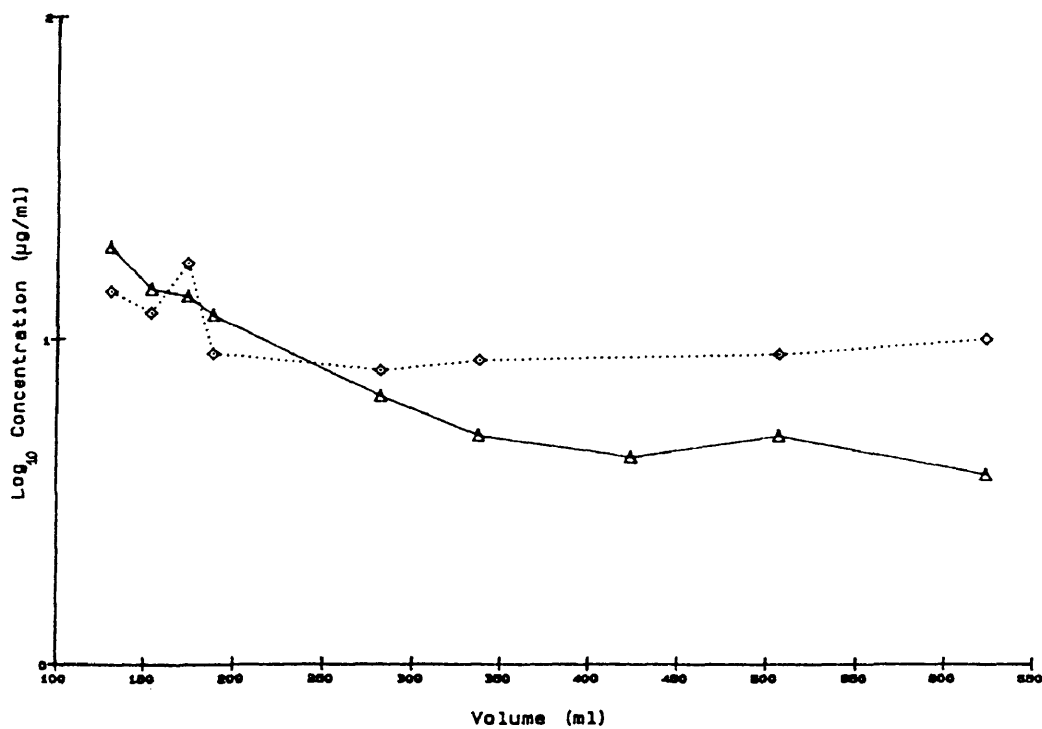
Figure 12d

Comparison of Al, Ca, Fe, Mn, and Si levels in  
pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 81



Element Concentration versus Volume Eluted from Column 82



KEY

—△— Ca  
 .....◇..... Si

Figure 13a

Comparison of As, Cu, and Fe levels in pH 3, pH 5, and pH 8 columns

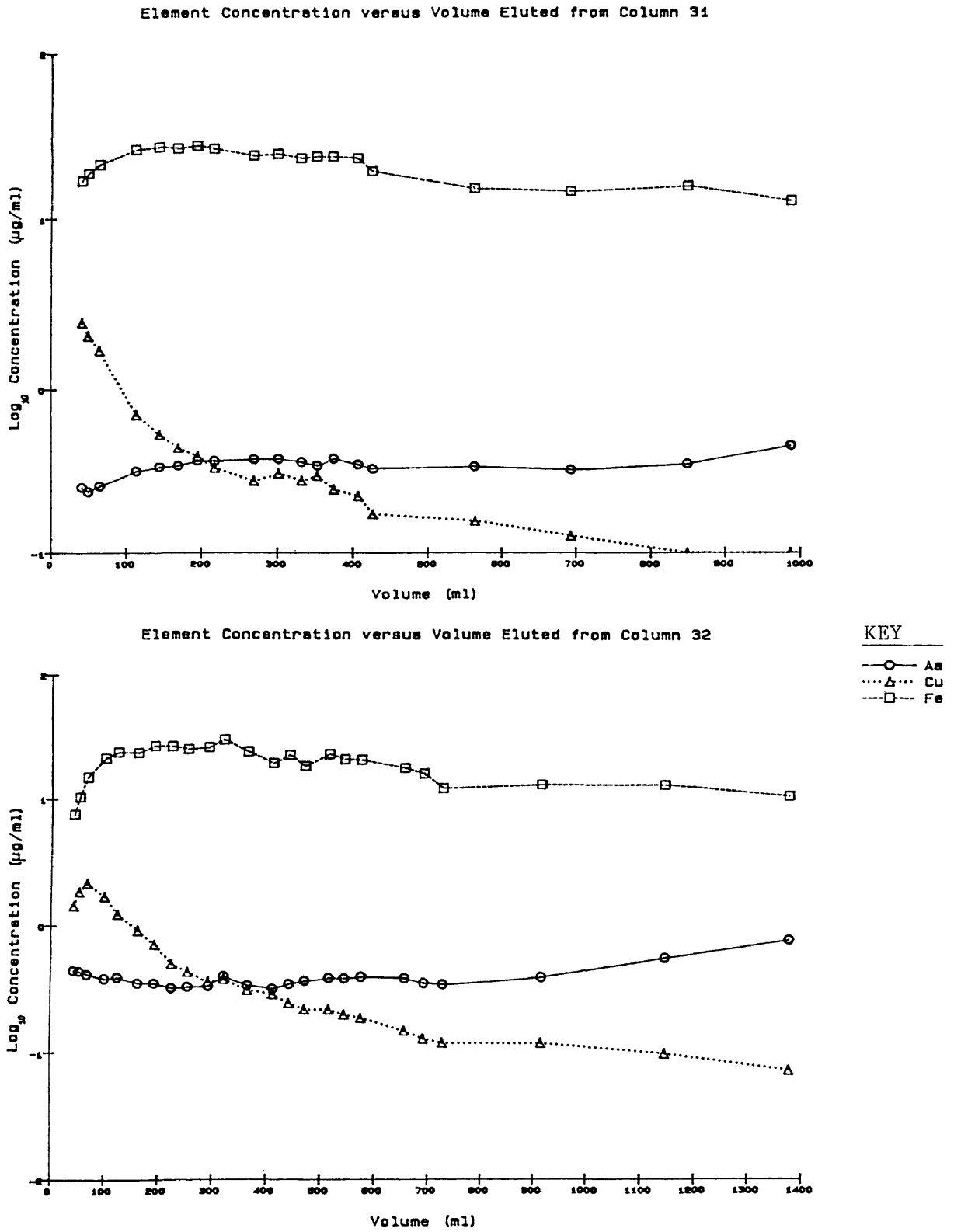


Figure 13b

Comparison of As, Cu, and Fe levels in pH 3, pH 5, and pH 8 columns

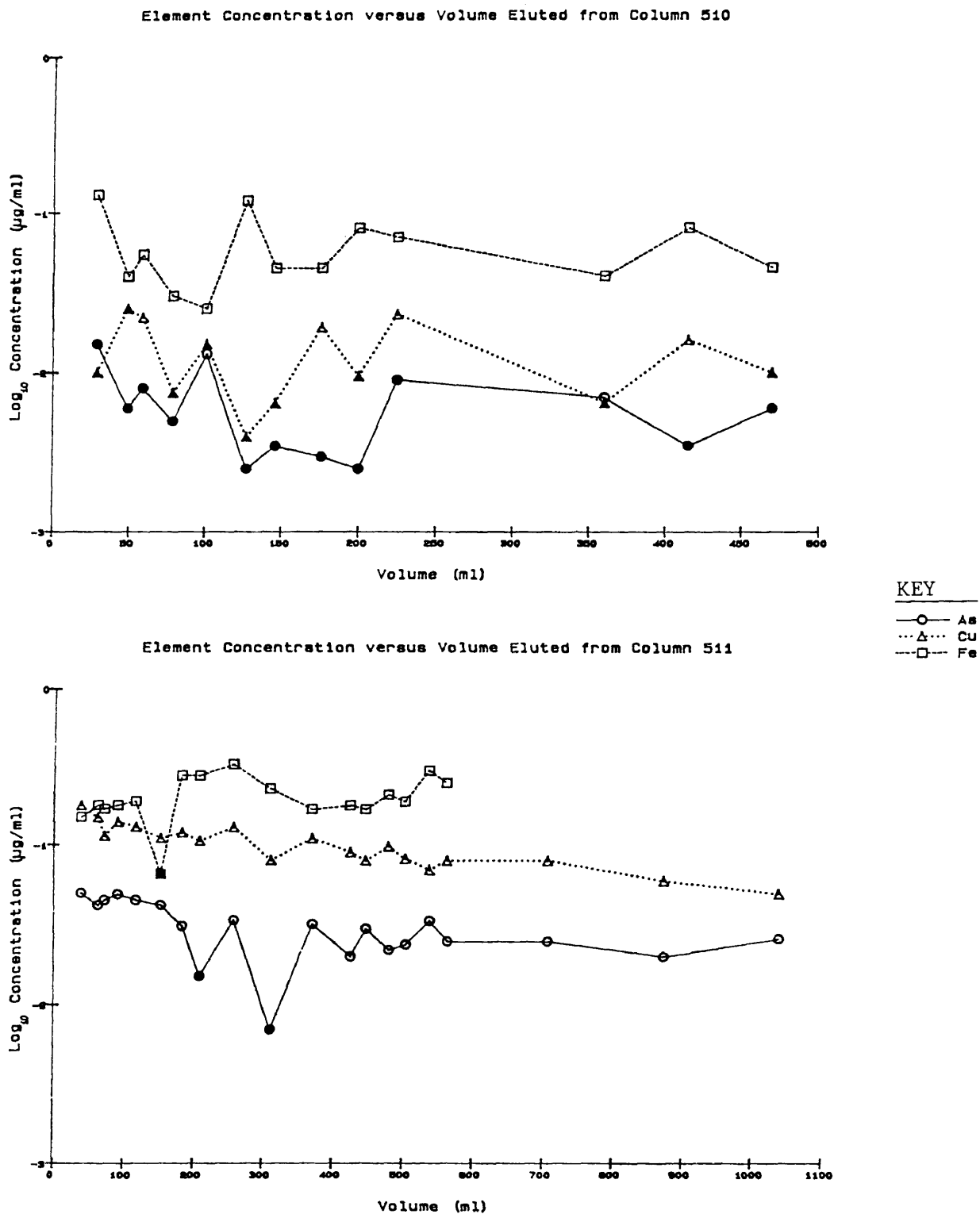


Figure 13c

Comparison of As, Cu, and Fe levels in pH 3, pH 5, and pH 8 columns

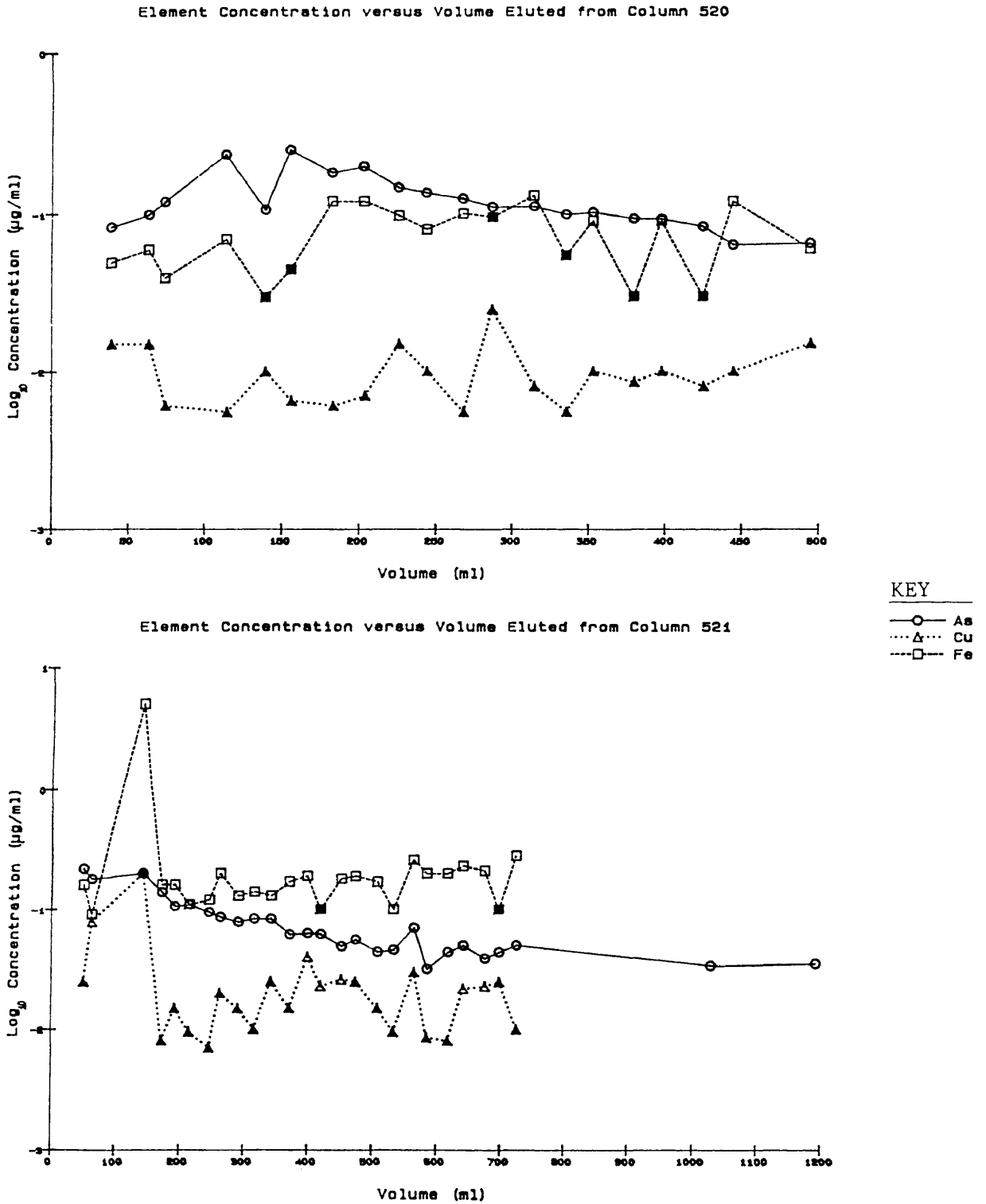


Figure 13d

Comparison of As, Cu and Fe levels in pH 3, pH 5, and pH 8 columns

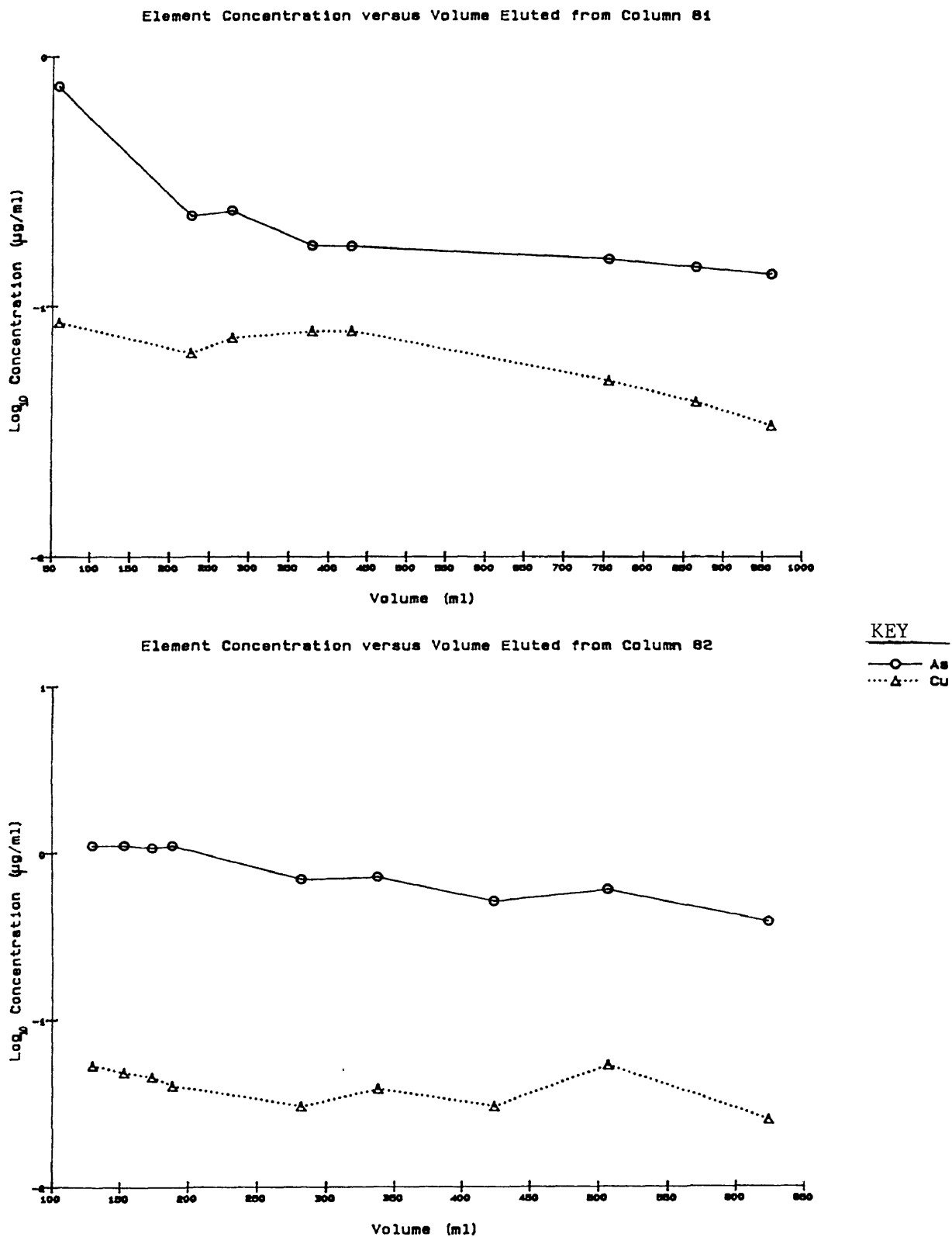
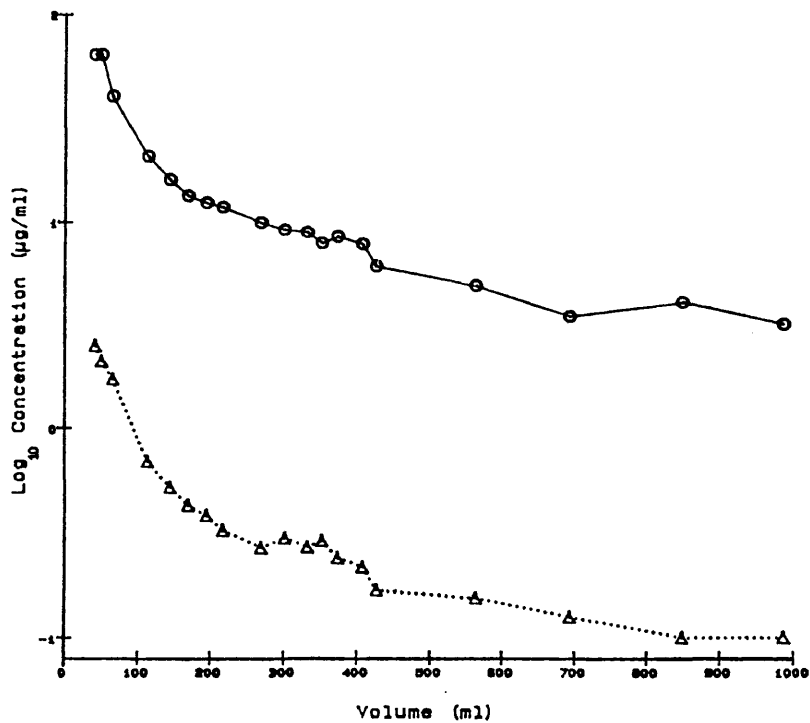


Figure 14a

Comparison of Ca and Cu levels in pH 3 and pH 8 columns

Element Concentration versus Volume Eluted from Column 31



Element Concentration versus Volume Eluted from Column 32

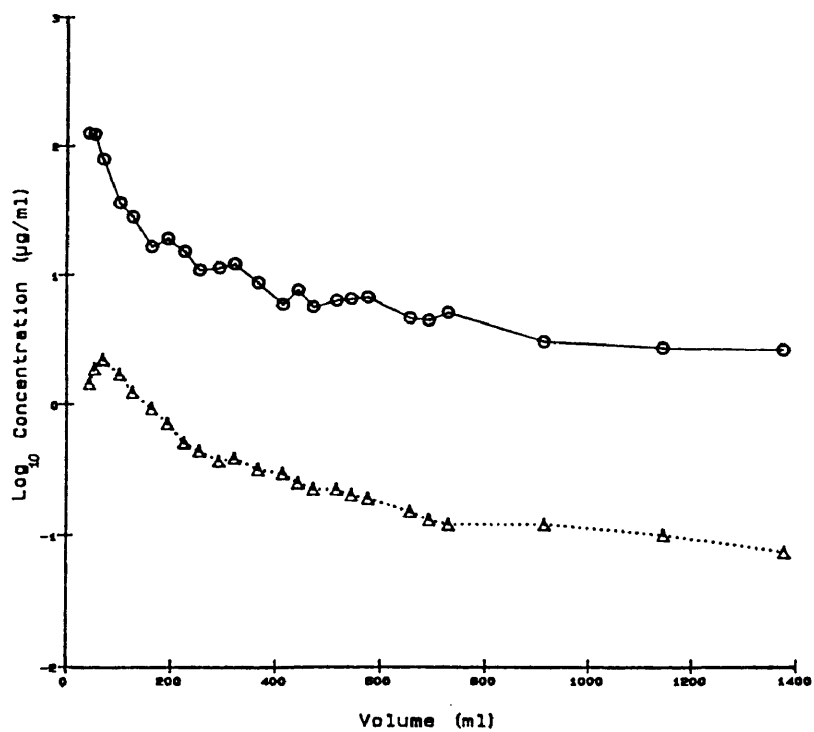
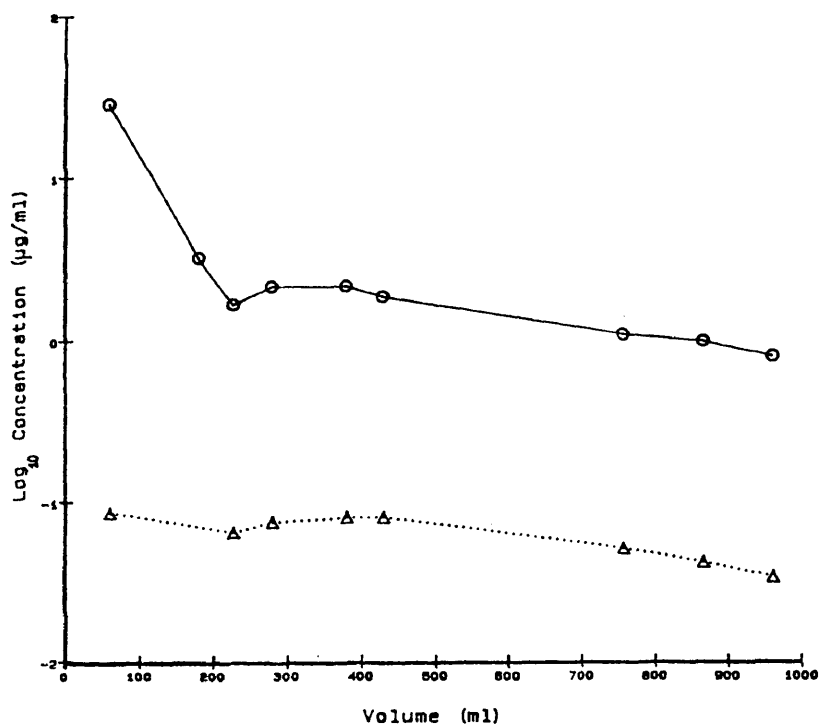
KEY: —○— Ca  
···△··· Cu

Figure 14b

Comparison of Ca and Cu levels in pH 3 and pH 8 columns

Element Concentration versus Volume Eluted from Column 81



KEY: —○— Ca  
 .....△..... Cu

Element Concentration versus Volume Eluted from Column 82

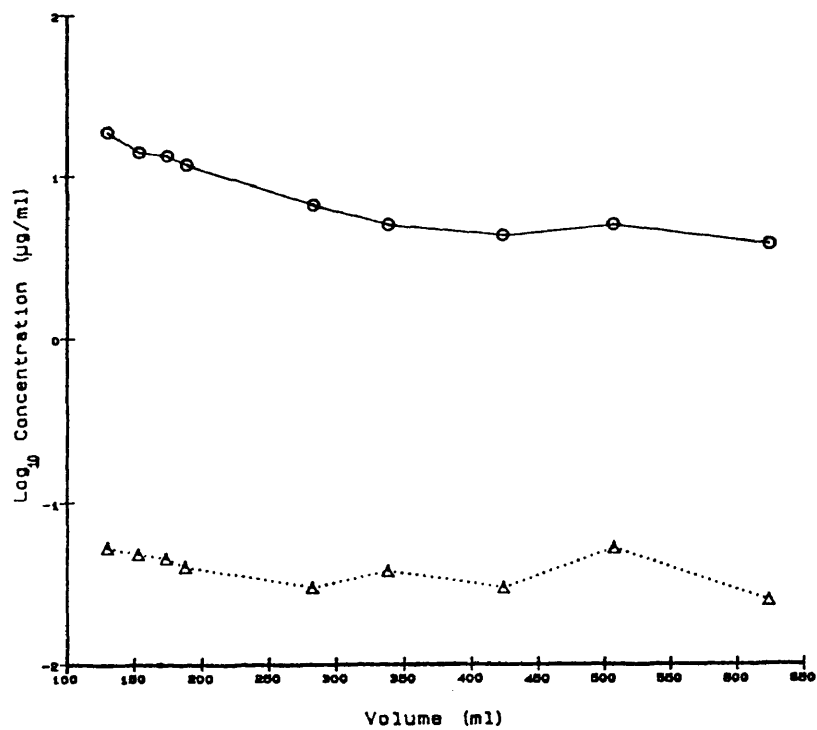
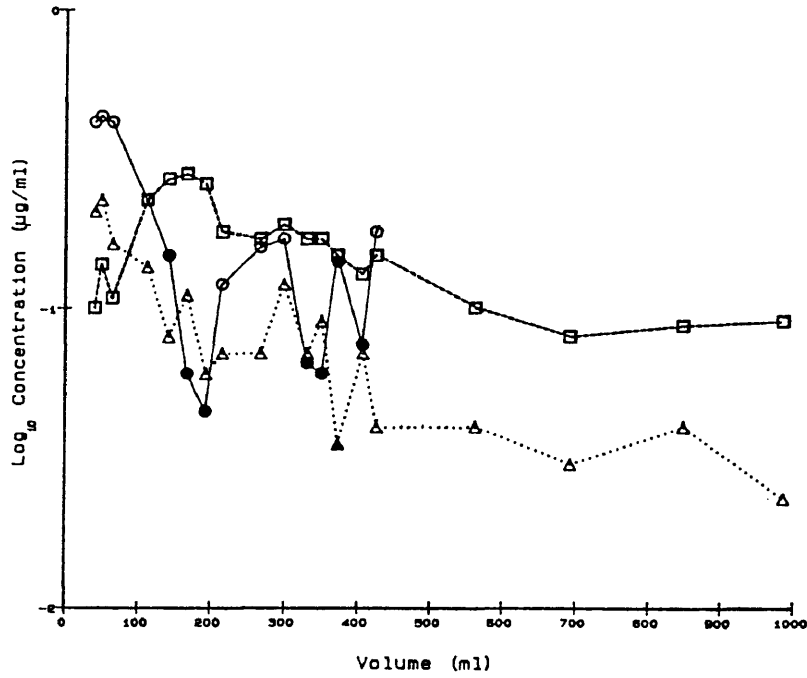


Figure 15

Comparison of Mn, Ni, and Pb levels in pH 3 columns

Element Concentration versus Volume Eluted from Column 31



KEY: —○— Mn  
.....△..... Ni  
—□— Pb

Element Concentration versus Volume Eluted from Column 32

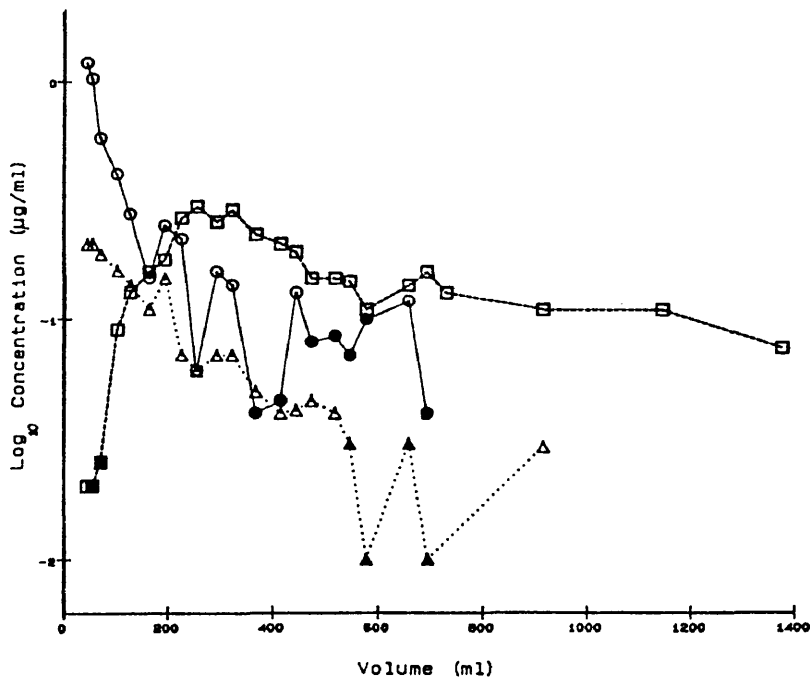
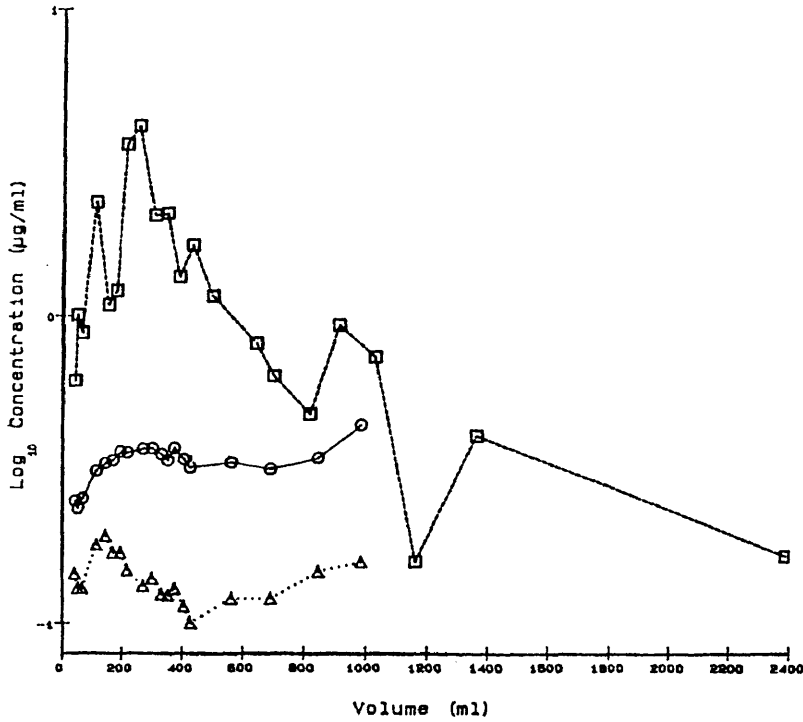


Figure 16a

Comparison of As, Se, and V levels in pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 31



KEY: —○— As  
 .....△..... Se  
 —□— V

Element Concentration versus Volume Eluted from Column 32

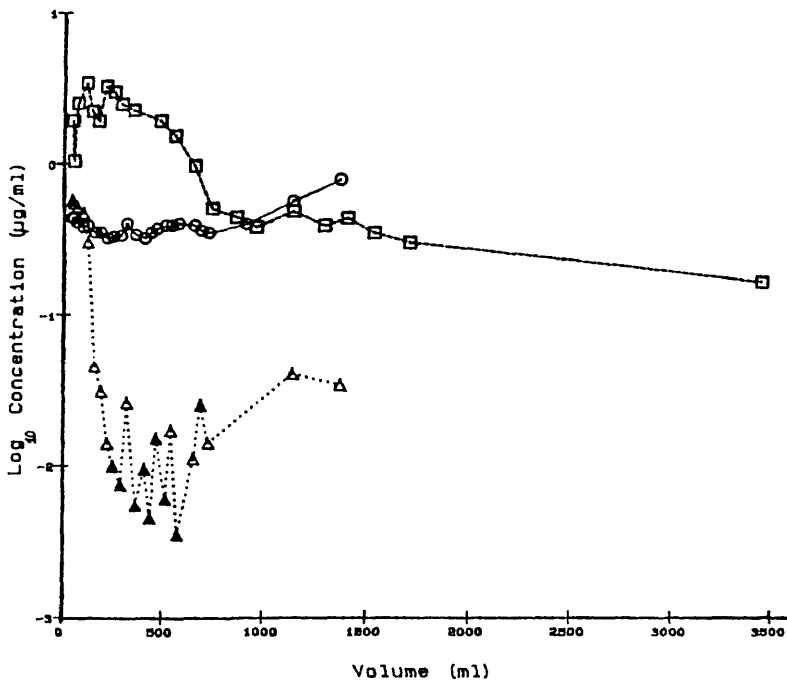
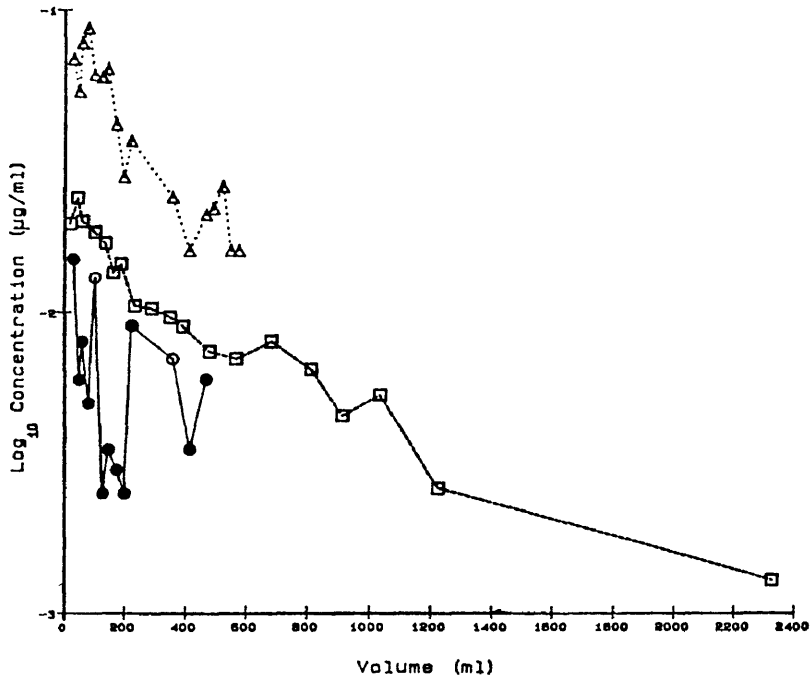


Figure 16b

Comparison of As, Se, and V levels in pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 510



KEY: ○ As  
△ Se  
□ V

Element Concentration versus Volume Eluted from Column 511

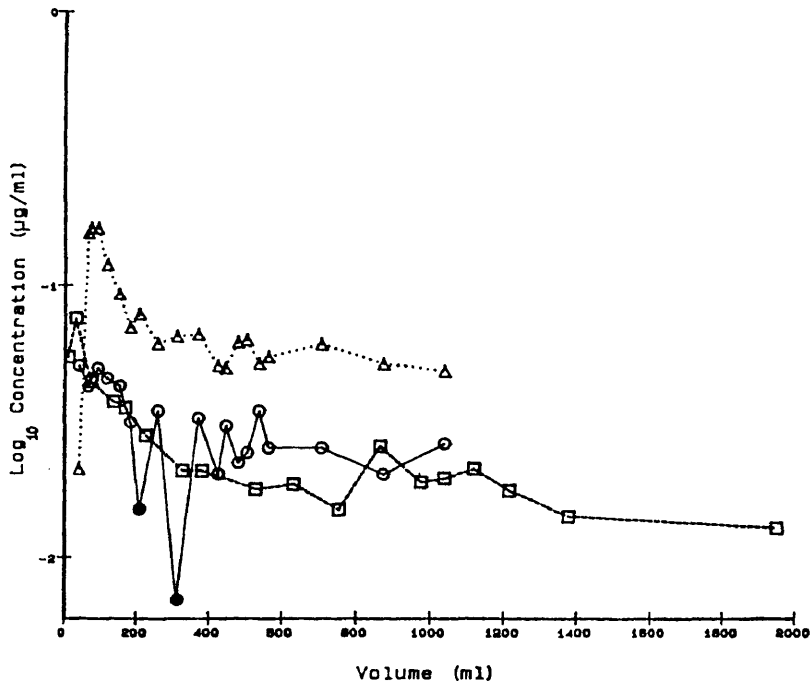
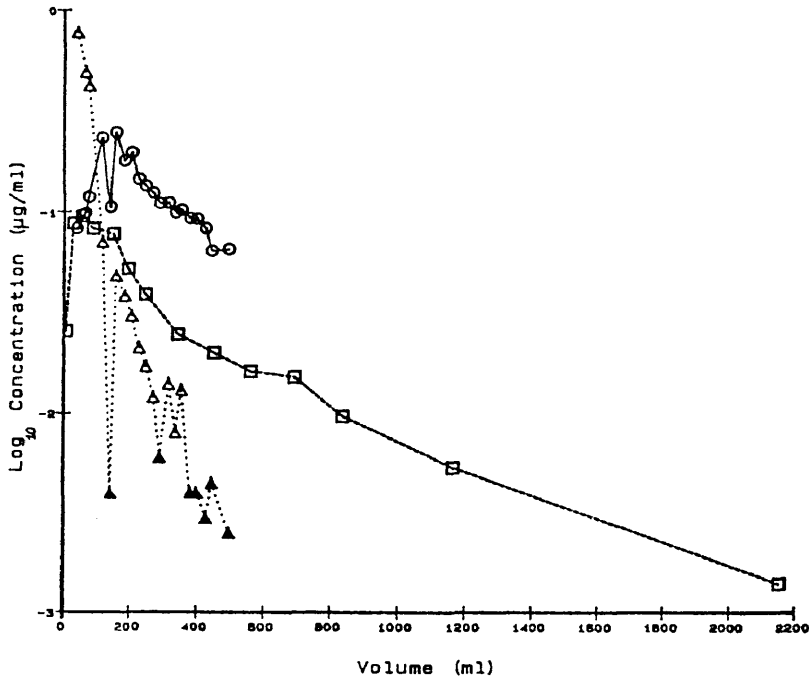


Figure 16c

Comparison of As, Se, and V levels in pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 520



Element Concentration versus Volume Eluted from Column 521

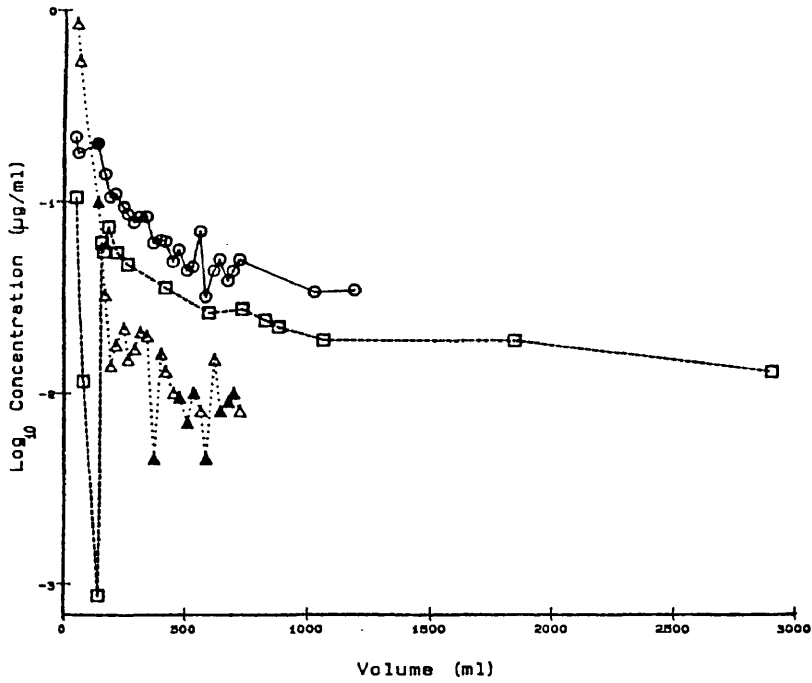
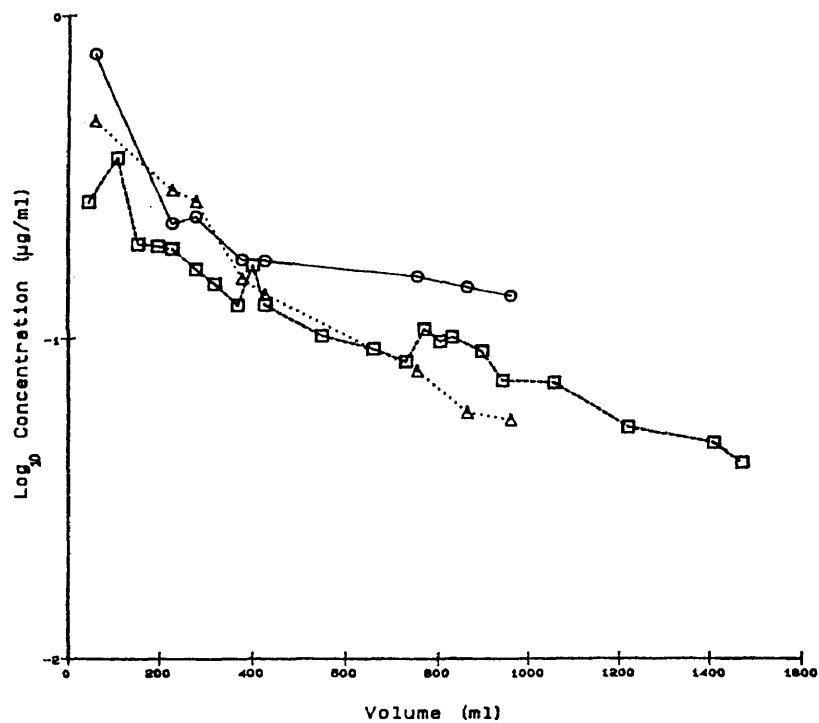


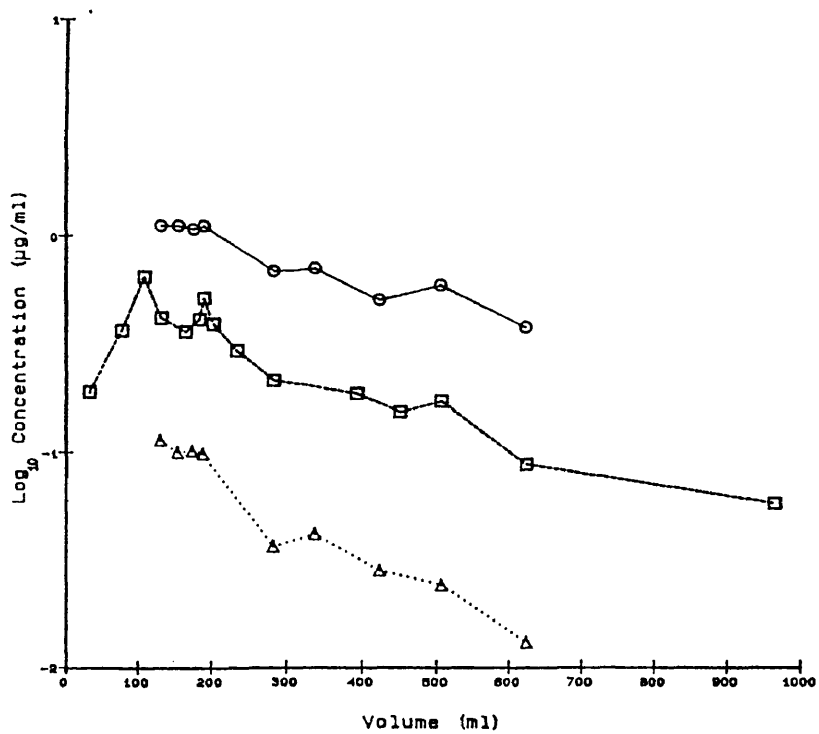
Figure 16d

Comparison of As, Se, and V levels in pH 3, pH 5, and pH 8 columns

Element Concentration versus Volume Eluted from Column 81



Element Concentration versus Volume Eluted from Column 82



○ As  
 △ Se  
 □ V

Table 9

Concentration of elements in 5N nitric acid  
leachates of Site 1 and Site 2 fly ash  
(concentration in ug/g - '\*' denotes concentration in mg/g)

('<' indicates concentration below detection limits)

	Si	Ca	Mn	Fe	Ni	Al
Site 1	37.0*	1480.0	<70.0	43.0*	53.0	33.0*
Site 2	28.1*	1910.0	<60.0	48.8*	46.0	25.0*
	As	V	Se	Cu	Pb	Rb
Site 1	147.0	240.0	16.4	95.0	61.0	87.0
Site 2	244.0	250.0	10.1	97.0	67.0	76.0
	Sr	Y	Ba			
Site 1	595.0	51.0	1520.0			
Site 2	680.0	49.0	1600.0			

## CHAPTER V

## SUMMARY AND CONCLUSIONS

The research presented in this paper has demonstrated the potential environmental hazards of weathered fly ash. Elements that pose these risks, such as vanadium, selenium, arsenic and nickel, were found at detectable levels after fly ash had undergone a long period of leaching in the laboratory. Vanadium was found in the leachates in the 1-10  $\mu\text{g}/\text{ml}$  range. Arsenic, selenium, and nickel were found to exist in the .1-1  $\mu\text{g}/\text{ml}$  range. Furthermore, the profile of these elements were still changing at the end of the study. In many cases, the concentrations were still above instrument detection limits.

In some cases, element levels varied significantly between site 1 and site 2. This illustrates the variability of fly ash within a single disposal site. Analysis of leachates from the .10 ionic strength pH 5 columns suggested possible suppression in solubility of certain elements due to the higher ionic strength. However, the reactions occurring between compounds in fly ash are complex and difficult to predict.

The ISAAC/Apple II+ system was an invaluable tool for automating the atomic absorption analysis of vanadium in fly ash leachates. The salt content of the buffer solutions accelerated graphite tube deterioration. Real-time plots of the data on the acquisition

system showed when this process started to occur. The data acquisition system could be implemented in other difficult GFAA analyses to give similar benefits. The major drawback of the Apple II+ computer was the length of time required to complete an analysis of an entire run. In this situation, the PDP-11 computer was a far superior system. If the data acquisition system was implemented today, far more powerful microcomputers could be substituted for the Apple II+.

It is satisfying to report that conditions at the fly ash disposal site have improved since this study was undertaken. Money from the Environmental Protection Agency's super fund has been used to level and 'cap' the fly ash with a special clay, which should reduce element leaching and ash transport by wind.

## APPENDIX A

## Data Acquisition Software and Calculations

Table A-1 includes all computations performed during the enhanced data acquisition mode. The top portion represents computations performed during the instrument char cycle and the bottom portion contains computations performed during the instrument atomization cycle. Certain characters in the equations denote use of a real versus an integer variable. For example, the '%' is used to represent an integer value in Apple II+ BASIC. The other variable names without the '%' are used to represent real values, which require more storage space on the Apple II+. In many cases, it was only necessary to use integer variables to store many of the numbers obtained from the acquisition system since they were digitized voltages. In some equations with mixed variable types, the final result is stored in an integer variable with use of the 'INT' function. This function saves the integer portion of a real number for storage into an integer variable. The 'ABS' function shown in some equations is used to take the absolute value of a number. A listing of the enhanced data acquisition program is included in this appendix after Table A-1. At the start of the enhanced data acquisition program, the operator is asked to select the length of time, in seconds, for acquiring the atomization signal. The period selected is based

on the element about to be analyzed. For vanadium, this period was normally five seconds which translates to a total of 300 points collected using a 60 Hz acquisition frequency. During the instrument char cycle, the deuterium and hollow cathode sample and reference beam signals were acquired for the same length of time these signals would be acquired during the atomization cycle. The purpose of acquiring these signals prior to the actual sample atomization was to obtain 'baseline' values for each signal. These baseline values would be used for later computations to obtain the corrected hollow cathode absorbance. The average deuterium sample beam signal (S0) is computed in equation 1, the average hollow cathode sample beam signal (S1) is computed in equation 2, the average deuterium reference beam signal (S2) is computed in equation 3, and the average hollow cathode reference beam signal (S3) is computed in equation 4. The number of points sampled during the char cycle is represented by  $n_1$  in equations 1 - 4.

Equations 5 - 10 were only computed during the instrument atomization cycle. As previously mentioned, the deuterium sample beam signal underwent a correction to compensate for the difference in time between when the signal was sampled and when the signal was updated by the instrument. Equation 5 shows how this correction was applied to the deuterium sample beam signal, which was stored in  $S(0,ii)$ . The corrected deuterium sample beam signal, stored in  $S(ii)$ , was then used to compute the background absorbance,  $ABG(ii)$ , at each point during the atomization cycle, as shown in equation 6. Note it is not

necessary to use the deuterium reference beam signal to compute  $ABG\%(ii)$  in equation 6. The average deuterium sample beam signal obtained during the char cycle,  $S_0$ , was used instead. The total hollow cathode absorbance,  $AHC\%(ii)$ , is computed in equation 7 using the same logic.  $AHC\%(ii)$  is computed for each point sampled during the atomization cycle using the hollow cathode sample beam signal,  $S\%(1,ii)$ , and the average hollow cathode sample beam signal obtained from the char cycle,  $S_1$ . The corrected hollow cathode absorbance,  $ACRRT\%(ii)$ , is obtained in equation 8 by subtracting the background absorbance,  $ABG\%(ii)$ , from the total hollow cathode absorbance,  $AHC\%(ii)$ .  $ACRRT\%(ii)$  represents only monochromatic absorbance with all other absorbance and scattering components subtracted out.

Finally, the average deuterium lamp drift ( $D_2$ ) and the average hollow cathode lamp drift ( $LD$ ) values are computed in equations 9 and 10, respectively. The deuterium lamp drift is a measure of the average change in the deuterium reference beam signals acquired during the atomization cycle,  $S\%(2,ii)$ , from the average deuterium reference beam signal obtained from the char cycle,  $S_2$ . The variable  $n_2$  is the total number of points sampled during the atomization cycle. The hollow cathode lamp drift is a measure of this change for the hollow cathode lamp.

Table A-1  
Calculations performed during data acquisition

Char Cycle Computations

- 1)  $S0 = \sum (S\%(0,i))/n_1$  \* average deuterium signal -sample beam (BG)
- 2)  $S1 = \sum (S\%(1,i))/n_1$  average hollow cathode signal -sample beam (I)
- 3)  $S2 = \sum (S\%(2,i))/n_1$  average deuterium signal -reference beam (BG0)
- 4)  $S3 = \sum (S\%(3,i))/n_1$  average hollow cathode signal -reference beam (I0)

\* ' $n_1$ ' represents total number of points collected during char cycle; ' $i$ ' represents individual signal values, which were summed over collection period. '%' sign on arrays indicates integer values are stored.

Atomize Cycle Computations

- 5)  $S(ii) = S\%(0,ii-1) \times .826 + S\%(0,ii) \times .174$  \*  
phase corrected deuterium signal-sample beam
- 6)  $ABG\%(ii) = INT(1000 \times (LOG_{10}(S0 / S(ii)) / 2.302))$  \*\*  
background absorbance
- 7)  $AHC\%(ii) = INT(1000 \times (LOG_{10}(S1 / S\%(1,ii)) / 2.302))$   
total absorbance
- 8)  $ACRRIT\%(ii) = AHC\%(ii) - ABG\%(ii)$   
corrected absorbance (monochromatic)
- 9)  $D2 = (100 \times (ABS(S2 - S\%(2,ii)) / S2)) / n_2$  \*\*\*  
average deuterium lamp drift
- 10)  $LD = (100 \times (ABS(S3 - S\%(3,ii)) / S3)) / n_2$   
average hollow cathode lamp drift

\* ' $ii$ ' represents individual signal values collected during atomize cycle.

\*\* 'INT' refers to taking the integer equivalent of a real number - decimal portions of the real number are truncated.

\*\*\* ' $n_2$ ' represents total number of points collected during atomize cycle. Individual deuterium lamp drift and hollow cathode lamp drift values were computed during atomize cycle; sum of these values were averaged at end of atomize cycle. 'ABS' refers to taking the absolute value of a number.

## Enhanced Data Acquisition Program

```

0 IF Y3 = 1 OR Y3 = 2 THEN G = 6 + 2: GOTO 4004
5 TEXT
10 D8 = CHR$(4)
12 GOTO 890
20 HOME: HTAB 1: VTAB 22: PRINT "DO YOU WISH TO END RUN(1), INTERRUPT RUN(2) OR RETURN TO COLLECT DATA(3)?": INPUT O4
22 IF O4 (1 OR O4) 3 THEN GOTO 20
23 IF O4 = 1 THEN GOTO 4770
27 IF O4 = 3 THEN HOME: HTAB 1: VTAB 23: PRINT "(1) TO SAVE RAW DATA: HTAB 1: VTAB 24: PRINT "(2) TO SAVE RAW DATA/PRINT RAW DATA: GOTO 40
30 PRINT "INTERUPTING": GOTO 20
40 RETURN
44 HOME: HTAB 1: VTAB 22: PRINT "STORING RAW DATA"
45 PRINT O4;"OPEN":I98;"L":PI;"D":REX
47 PRINT O4;"WRITE":I98;"R":BI;"B":PRINT "":PI = 6 + I:I7 = 0
51 FOR PP = 1 TO 2
53 PRINT O4;"WRITE":I98;"R":PI
55 FOR K = 0 TO 1
56 W9 = K + Y7
57 FOR I = ED TO F STEP 2
58 PRINT S(I),I)
61 NEXT I
71 NEXT K
74 PI = PI + I:I7 = 2
77 NEXT PP
80 PRINT O4;"CLOSE":I98
81 PRINT "STOP"
82 IF Y3 = 177 GOTO 98
84 POKE 33,33: PR# 1: PRINT CHR$(15)
87 FOR I = ED TO F STEP 2
90 PRINT "SX(0, I),I":SX(0, I): SX(1, I):SX(1, I): SX(2, I):SX(2, I): SX(3, I):SX(3, I)
92 NEXT I
94 PR# 0
98 POKE 33,40: RETURN
100 FOR I = ED TO F - 4:I0 = 0.0:E = 0.0
110 FOR K = I TO I + 4
120 D = D + SX(0,K):E = E + SX(1,K)
130 NEXT K
140 SX(0, I + 2) = D / 5.0: SX(1, I + 2) = E / 5.0
150 IF I = ED THEN BB = 0: GOSUB 190
160 IF I = F - 4 THEN BB = F - I: GOSUB 190
170 NEXT I
180 RETURN
190 FOR N = BB TO BB + 1
200 SX(0, N) = D / 5.0: SX(1, N) = E / 5.0
210 NEXT N
220 RETURN
300 PMAI = 0:REX = 0
480 FOR I = 0 TO NN
485 IF ACRTX(I) PMAI THEN PMAI = ACRTX(I):LOC = I
490 NEXT I
495 HOME
500 HTAB 24: VTAB 23: PRINT "HT=";PMAI: HTAB 33: VTAB 23: PRINT "N=";LOC: HTAB 26: VTAB 24: PRINT "TRANSIENT#";IG
505 RETURN
890 PRINT O4;"BLDAD PIC:A16384,D1"
891 PRINT O4;"BLDAD FREECAT.08J:A38350"
892 PRINT O4;"BLDAD FFFF:A36847": POKE 233, INT (36847 / 256): POKE 232, (36847 / 256) - INT (36847 / 256) * 256: HIMEM = 36846
895 PRINT O4;"BLDAD WORKINGSE.08J:A7800": LOMEN = 24576
897 O4 = CHR$(4):I6 = 0

```

```

900 PRINT "ENTER NAME OF FILE AND DRIVE # FOR DATA STORAGE (SEPARATE RESPONSES BY A COMMA)"; INPUT Z9$,R2$
902 IF R2$ ( 1 OR R2$ ) 2 THEN GOTO 900
904 PRINT "ENTER ELEMENT NAME, # OF SECONDS FOR TRANSIENT (SEPARATE RESPONSES BY COMMA AND ONLY INTEGERS FOR TIME"; INPUT S9$,N1:LN = N1 * 50;L = 300 - 8;IL = L + 1 + N1F = IL;ED = L + 1
906 R1 = INT ((65.0 / 12.0) * N1) + 33
907 R0 = INT ((N / 3.0) * 4.0) + 2 * N + 29;Z9$ = Z9$ + STR$(R1)
909 PRINT D0;"OPEN";Z9$;"L";R1;"D";R2$
910 IF PEEK (-18982) ( 2 THEN PRINT D0;"CLOSE";Z9$; GOTO 930
915 PRINT D0;"CLOSE";Z9$
920 PRINT "FILE ALREADY EXISTS -DO YOU WISH TO OVERWRITE (1) OR TO CHOOSE A NEW NAME (2)"; INPUT R3$
922 IF R3$ ( 1 OR R3$ ) 2 THEN GOTO 920
925 IF R3$ = 2 THEN GOTO 900
927 PRINT D0;"DELETE";Z9$
930 NORMAL
933 POKE PEEK (966) + PEEK (967) * 256;0;ADR = 7600
940 DIM A$(3),S$(3,1),AB$(N),ACRT$(N),D$(9),S(N),A$(N)
953 Z = .826;Y = .174;X = 2.302585;H = 1.0 / 5.0;V = .200;U = 258.9 / (N * 1.000001);T = 1000
956 HOME :50 = 0:51 = 0:52 = 0:53 = 0:5 = 100
964 INVERSE
965 POKE 7799,00; POKE 7798,17
999 HTAB 1: VTAB 23: PRINT "(1) TO SAVE RAW DATA"; HTAB 1: VTAB 24: PRINT "(2) TO SAVE RAW DATA/PRINT RAW DATA";Y3 = 0;Y5 = 0
1000 & B1M, (TV) = 0, (AM) = 64
1001 HTAB 1: VTAB 21: PRINT "WAITING FOR RECORDER-(ESC) FOR MENU"
1003 Y4 = PEEK ( - 16384); POKE - 16368,0
1004 IF Y4 = 177 OR Y4 = 178 THEN Y5 = Y4
1005 IF Y4 ( ) 155 THEN GOTO 1010
1006 GOSUB 20
1010 IF 0 ( ) 0 THEN GOTO 1000
1020 FOR I = 0 TO L
1030 CALL ADR,AS,0,1
1040 NEXT I
1045 & B2DM, (TV) = P, (AM) = 63;P = P - 4
1050 & B1M, (TV) = 0, (AM) = 256
1055 HTAB 1: VTAB 21: PRINT "WAITING FOR ATOMIZE
1060 IF 0 ( ) 0 THEN GOTO 1050
1067 HOME
1070 FOR K = ED TO F
1080 CALL ADR,AS,0,1
1090 NEXT K:6 = 6 + 1
1091 IF Y5 = 177 OR Y5 = 178 THEN Y3 = Y5; GOTO 1094
1092 Y3 = PEEK ( - 16384); POKE - 16360,0
1094 IF Y3 = 177 OR Y3 = 178 THEN NORMAL : GOSUB 44
1095 HTAB 1: VTAB 23: PRINT "(ESC) TO PREVENT DATA STORAGE"; HTAB 1: VTAB 24: PRINT "(RTN) TO MARK RECORD FOR UNUSUAL DATA"; HTAB 1: VTAB 21: PRINT "COMPUTING
1100 FOR I = 0 TO L
1105 REM RINT "1";1;" S0;S$(0,1);" S1;S$(1,1);" S2;S$(2,1);" S3;S$(3,1)
1120 S1 = S1 + S$(1,1);S2 = S2 + S$(2,1);S3 = S3 + S$(3,1);S0 = S0 + S$(0,1)
1150 NEXT I
1170 S0 = S0 / I;S1 = S1 / I;S2 = S2 / I;S3 = S3 / I
1175 REM RINT "RNG: S0";S0;" S1";S1;" S2";S2;" S3";S3
1180 NN = 0
1190 FOR K = ED TO F
1200 IF K = F THEN S(NN) = S$(0,K); GOTO 1220
1210 S(NN) = S$(0,K) * Z + S$(0,K + 1) * Y
1220 AB$(NN) = INT (T * ( LOG (S0 / S$(1,K)) / K))
1230 AC$(NN) = INT (T * ( LOG (S1 / S$(1,K)) / K))
1250 ACRT$(NN) = A$(K) * NN - AB$(NN)
1265 REM RINT "S(NN)";S(NN);" S1";S$(1,K);" S2";S$(2,K);" S3";S$(3,K);" AB$";AB$(NN);" AC$";ACRT$(NN)
1270 IF K = F THEN GOTO 1280
1275 NN = NN + 1
1280 NEXT K
1295 GOSUB 300: REM AREA SUBROUTINE

```

```

1296 CALL - 182: POME 71,0: CALL - 193: HRR : ROT= 0: SCALE= 1
1297 POME 60,0: POME 61,64: POME 62,255: POME 63,95: POME 66,0: POME 67,32
1298 CALL - 468
1299 HCOLOR= 3
1300 LNS = STR$ ( INT (LNN)/1024 = ( LEFT$ ( STR$ (LNN / 2.0), 3) ): X5 = 142
1301 FOR I = 1 TO LEN (LNS)
1302 DRAW ( ASC ( MID$ (LNS, I, 1) ) - 31) AT X5, 150
1303 X5 = X5 + 5
1304 NEXT I
1307 DRAW ( ASC (LNS) - 31) AT 274, 150
1308 HCOLOR= 2
1309 FOR I = 0 TO NN STEP 2
1310 IF AB6X(I) > 699 OR AB6X(I) < - 99 THEN GOTO 1320
1312 PLOT INT (I * U) + 20, INT (136 - (AB6X(I) * V))
1320 NEXT I
1330 HCOLOR= 6
1340 FOR I = 0 TO NN STEP 2
1342 IF ACRTX(I) > 699 OR ACRTX(I) < - 99 THEN GOTO 1352
1350 PLOT INT (I * U) + 20, INT (136 - (ACRTX(I) * V))
1352 NEXT I
1353 HCOLOR= 1
1354 FOR I = 0 TO NN STEP 4
1355 IF AHX(I) > 699 OR AHX(I) < - 99 THEN GOTO 1360
1358 PLOT INT (I * U) + 19, INT (136 - (AHX(I) * V))
1360 NEXT I
1361 YA = PEEK ( - 16384): POME - 16368, 0
1362 IF YA = 155 THEN G = 6 - 1: GOTO 4000
1363 IF YA = 141 THEN REX = 1
1365 PRINT CHR$ (4): DS = CHR$ (4)
1368 PRINT D4;"OPEN"; Z94;"L"; R1;"D"; REX
1369 PRINT D4;"WRITE"; Z94;"R"; G;"80"; PRINT REX
1370 PRINT D4;"WRITE"; Z94;"R"; G;"82"
1375 PRINT P: PRINT LOC
1380 PRINT D4;"WRITE"; Z94;"R"; G;"814"
1384 II = 0
1385 FOR I = 0 TO NN STEP 31
1387 D2(II) = S * ( ABS (S2 - S*(2, II) / S2): DSUM = DSUM + D2(II)
1389 LD(II) = S * ( ABS (S3 - S*(3, II) / S3): LSUM = LSUM + LD(II)
1392 II = II + 1
1395 NEXT I
1400 DSUM = DSUM / II: IF DSUM < .01 THEN DSUM = 0.0
1405 LSUM = LSUM / II: IF LSUM < .01 THEN LSUM = 0.0
1410 PRINT LEFT$ ( STR$ (DSUM), 3): PRINT LEFT$ ( STR$ (LSUM), 3)
2010 PRINT D4;"WRITE"; Z94;"R"; G;"825"
2015 NO = NN / 2: NO = NN / 2 + 1
2020 FOR I = 0 TO NN
2030 PRINT ACRTX(I)
2040 NEXT I
2050 PRINT D4;"WRITE"; Z94;"R"; G;"8"; RP
2060 FOR I = 0 TO NO
2070 PRINT AB6X(I)
2072 NEXT I
2074 FOR I = NO TO NN STEP 4
2076 PRINT AB6X(I)
2080 NEXT I
2095 PRINT D4;"CLOSE"; Z94
3000 CALL 38350
3010 IF ( PEEK (38349) * 256 + PEEK (38348) ) = INT ((161 * 1.000001) / 256.0) + 1.0: GOTO 4000
3012 & BUZZ ON : PRINT "NEXT TRANSIENT MUST BE PLACED ON NEW DISK -DO YOU WISH TO CHANGE DISKS (1) OR END RUN (2)?": INPUT H5
3014 IF H5X ( 1 OR H5X ) 2 THEN PRINT CHR$ (7): GOTO 3012

```

```
3015 & BUZZ STOP : IF HEX = 2 GOSUB 20
3018 PRINT "HIT ANY KEY AFTER NEW DISK IS INSERTED": INPUT **;KEY$: HOME
4000 IF Y3 = 177 OR Y3 = 178 THEN G = G + 2
4004 GOTO 556
4770 PRINT D$;"OPEN";Z9$;"L";R1;"D";R2$
4772 PRINT D$;"WRITE";Z9$;"R0": PRINT G: PRINT S$: PRINT N: PRINT R1: PRINT R2
4774 PRINT D$;"CLOSE";Z9$
4780 END
```

## APPENDIX B

## Data Analysis Software and Calculations

The details of the post-acquisition calculations are discussed in this section. A list of important equations used by the two primary analysis programs are included in Table B-2. Computer listings of the analysis programs as well as a reporting program are included in this section.

A summary of the post-acquisition calculations would not be complete without a discussion of difficulties encountered in integrating vanadium peaks collected during data acquisition. One of the more challenging tasks was to determine an algorithm that could reproducibly determine peak area for very small vanadium peaks as well as the larger peaks produced by standards. The vanadium peaks were subject to spiking at peak maximum (due to graphite tube deterioration), prolonged trailing edges (due to processes involved in the decay of atoms after atomization), and unpredictable peak fronts (due to matrix interferences). The slope at the beginning of most vanadium peaks was very gradual. This made peak versus noise discrimination difficult. The final algorithm included three tests to determine if a peak was 'eligible' for integration. The first test, to mark 'start of peak', required an increasing difference between five

successive data points. The average difference between each of the five points was saved and used for later tests. The second test required that the difference in three successive data points, located after the peak maximum, be less than the average difference determined from the first test. Satisfying the second requirement guaranteed that a decreasing trend occurred just after the peak maximum. The third test required that the average of three successive points, located after the points that satisfied the second test, be less than 4% of the peak maximum. If the third test was satisfied, it indicated the data points had returned to some baseline value. If all three tests were satisfied, area integration began at the first data point comprising the set of five 'beginning' points. Area integration stopped at the first data point comprising the set of three 'ending' points. If the 'peak start' was not located before the peak maximum, area calculations were aborted. The peak was also flagged and not used as a replicate in the calculation of average peak area. If this occurred on all replicates of a sample or standard, the average area computation was aborted and flagged for future reference.

After area computations and the sample labelling step were completed, the next task was to perform a second order non-linear regression on the data. The non-linear regression equation is shown on line A in Table B-2. The equation is also shown below:

$$A/C = P_0 + P_1 \times A + P_2 \times A^2 \quad (\text{Routh, 1981})$$

Concentrations were determined for all solutions analyzed in the run, including standards. Equation B in Table B-2 shows the computation used to obtain the solution concentration, which was not yet corrected for instrument sensitivity changes. Recalibration occurred every seven to eight samples to determine the direction and amount of the instrument sensitivity change. A correction factor, CORR(i), was computed to compensate for this sensitivity change (see equation C in Table B-2). When CORR(i) values were greater than one, this indicated the sensitivity of the instrument had increased during the run. For groups or blocks of standards run together, an average correction factor was computed as AVGCORR(i) (see equation D in Table B-2). Finally, an average AVGCORR(i) value, represented by AVGCORR2(i), was computed using the two sets of standards which surrounded a group of samples (see equation E in Table B-2). Samples bracketed by two sets of standards had an average sensitivity correction factor applied to their concentration values (see equation F in Table B-2). The adjusted sample weight, ADJWT(i), was folded into the final equation for corrected solution concentration in equation G. The mean relative standard deviation, MRSD, and relative mean standard deviation, RMSD, were computed for the first group of standards used in the regression, as shown in equations H and I in Table B-2. A solution concentration error, SCEERR(i), was

also calculated for each sample analyzed in the run (see equation J in Table B-2).

Table B-1

Functions available from post acquisition processing programs

Main Menu Available from Data Analysis Program

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- A) Area calculations
- B) Second pass through data
- C) Make labels
- D) Edit labels
- E) Transfer weight/tray position to 'C' file
- F) Exit

Main Menu Available from Nonlinear Regression Program

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- A) Peak Height / Area Calibration and Regression
- B) Peak Height Calibration and Regression
- C) Peak Area Calibration and Regression
- D) Calibration Plot/Hardcopy
- E) Exit

Table B-2  
Equations for non-linear regression and  
corrected solution concentration

- A)  $A/C = P_0 + P_1 \times A + P_2 \times A^2$ \*  
general form of non-linear regression equation.
- B)  $C(i) = A(i) / (P_0 + P_1 \times A(i) + P_2 \times A(i)^2)$   
concentration not corrected for instrument sensitivity changes.
- C)  $CORR(i) = C(i) / SOLNC(i)$ \*\*  
instrument sensitivity correction factor.
- D)  $AVGCOORR(i) = \sum (CORR(i)) / NSTDS$ \*\*\*  
average instrument sensitivity correction factor.
- E)  $AVGCOORR2(i) = (AVGCOORR(i-1) + AVGCOORR(i)) / 2.0$ \*\*\*\*  
block averaged instrument sensitivity correction factor.
- F)  $CONC(i) = (A(i) / AVGCOORR2(j)) / DIL(i)$   
sample concentration corrected for average instrument sensitivity  
change and dilution factor (DIL(i)).
- G)  $CONC(i) = ADJWT(i) \times CONC(i)$   
sample concentration corrected for adjusted sample weight (ADJWT(i))
- H)  $MRS D = (\sqrt{(\sum (SD(i) / A(i))^2) / N}) \times 100.0$ \*\*\*\*\*  
mean relative standard deviation.
- I)  $RMS D = \sqrt{(\sum (1 - CORR(i))^2) / N}$ \*\*\*\*\*  
relative mean standard deviation.
- J)  $SCERR(i) = \sqrt{((SD(i)^2) / (P_0 + P_1 \times A(i) + P_2 \times A(i)^2)) + ((RMS D \times C(i))^2)}$   
sample solution concentration error.

\* in the regression equation, X is absorbance (A) and Y is absorbance divided by solution concentration (C); P<sub>0</sub>, P<sub>1</sub>, and P<sub>2</sub> are regression coefficients.

\*\* 'SOLNC(i)' is solution or 'known' concentration; equation C only applied to standards.

\*\*\* 'NSTDS' is number of standards analyzed together in a set; equation D only applied to standards.

\*\*\*\* equation E applied to pairs of standard sets surrounding a group of samples.

\*\*\*\*\* equation H computed with first group of standards analyzed in run; 'N' is number of standards in the first group. 'SD(i)' is relative standard deviation (computed with solution concentration, SOLNC(i), and concentration obtained from regression, C(i)).

\*\*\*\*\* equation I computed with first group of standards analyzed in run.

## Data Analysis Program

```

1 TEXT D4 = CHR$(4): GOTO 3820
10 HOME : IF ADJ$( ) = "*" THEN PRINT "SAMPLE LABELS PRESENT- DO YOU WISH TO REDO?": INPUT Y$: IF LEFT$(Y$,1) = "N" GOTO 499
15 DIM TIC$(10), TEG$(10), NNTX$(10,15), NUMR$(10,15), NSTX$(10,15), NIX$(10,15)
20 FN = 0: I0 = 0
50 FOR I = 1 TO 10
60 IF LBL$(I) = "STD" THEN I0 = I0 + 1: GOTO 90
62 IF LEFT$(LBL$(I),3) = "EPA" OR LEFT$(LBL$(I),3) = "TEG" OR LEFT$(LBL$(I),3) = "MTX" THEN I0 = I0 + 1: GOTO 90
63 IF FN = 1 GOTO 90
64 V9 = 0: SPEED= 80
65 FOR II = 1 TO LEN(NMB$(I))
70 IF MID$(NMB$(I),II,1) = "-" THEN V9 = V9 + 1
75 IF V9 = 2 THEN NUMR$(I) = LEFT$(NMB$(I),II - 1): NIX$(I) = 1: IF = 1: TA = 1: NSTX$(I,TA) = NMB$(I): NNTX$(I,TA) = 1: IFM = 1: GOTO 90
80 NEXT II
90 NEXT I
9A FOR K = 1 TO 10
100 FOR I = 1 TO 10
110 IF LBL$(I) = "STD" GOTO 200
115 IF LEFT$(LBL$(I),3) = "EPA" OR LEFT$(LBL$(I),3) = "TEG" OR LEFT$(LBL$(I),3) = "MTX" GOTO 200
120 IF TA = 0 GOTO 178
122 STR = 0
125 FOR II = 1 TO TF
130 IF LEFT$(NMB$(I), (LEN(NMB$(II)))) = NUMR$(II) THEN STR = STR + 1
135 NEXT II: IF STR < > 0 GOTO 200
140 IF = TF + 1
145 V9 = 0
150 FOR J = 1 TO LEN(NMB$(I))
155 IF MID$(NMB$(I),J,1) = "-" THEN V9 = V9 + 1
160 IF V9 = 2 THEN NUMR$(I) = LEFT$(NMB$(I),J - 1): NIX$(I) = J: GOTO 175
165 NEXT J: NUMR$(I) = NMB$(I): NIX$(I) = 1
175 TA = 1: NSTX$(I,TA) = NMB$(I)
176 GOTO 200
178 IF NMB$(I) = NSTX$(I,1) GOTO 200
180 IF LEFT$(NMB$(I), (LEN(NMB$(I)))) = NUMR$(I) THEN TA = TA + 1: NSTX$(I,TA) = NMB$(I): NNTX$(I,TA) = 1: NIX$(I) = TA
200 NEXT I
201 TA = 0: NSUMX = 0
202 FOR J = 1 TO TF
20A NSUMX = NSUMX + NIX$(J)
205 NEXT J
207 IF (NSUMX + I0) = 0 THEN GOTO 220
210 NEXT K
220 PRINT "FILES TO BE READ"
230 PRINT "FILENAME AND # OF ENTRIES IN THAT SERIES"
235 FOR J = 1 TO TF
240 PRINT NUMR$(J); " "; NIX$(J)
245 NEXT J
260 FOR J = 1 TO TF
270 PRINT "READY TO LOCATE DATA: BP "; NUMR$(J); " SERIES"
280 PRINT "CATALOG TO LOCATE FILE": INPUT Y$
290 IF LEFT$(Y$,1) < > "Y" GOTO 310
300 PRINT D4; "CATALOG, D1"
305 GOTO 280
310 PRINT D4; "MON, C, 1, 0"
311 PRINT D4; "OPEN BP "; NUMR$(J); ", L70"
315 FOR BV = 1 TO NIX$(J)
317 NIX$(BV) = ""
318 NEXT BV
320 IF PEEK( - 18962) < 2 THEN PRINT D4; "CLOSE BP "; NUMR$(J): GOTO 280

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330 PRINT D$;"READ BP ";NUMRS(J);",R0"; INPUT S:STR = 0;ACTR = 0
340 FOR JK = 1 TO 5
350 PRINT D$;"READ BP ";NUMRS(J);",R";JK; INPUT SN$
360 FOR JL = 1 TO NIX(J)
370 IF NIX(JL) = "9" GOTO 400
375 IF SN$ ( ) NSTX$(J,JL) GOTO 400
380 NCTR = NCTR + 1
385 PRINT D$;"READ BP ";NUMRS(J);",R";JK; INPUT U1$: INPUT U2: INPUT U3$: INPUT U4: INPUT U5: INPUT U6$
388 NIX(JL) = "9"
389 A%(NIX(J,JL)) = U2
390 TICS(NIX(J,JL)) = U3$
392 TCR$(NIX(J,JL)) = U6$
395 IF NCTR = NIX(J) THEN PRINT D$;"CLOSE BP ";NUMRS(J); GOTO 430
398 GOTO 410
400 NEXT JL
410 NEXT JK; PRINT D$;"CLOSE BP ";NUMRS(J)
412 IF NCTR = NIX(J) GOTO 430
414 PRINT "SAMPLES IN BP ";NUMRS(J);" SERIES NOT SATISFIED"
416 PRINT "NUMBER IN SERIES ";NIX(J)
418 PRINT "NUMBER FOUND ";NCTR
419 FOR HP = 1 TO 3000; NEXT HP
430 NEXT J
440 I = 01
458 PRINT "INSERT DISK WITH FILE";Z9$;" AND HIT ANY KEY TO CONTINUE"; INPUT Y$:Y$ = "?"
459 RETURN
500 FOR I = 1 TO 3000; NEXT I; GOTO 1450
510 PRINT "SUBROUTINE"
520 PA(R - 1) = (IP2 * 1.000001) / RE1X(R - 1) : PA$(R - 1) = STR$(PA(R - 1))
540 RE1 IFYY = 0 THEN A$(R - 1) = "0*"; GOTO 560
550 RE1 VPI=(42 * 1.000001) / YI:A$(R - 1) = STR$(VPI):A$(R - 1) = LEFT$(A$(R - 1),7)
570 I1 = 0.00012 * 0.00012 : SID(R - 1) = 0.00012 : SID(R - 1) = 0.00012 : IANT = 0
575 IF RE1X(R - 1) = 1 THEN SID(R - 1) = 0.0; GOTO 610
578 IF PA(R - 1) = 0 THEN SID(R - 1) = 0.0; GOTO 610
580 FOR I = 1 TO RE1X(R - 1)
590 I1 = I1 + (ABS(PA(R - 1) - PA$(R - 1,I))) ^ 2
600 NEXT I:SID(R - 1) = ((SQR(I1) / (RE1X(R - 1) - 1))) / PA(R - 1) * 100.0
610 RE1 IFYY = 1 THEN S2D(R - 1) = 0.0
620 RE1 IFYY = 0 OR YY = 1 GOTO 650
625 RE1 IF VAL(A$(R-1)) < 1 THEN GOTO 650
630 FOR I = 1 TO YY
632 IF RE1X(R - 1,I) = "0*" GOTO 636
634 IANT = IANT + 1
636 NEXT I
638 IF IANT = 0 THEN A$(R - 1) = "0*"; GOTO 650
642 VR = (42 * 1.000001) / IANT:A$(R - 1) = STR$(VR):A$(R - 1) = LEFT$(A$(R - 1),7)
644 IF IANT = 1 THEN S2D(R - 1) = 0.0; GOTO 650
646 IF (VAL(A$(R - 1))) = 0 THEN S2D(R - 1) = 0.0; GOTO 650
648 FOR I = 1 TO YY
650 IF RE1X(R - 1,I) = "0*" GOTO 670
660 I2 = I2 + (ABS(VAL(ORER(R - 1,I)) - VAL(A$(R - 1,I)))) ^ 2
670 NEXT I
690 Y1Y$(R - 1) = YY
700 A2 = 0:P2 = 0:YY = 0:TP = P
705 ERE = FIRE (0)
710 RETURN
720 IF RIGHT$(Z9$,1) = "C" THEN PRINT D$;"CLOSE";Z9$; PRINT "INCORRECT NAME FORMAT FOR READING RAW DATA FILE- DO NOT APPEND NAMES WITH A 'C'"; GOTO 500
730 IF PEEX (-.18962) < 2 THEN PRINT D$;"CLOSE";Z9$; PRINT "FILE HAS NO RAW DATA"; GOTO 500
770 PRINT D$;"CLOSE";Z9$
780 IF D < 0 THEN PRINT "AREA IS READY CALCULATED- DO YOU WISH TO REDO?"; INPUT D0$: IF LEFT$(D0$,1) < "Y" GOTO 1450

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790 PRINT D$;"READ";Z9$;"R0,B0"; INPUT G; INPUT S$; INPUT N; INPUT R1; INPUT RP; PRINT D$;"CLOSE";Z9$
800 DIM ACRTX(N),PMAK(6,9),PA(G),RE1X(6),RE2X(6,9),PAK(6,9),Y1X(6),ADM(6),SD(6),PMAK(6,9),PAK(6)
810 PRINT D$;"OPEN";Z9$;"L";RI
811 PRINT "HOW MANY SIDES OF DISKS USED FOR DATA"; INPUT IY$
812 IF IY$ ( = 0 GOTO 811
813 FOR IY = 1 TO IY$
814 PRINT "ENTER LAST TRANSIENT # ON SIDE";IY; INPUT ICZX(IY)
815 IF ICZX(IY) ( = 0 THEN GOTO 814
816 NEXT IY
818 XSX = 0;E1X = 0;S1X = 0
820 FOR M = 1 TO 6
821 FOR IY = 1 TO IY$
822 IF M = (ICZX(IY) + 1) THEN PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)"; INPUT Z$
823 NEXT IY
825 PRINT D$;"OPEN";Z9$;"L";RI
829 SUM = 0;AREA = 0;RI = 0;CTRL = 0;CTRL = 0;HI = 0;LAGE = 0;RR = 0
830 PRINT D$;"READ";Z9$;"R";M;"B1"; INPUT P
860 IF M = 1 THEN TP = P;R = 1;PR = 1
865 PRINT D$;"READ";Z9$;"R";M;"B165A"; INPUT FLZ$; IF FLZ$ = "*" THEN PRINT D$;"CLOSE";Z9$; GOTO 1410
870 IF P ( ) TP THEN RE1X(R) = PR - 1;R = R + 1;PR = 1
878 IF R ) 5 AND XSX ) 0 THEN S1X = S1X / XSX;E1X = E1X / XSX;XSX = 0
880 PRINT D$;"READ";Z9$;"R";M;"B1"; INPUT P; INPUT LOC:PMAK(R,PR) = STR$(PMAK(R,PR))
890 PRINT D$;"READ";Z9$;"R";M;"B25"
900 FOR I = 0 TO N
910 INPUT ACRTX(I)
920 NEXT I
930 PRINT D$;"CLOSE";Z9$
932 IF PMAK(R,PR) ) 40 OR PMAK(R,PR) ( = 10 GOTO 940
934 IF E1X = 0 GOTO 940
935 FOR I = S1X TO E1X
936 AREA = AREA + ACRTX(I)
938 NEXT I; GOTO 1360
940 FOR I = 0 TO N
950 IF I = N AND PMAK(R,PR) ) 40 THEN AREA$ = "0*"; GOTO 1320
960 IF I = N THEN PRINT "NO 5 POINTS THAT EXCEED THRESHOLD";AREA = 0.0; GOTO 1300
970 IF ACRTX(I) ( 0 GOTO 1050
980 IF CTRL ) 0 GOTO 1010
990 IF (ACRTX(I + 1) - ACRTX(I)) ) 0 THEN RR = (ACRTX(I + 1) - ACRTX(I));CTRL = 1
1000 GOTO 1050
1010 IF (ACRTX(I + 1) - ACRTX(I)) ) = RR THEN CTRL = CTRL + 1;SUM = SUM + (ACRTX(I + 1) - ACRTX(I)); GOTO 1040
1020 CTRL = 0
1030 SUM = 0.0
1040 IF CTRL = 5 THEN RR = SUM / 5.0; GOTO 1060
1050 NEXT I
1060 CTRL = 0
1070 IF (I - 9) ( 0 THEN AREA$ = "0*"; GOTO 1320
1090 SPEED = 253
1100 FOR K = (I - 4) TO N
1110 IF K = N THEN AREA$ = "0*"; PRINT " AREA$";AREA$; GOTO 1320
1130 IF K ( LOC GOTO 1170
1140 IF ABS (ACRTX(K) - ACRTX(K + 1)) ) = RR THEN RI = 0; GOTO 1160
1150 RI = RI + 1
1160 IF RI = 3 THEN CTRL = CTRL - 2; GOTO 1190
1170 AREA = AREA + ACRTX(K);CTRL = CTRL + 1
1180 NEXT K
1190 REM
1200 REM THE ABOVE LOOP HAS POINTS INITIALLY THAT ALL DONT EXCEEDTHRESHOLD SO R2 COUNTS- IT MUST FIND 3 CONSECUTIVE POINTS THAT EXCEED THRESHOLD AGAIN SO THAT NEXT LOOP CAN BE ENTERED
1210 RR = PMAK(R,PR) * .04
1220 FOR H = K - 2 TO N; REM PRINT"H";H
1230 HI = HI + 1

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1240 IF H = N - 1 THEN GOTO 1300
1250 IF ACRTX(H) ) RR GOTO 1270
1260 IF ((ACRTX(H) + ACRTX(H + 1) + ACRTX(H + 2)) * 1.000001) / 3.0 ( = RR GOTO 1300
1270 IF H1 ) 2 THEN AREA = AREA + ACRTX(H)
1280 NEXT H
1290 REM THE ABOVE LOOP HAS ALL POINTS ENTERING WHICH EXCEED THE THRESHOLD ON THE SLOPE DOWNSHING- R3 MUST COUNT 3 CONSECUTIVE POINTS THAT DONT EXCEED IN ORDER TO STOP AREA CALCULATIONS
1300 AREA# = STR# (AREA)
1310 REM SPEED=2
1320 IF TP ( ) P THEN GOSUB 510
1330 IF AREA# = "0" GOTO 1350
1335 IF R = 5 THEN XS# = XS# + 1:SI# = SI# + H:EI# = EI# + H
1340 A2 = A2 + AREA
1350 P2 = P2 + PMAX(R,PR):REAR(R,PR) = AREA#*YY + Y1 + 1
1370 PR = PR + 1
1380 PRINT D#;"MOM",1,0"
1400 SPEED= 253
1410 NEXT WHEREX(R) * PR - 1:R = R + 1: GOSUB 510
1420 R = R - 1
1430 PRINT "PLACE SIDE 1 BACK IN DRIVE AND HIT ANY KEY AND (RTN)": INPUT Z#
1438 PRINT D#;"UNLOCK";Z#
1440 PRINT D#;"WRITE";Z#;";RO,B100"; PRINT "A"; PRINT D#;"WRITE";Z#;";RO,B102"; PRINT R: PRINT D#;"WRITE";Z#;";RO,B107"; PRINT L9
1450 PRINT D#;"CLOSE";Z#;";PRINT D#;"LOCK";Z#
1460 PRINT "ENTER DISK FOR CALCULATED DATA AND HIT ANY KEY AND (RTN) TO STORE CALCULATIONS": INPUT I#
1470 Z# = Z# + "C";I# = I# + 2 = R:I# = R
1480 GOSUB 3460
1490 RETURN
1500 VTAB SX(L): HTAB 5: PRINT NMB1$(L): VTAB SX(L): HTAB 14: PRINT LBL1$(L): VTAB SX(L): HTAB 27: PRINT DIL1$(L): VTAB SX(L): HTAB 37: PRINT REP1$(L): RETURN
1510 GK = SH$(L):PK = 2: INVERSE
1520 FOR IO = 1 TO REIX(L)
1530 VTAB (GK): HTAB (PK): PRINT PMA1$(L,IO):PK = PK + 5: IF PK ( = 35 THEN PK = 2:GK = GK + 1
1540 NEXT IO
1550 HTAB (GK): VTAB (GK): PRINT LEFT$(P4$(L),6): RETURN
1560 GK = GS$(L):PK = 2
1570 FOR IO = 1 TO YIY$(L)
1580 VTAB (GK): HTAB (PK): PRINT REAR$(L,IO):PK = PK + 7: IF PK ( = 33 THEN PK = 2:GK = GK + 1
1590 NEXT IO
1600 HTAB (GK): VTAB (GK): PRINT LEFT$(A4$(L),8): RETURN
1610 VTAB (20): HTAB (1): PRINT "ENTER RECORD # YOU WISH TO MODIFY (1 AT A TIME) OR HIT (RETURN) FOR NO CHANGES"
1620 INPUT "I#": IF L# = "" GOTO 2270
1630 L = VAL (L#): IF L ( 1 OR L ) X GOTO 1610
1640 IF L ( NM OR L ) (NM + 4) GOTO 1610
1650 O1$ = LBL1$(L):O2$ = NMB1$(L):O3$ = DIL1$(L):O4$ = REP1$(L)
1660 VTAB SX(L): HTAB (5): PRINT NMB1$(L): VTAB SX(L): HTAB 4: INPUT "O2#"
1670 IF LEN (O2#) ) 9 GOTO 1660
1680 IF LEN (O2#) ) 0 THEN NMB1$(L) = O2$
1690 GOSUB 1500
1700 VTAB SX(L): HTAB (14): PRINT LBL1$(L): VTAB SX(L): HTAB 13: INPUT "O1#"
1710 IF LEN (O1#) ) 4 GOTO 940
1720 IF LEN (O1#) ) 0 THEN LBL1$(L) = O1$
1730 GOSUB 1500
1740 VTAB SX(L): HTAB (27): PRINT DIL1$(L): VTAB SX(L): HTAB 26: INPUT "O3#"
1750 IF LEN (O3#) ) 6 GOTO 1740
1760 IF LEN (O3#) ) = 0 GOTO 1810
1770 IF VAL (O3#) ( = 0 GOTO 1740
1780 FOR I1 = 1 TO LEN (O3#)
1790 IF ASC ( MID$( O3#,I1,1) ( 46 OR ASC ( MID$( O3#,I1,1) ( 57 GOTO 1740
1800 NEXT I1:DIL1$(L) = O3$
1810 GOSUB 1500
1820 VTAB SX(L): HTAB 37: PRINT REP1$(L): VTAB SX(L): HTAB 36: INPUT "O4#"
1830 IF LEN (O4#) ) 2 GOTO 1820

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2970 FOR II = 1 TO LEN (Q3$)
2980 IF ASC ( MID$ (Q3$,II,1) ) ( 46 OR ASC ( MID$ (Q3$,II,1) ) ) 57 GOTO 2930
2990 NEXT II:DILL$(II) = Q3$
3000 HTAB 1: VTAB 15: PRINT "ENTER *Y*,";"*I*;" 2 CHARACTERS ALLOWED"
3010 INPUT *;Q4$: IF LEN (Q4$) > 2 GOTO 3000
3020 IF LEN (Q4$) = 0 GOTO 3070
3030 IF VAL (Q4$) ( = 0 GOTO 3010
3040 FOR II = 1 TO LEN (Q4$)
3050 IF ASC ( MID$ (Q4$,II,1) ) ( 46 OR ASC ( MID$ (Q4$,II,1) ) ) 57 GOTO 3000
3060 NEXT II:REP$(II) = Q4$
3070 X = I: I = I + 1
3075 IF Q2 = 0 GOTO 3060
3077 IF I > 1 THEN PRINT "8 DATA ENTRIES=";Q2;" CANNOT ENTER MORE LABELS": FOR HQ = 1 TO 1000: NEXT HQ: GOTO 3090
3080 GOTO 2840
3090 RES
3100 HOME : VTAB (1): HTAB (2): PRINT M$: VTAB (1): HTAB (14): PRINT X$
3110 VTAB (1): HTAB (26): PRINT Y$: VTAB (1): HTAB (34): PRINT Z$
3120 FOR NN = 1 TO X STEP 5:S = 4: HOME
3130 FOR NN = NN TO NN + 4
3140 IF NN > X GOTO 3380
3150 SX(NN) = INT (S)
3160 VTAB (5): HTAB (1): PRINT NN;"": VTAB (5): HTAB (5): PRINT NBB$(NN)
3170 VTAB (5): HTAB (14): PRINT LBL$(NN)
3180 VTAB (5): HTAB (27): PRINT DILL$(NN)
3190 VTAB (5): HTAB (37): PRINT REP$(NN)
3200 IF Q2 = 0 GOTO 3370
3210 IF JX ( 4 GOTO 3370
3220 INVERSE : S = S + 1
3230 PE = 2:SHK(NN) = INT (S)
3240 FOR JK = 1 TO REIX(NN)
3250 HTAB (PE): VTAB (S): PRINT PNO$(NN,JK)
3260 PE = PE + S: IF PE = 35 THEN S = S + 1:PE = 2
3270 NEXT JK
3280 HTAB (PE): VTAB (S)
3290 PRINT LEFT$( P4$(NN),6):S = S + 1:PE = 2
3300 SSX(NN) = INT (S)
3310 FOR IK = 1 TO YIY(NN)
3320 HTAB (PE): VTAB (S): PRINT REA$(NN,IK)
3330 PE = PE + 7: IF PE = 33 THEN S = S + 1:PE = 2
3340 NEXT IK
3350 HTAB (PE): VTAB (S)
3360 PRINT LEFT$( Q4$(NN),8)
3370 S = S + 1: NORMAL
3380 NEXT NN
3390 HTAB 1: VTAB 20: PRINT "PRESS (1) TO CONTINUE OR (2) TO MODIFY
3400 INPUT Q3$
3410 IF Q3$ ( 1 OR Q3$ ) 2 GOTO 3400
3420 IF Q3$ = 2 THEN GOSUB 1610
3430 NEXT NN
3440 HOME : PRINT "DO YOU WISH TO GET A LISTING OF RECORDS, FIVE ITEMS AT A TIME? * : INPUT Q5: IF RIGHT$( Q5,1) = "Y" GOTO 3100
3450 PRINT D$;"UNLOCK";Z9$
3460 PRINT D$;"OPEN";Z9$;" :L350";" :D";R2X
3470 IF PEEK ( - 18962 ) ( 2 THEN FD = 2
3480 PRINT D$;"MON C,1,0"
3490 FOR N = 1 TO 1
3500 IF W ) 0 GOTO 3560
3505 IF FX = 1 GOTO 3732
3510 PRINT D$;"WRITE";Z9$;" :R";H$;" :BC"
3520 PRINT NBB$(NN): PRINT LBL$(NN)
3530 PRINT DILL$(NN): PRINT REP$(NN)

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3540 PRINT D$;"WRITE";Z9$;"R";N$;"B52"
3550 PRINT R$H(N)
3560 IF Q2 = 0 GOTO 3740
3565 IF Q8$ = 3 OR Q8$ = 4 GOTO 3740
3570 IF J$ ( 4 GOTO 3740
3580 PRINT D$;"WRITE";Z9$;"R";N$;"B77"; PRINT RE1$(N)
3590 PRINT D$;"WRITE";Z9$;"R";N$;"B80"; PRINT LEFT$(P4$(N),6)
3600 PRINT D$;"WRITE";Z9$;"R";N$;"B88"
3610 FOR I1 = 1 TO RE1$(N)
3620 PRINT PWR4$(N,I1)
3630 NEXT I1
3640 PRINT D$;"WRITE";Z9$;"R";N$;"B140"; PRINT LEFT$( ( STR$(S(D(N))),4)
3650 PRINT D$;"WRITE";Z9$;"R";N$;"B177"; PRINT Y1Y$(N)
3660 PRINT D$;"WRITE";Z9$;"R";N$;"B180"; PRINT LEFT$(A4$(N),8)
3670 PRINT D$;"WRITE";Z9$;"R";N$;"B190"
3680 FOR I1 = 1 TO Y1Y$(N)
3690 PRINT RE4$(N,I1)
3700 NEXT I1
3710 PRINT D$;"WRITE";Z9$;"R";N$;"B254"; PRINT LEFT$( ( STR$(S(D(N))),4)
3720 IF FD ( 2 THEN GOTO 3740
3730 PRINT D$;"WRITE";Z9$;"R";N$;"B52"; PRINT LEFT$( ("1.0000000",5); GOTO 3740
3732 PRINT D$;"WRITE";Z9$;"R";N$;"B40"; PRINT LEFT$(TIC$(N),10); PRINT LEFT$(TZ$(N),10)
3735 PRINT D$;"WRITE";Z9$;"R";N$;"B52"; PRINT LEFT$( ( STR$(R$H(N)),8)
3740 NEXT N
3750 IF W ( 0 OR J$ = 4 THEN PRINT D$;"WRITE";Z9$;"R";N$;"B4"; PRINT Q2; PRINT D$;"WRITE";Z9$;"R";N$;"B0"; PRINT 6
3760 IF Q8$ = 3 OR Q8$ = 4 THEN PRINT D$;"WRITE";Z9$;"R";N$;"B0"; PRINT X
3770 PRINT D$;"WRITE";Z9$;"R";N$;"B100"; PRINT 1
3780 IF FD = 2 THEN PRINT D$;"WRITE";Z9$;"R";N$;"B0"; PRINT 0; PRINT D$;"WRITE";Z9$;"R";N$;"B15"; PRINT "*"
3785 IF Q8$ = 5 THEN PRINT D$;"WRITE";Z9$;"R";N$;"B15"; PRINT "*"
3790 PRINT D$;"CLOSE";Z9$
3800 PRINT D$;"LOCK";Z9$
3810 RETURN
3820 TEXT : HOME : PRINT "MENU OPTIONS": CLEAR :D$ = CHR$( 4)
3830 HTAB 1: VTAB 5: PRINT "(1) AREA CALCULATIONS"
3840 PRINT "(2) END PASS THROUGH DATA-EDIT DATA/LABELS"
3850 PRINT "(3) NAME LABELS"
3860 PRINT "(4) EDIT LABELS"
3870 PRINT "(5) INPUT SAMPLE WTS./LABELS FROM DISK"
3880 PRINT "(6) QUIT"
3890 INPUT Q8$
3900 IF Q8$ ( 1 OR Q8$ ) 6 GOTO 3890
3910 IF Q8$ = 6 GOTO 4020
3920 PRINT "CATALOGS TO LOCATE FILE? (Y/N)"; INPUT Y$
3930 IF ( LEFT$(Y$,1) ) = "Y" THEN PRINT "DRIVE B?"; INPUT R2$; IF R2$ = 1 OR R2$ = 2 THEN PRINT D$;"CATALOG";D";R2$
3940 PRINT "ENTER FILENAME AND DRIVE # (SEPARATE RESPONSES BY COMMA) - FOR OPTIONS 2,3,4 AND 5 'FILENAME' REFERS TO CALCULATED DATA FILE AND NAME APPENDED WITH A 'C' "; INPUT Z9$,R2$
3950 IF R2$ ( 1 OR R2$ ) 2 GOTO 3940
3960 IF R2$ ( LEFT$(Z9$,1) ) ( 65 OR R2$ ( LEFT$(Z9$,1) ) 90 GOTO 3940
3970 PRINT D$;"OPEN";Z9$;"L350";D";R2$
3980 IF Q8$ = 1 THEN PR = 1: GOSUB 720
3990 IF Q8$ = 2 OR Q8$ = 3 OR Q8$ = 4 OR Q8$ = 5 THEN GOSUB 2280
4000 IF Q8$ = 6 GOTO 4020
4010 GOTO 3820
4020 END

```

# Non-linear Regression Program

```

10 HOME
15 DS = CHR$(4)
20 GOTO 2660
25 FOR I = 1 TO 3000: NEXT I
27 GOTO 2740
30 K = K + 1: REM K IS INCREMENTED EACH TIME SUB IS REACHED SO THAT SUMMED RATIOS CAN BE DIVIDED BY # OF STDS IN A BLOCK
35 REM NRFT IS THE RESULT OF SUMMED RATIOS(CRFT) WHICH ARE DIVIDED BY THE # OF STDS IN PARTICULAR BLOCK
40 SUM = SUM + CRFT(I)
45 IF I = 02 THEN J = J + 1:NRFT(J) = SUM / N:K = 0:SUM = 0: PRINT "NRFT";J;"=";NRFT(J): GOTO 60: REM ECITED ONLY IF AT LAST POINT IN ARRAY
50 IF LBL$(I + 1) ( ) "STD" THEN J = J + 1:NRFT(J) = SUM / N:K = 0:SUM = 0: PRINT "NRFT";J;"=";NRFT(J): REM MAKING AN AVERAGE NOW IF NEXT POINT IS NOT A STD
55 REM F P = 0 AND LBL$(I + 1) ( ) "STD" THEN RMSD = SUR (RMSD / CTR)
60 RETURN
65 FOR IL = 1 TO 2
66 CTR = 0
67 IF OPS = 2 AND IL = 2 GOTO 81
69 IF OPS = 3 AND IL = 1 GOTO 81
71 FOR I = 1 TO 01
73 IF I = 01 THEN PRINT "NO CONSECUTIVE STDS IN FILE": GOTO 83
74 IF LBL$(I) ( ) "STD" THEN CTR = 0: GOTO 79
75 IF IL = 1 AND P4$(I) = "04" GOTO 79
76 IF IL = 2 AND P4$(I) = "04" GOTO 79
77 CTR = CTR + 1:CSX(CTR) = I
78 IF CTR = 1 AND LBL$(I + 1) ( ) "STD" THEN GOTO 80
79 NEXT I
80 A(I) = CTR: BOSUB 84
81 PRINT "NRFT": PRINT IL
83 NEXT IL: RETURN
84 D = 2: IF IL = 2 THEN RETURN
85 FOR UJ = 1 TO CTR
86 PRINT "UJ=";UJ;" NUM=";CSX(UJ)
87 I = CSX(UJ)
88 YX = VAL (DILL$(I)):C(UJ) = YX: PRINT "C=";C(UJ)
90 X = VAL (P4$(I))
95 IF IL = 2 THEN X = VAL (P4$(I)): PRINT "X=";X
100 Y = X / YX
105 FOR J = 2 TO 2 * D + 1
110 A(J) = A(J) + X ^ (J - 1)
115 NEXT J
120 FOR K = 1 TO D + 1
125 R(K,D + 2) = T(K) + Y * X ^ (K - 1)
130 T(K) = T(K) + Y * X ^ (K - 1)
135 NEXT K
140 T(0 + 2) = T(0 + 2) + Y ^ 2
145 NEXT UJ
150 FOR J = 1 TO D + 1
155 FOR K = 1 TO D + 1
160 R(J,K) = A(J + K - 1)
165 NEXT K
170 NEXT J
175 FOR J = 1 TO D + 1
180 FOR K = J TO D + 1
185 IF R(K,J) ( ) 0 THEN 205
190 NEXT K
195 PRINT "NO UNIQUE SOLUTION"
200 GOTO 225
205 FOR I = 1 TO D + 2
210 S = R(J,I)

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215 R(I,1) = R(I,1)
220 R(I,1) = S
225 NEXT I
230 Z = 1 / R(I,J)
235 FOR I = 1 TO D + 2
240 R(I,1) = Z * R(I,1)
245 NEXT I
250 FOR K = 1 TO D + 1
255 IF K = J THEN 280
260 Z = -R(I,J)
265 FOR I = 1 TO D + 2
270 R(I,1) = R(I,1) + Z * R(I,1)
275 NEXT I
280 NEXT K
285 NEXT J
290 PRINT
295 PRINT " CONSTANT=";
300 P0 = R(I,D + 2)
305 PRINT P0
310 FOR J = 1 TO D
315 PRINT J;"DEGREE COEFF=";
320 IF J = 1 THEN P1 = R(J + 1,D + 2); PRINT P1
325 IF J = 2 THEN P2 = R(J + 1,D + 2); PRINT P2
330 NEXT J:P = 0:SUM = 0:K = 0:J = 0
335 FOR I = 1 TO Q2
338 IF IL = 1 AND P4*(I) = "0" GOTO 380
340 IF IL = 2 AND P4*(I) = "0" GOTO 380
345 R(I) = VAL (P4*(I))
350 IF IL = 2 THEN R(I) = VAL (P4*(I)); PRINT "R=";R(I)
355 NOK(I) = R(I) / (P0 + P1 * R(I) + P2 * (R(I) ^ 2))
356 FOR JK = 1 TO CTR
357 NA = CSX(JK)
358 IF NGB1*(I) = NGB1*(JK) GOTO 360
359 GOTO 367
360 CRT(I) = NOK(I) / C(KK); PRINT "CRT=";CRT(I);DK(I) = CRT(I);BOSUB 30
361 IF I) CSX(CTR) GOTO 367
363 MRSD = MRSD + (SD(IL,1) / R(I)) ^ 2
364 PRSD = PRSD + ((1 - CRT(I)) ^ 2)
365 REM IF SENSITIVITY HAS DROPPED THEN CRT WILL BE LESS THAN 1 - FOR ANY GROUP OF SAMPLES AFFECTED BY THIS DROP IN SENSITIVITY, THEIR CONCENTRATION VALUES AS RETURNED FROM THE CURVE SHOULD BE INCREASED (DONE BY DIVIDING BY CRT)
367 NEXT JK
380 NEXT I
385 MRSD = SQ (MRSD / CTR); PRINT "MRSD=";MRSD
388 PRSD = SQ (PRSD / CTR); PRINT "PRSD=";PRSD
390 IF MRSD (.01) THEN MRSD = .01
392 MRSD = MRSD * 100.0
395 P = 0; REM PRSD=0;
400 FOR I = 1 TO Q2; REM THIS LOOP FOR ALL STDS W/R/T CONCEN RETURNED FROM CALIB FOR 1ST GROUP OF STDS
405 IF IL = 1 AND P4*(I) = "0" GOTO 460
410 IF IL = 2 AND P4*(I) = "0" GOTO 460
450 IF SD(IL,1) ( MRSD THEN SD(IL,1) = MRSD
455 SCER(I) = SQ ((SD(IL,1) ^ 2) / (P0 + P1 * R(I) + P2 * (R(I) ^ 2)) + ((PRSD * NOK(I)) ^ 2))
457 PRINT "SCER=";SCER(I)
460 NEXT I
465 NA = 1
470 FOR I = 2 TO J; REM THIS LOOP TO GET AVERAGES FOR BLOCKS OF STDS SURROUNDING A GROUP OF SAMPLES
475 IF NA = 1 AND D(L,1) ( ) "STD" THEN INCR(TNA) = NRT(I);NA = NA + 1
480 INCR(TNA) = (INCR(T) - 1) + NRT(I) / 2.0; PRINT "INCR(T)=";INCR(T) - 1)
485 REM INCR(T) IS THE AVERAGE OF INCR(T) SURROUNDING A BLOCK OF DATA
490 NA = NA + 1

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495 NEXT I
500 IF LBL$(I2) ( ) "STD" THEN INCRBT (RM) = NBT(I)
505 J = 0
510 IF LBL$(I) ( ) "STD" THEN J = 1
515 FOR I = 1 TO I2: REM THIS LOOP DETERMINES IF SAMPLE IS A STD OR NOT -IF IT IS A REGULAR SAMPLE THEN THE PROPER VALUE OF J IS ASSIGNED, VALUE GOES TO A SUB AND A NEW NMC IS ASSIGNED BY DIVIDING BY THE PROPER INCRBT
520 IF I = I2 GOTO 535
522 IF IL = 1 AND P4$(I) = "0*" GOTO 540
525 IF IL = 2 AND P4$(I) = "0*" GOTO 540
530 IF LBL$(I) = "STD" AND LBL$(I + 1) ( ) "STD" THEN J = J + 1
535 IF LBL$(I) ( ) "STD" THEN NMC(I) = (NMC(I) / INCRBT(I)) * VAL (DIL$(I));DX(I) = NMC(I) * AJM(I); PRINT "NMC=";NMC(I)
540 NEXT I
550 J = 1
552 PRINT "HIT ANY KEY TO CONTINUE BEFORE STORAGE": INPUT Y$
553 PRINT D$;"MON,C,I,0"
554 PRINT D$;"UNLOCK";?9$
555 PRINT D$;"OPEN";?9$;"L350"
560 FOR I = 1 TO 01
565 PRINT D$;"WRITE";?9$;"R";I;"B";L2K(IL): PRINT NMC(I)
570 PRINT D$;"WRITE";?9$;"R";I;"B";L6K(IL): PRINT LEFT$(STR$(SD(IL,I)),4)
572 SPEED= 255
575 PRINT D$;"WRITE";?9$;"R";I;"B";L4K(IL): PRINT SCR(I)
580 PRINT D$;"WRITE";?9$;"R";I;"B";L6K(IL): PRINT DX(I)
585 NEXT I
590 PRINT D$;"WRITE";?9$;"R0,B";L8K(IL): PRINT P1: PRINT P2
592 M$ = L8K(IL) + 40: PRINT D$;"WRITE";?9$;"R0,B";M$; PRINT RMSD;M$ = M$ + 16: PRINT D$;"WRITE";?9$;"R0,B";M$; PRINT CTR
593 M$ = L8K(IL)
594 FOR II = 1 TO CTR
595 PRINT D$;"WRITE";?9$;"R0,B";M$; PRINT CSK(II)
597 M$ = M$ + 4: NEXT II
598 PRINT D$;"WRITE";?9$;"R0,B18": PRINT "1"
600 PRINT D$;"CLOSE";?9$
602 PRINT D$;"LOCK";?9$
610 P# = 0
620 GOTO 700
650 FOR IL = 1 TO 2
652 PRINT D$;"MON,C,I,0"
653 SPEED= 50
655 PRINT D$;"UNLOCK";?9$;"D";R2$
660 PRINT D$;"OPEN";?9$;"L350"
662 PRINT D$;"READ";?9$;"R0,B18": INPUT R$; IF R$ = "1" GOTO 665
663 PRINT D$;"CLOSE";?9$; PRINT "REGRESSION NOT PREVIOUSLY DONE": FOR NB = 1 TO 1000: NEXT NB: GOTO 2560
665 PRINT D$;"READ";?9$;"R0,B";L8K(IL)
670 INPUT P0: INPUT P1: INPUT P2
675 PRINT D$;"CLOSE";?9$
680 PRINT D$;"LOCK";?9$
700 POME = 16304.0: POME = 16297.0: POME = 16299.0: POME = 16302.0
800 ROT= 0
808 X = 20;Y = 134;K = 17;P = 17
816 HGR2
824 HCOLOR= 3: SCALE= 1
832 HPLOT 20,0 TO 20,137: HPLOT 20,137 TO 279,0: HPLOT 279,0 TO 279,0 TO 20,0
840 FOR R = 1 TO 1
848 IF R = 2 THEN X = 274
856 FOR I = 140 TO 0 STEP - 20
864 DRAW 14 AT X,1
872 IF R = 2 THEN GOTO 920
880 IF 1 ( 1.0 THEN GOTO 920
888 DRAW 15 AT 6,1
896 IF P ) 26 THEN P = 17
904 DRAW P AT 11,1

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912 P = P + 1
920 NEXT I
928 NEXT R
936 FOR R = 1 TO 1: ROT = 16
944 IF R = 2 THEN Y = 0
952 FOR I = 12 TO 265 STEP 66
960 IF I < 30 THEN GOTO 1064
968 DRAW 14 AT 1,1: GOTO 1064
976 IF R = 2 THEN GOTO 1064
984 ROT = 0
992 IF K > 26 THEN GOTO 1016
1000 DRAW K AT 1,150
1008 GOTO 1056
1016 DRAW 18 AT 1,150
1024 IF K = 27 THEN DRAW 17 AT 1 + 5,150
1032 IF K = 28 THEN DRAW 18 AT 1 + 5,150
1040 IF K = 29 THEN DRAW 19 AT 1 + 5,150
1048 ROT = 16
1056 K = K + 1
1064 NEXT I
1072 NEXT R
1080 X = 0
1088 ROT = 0
1096 AS = "A"
1104 AS = "CONC"
1112 FOR I = 1 TO LEN (AS)
1120 DRAW (ASC (MID$(AS,I,1)) - 31) AT X,70
1128 X = X + 7
1136 NEXT I
1144 X = 133
1152 FOR I = 1 TO LEN (B#)
1160 DRAW (ASC (MID$(B#,I,1)) - 31) AT X,159
1168 X = X + 7
1176 NEXT I
1255 SCALE = 1: X2 = 150
1257 IF IL = 2 GOTO 1265
1260 V = .200: U = 298.9 / (700.0 / (P0 + P1 * 700.0 + P2 * (700.0 ^ 2)))
1261 CH# = STR$( (350.0 / (P0 + P1 * 350.0 + P2 * (350.0 ^ 2)))): CF# = LEFT$(CH#,5)
1263 CF# = STR$( (700.0 / (P0 + P1 * 700.0 + P2 * (700.0 ^ 2)))): CF# = LEFT$(CF#,5)
1264 IV = 650: IW = 10: GOTO 1275
1265 V = .002456: U = 253.9 / (57000 / (P0 + P1 * 57000 + P2 * (57000 ^ 2)))
1268 CH# = STR$( (28500 / (P0 + P1 * 28500 + P2 * (28500 ^ 2)))): CH# = LEFT$(CH#,5)
1272 CF# = STR$( (57000 / (P0 + P1 * 57000 + P2 * (57000 ^ 2)))): CF# = LEFT$(CF#,5)
1273 IV = 53000: IW = 815
1275 FOR I = 1 TO IV STEP IW
1280 PLOT INT ( (1 / (P0 + P1 * I + P2 * (I ^ 2))) * U) + 20, INT ( (136 - I * V)
1285 NEXT I
1290 FOR I = 1 TO LEN (Z99#)
1295 DRAW (ASC (MID$(Z99#,I,1)) - 31) AT X2,10
1300 X2 = X2 + 7
1305 NEXT I
1310 X2 = 130
1315 FOR I = 1 TO LEN (CH#)
1320 DRAW (ASC (MID$(CH#,I,1)) - 31) AT X2,150
1325 X2 = X2 + 6
1330 NEXT I
1335 X2 = 249
1340 FOR I = 1 TO LEN (CF#)
1345 DRAW (ASC (MID$(CF#,I,1)) - 31) AT X2,150
1350 X2 = X2 + 6

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1355 NEXT I
1360 POK% = STR% (P0):P1% = STR% (P1):P2% = STR% (P2):XE = 10
1365 FOR I = 1 TO LEN (STR% (P0))
1370 DRAW (ASC ( MID% (P0%,I,1)) - 31) AT XE,165
1385 XE = XE + 6
1390 NEXT I
1392 XE = 10
1395 FOR I = 1 TO LEN (STR% (P1))
1400 DRAW (ASC ( MID% (P1%,I,1)) - 31) AT XE,175
1410 XE = XE + 6
1420 NEXT I
1422 XE = 10
1425 FOR I = 1 TO LEN (STR% (P2))
1428 DRAW (ASC ( MID% (P2%,I,1)) - 31) AT XE,185
1430 XE = XE + 6
1435 NEXT I
1490 FOR PX = 1 TO 5000: NEXT PX
1500 TEXT : HOME
1505 A = 1:B = 0:C = 0:D = 1
1510 HTAB 1: VTAB 22: PRINT "(1): PRINT CURRENT PLOT"
1520 HTAB 1: VTAB 23: PRINT "(2) CHG PRINT FORMAT/VIEW INSTRUCTIONS"
1530 HTAB 1: VTAB 24: PRINT "(3) CONTINUE WITH ROUTINE"
1550 VTAB 24: HTAB 1: INPUT BJK
1560 IF BJK (1 OR BJK) 3 GOTO 1500
1570 IF BJK = 3 GOTO 2580
1580 IF BJK = 1 GOTO 1910
1600 HOME
1610 HTAB 1: VTAB 1: PRINT "TO PRINT A HITES SCREEN YOU MUST USE THE 'USR' FUNCTION"
1620 HTAB 1: VTAB 3: PRINT "PRINT USR(ABCD) MUST BE ENTERED WHERE A,B,C,D SUBFUNCTIONS ARE DESCRIBED BELOW"
1630 HTAB 1: VTAB 5: PRINT "A-HITES PAGE (0=PAGE 1;1=PAGE 2)"
1640 HTAB 1: VTAB 6: PRINT "B-SIZE (0=SMALL;1=LARGE)"
1650 HTAB 1: VTAB 7: PRINT "C-PICTURE TYPE (0=REG;1=INV.)"
1660 HTAB 1: VTAB 8: PRINT "D-PRINTER SLOT (1 TO 7)"
1670 HTAB 1: VTAB 9: PRINT "TYPING 'PRINT USR(1011)' MEANS DUMPING"
1680 HTAB 1: VTAB 10: PRINT "PAGE 1 OF GRAPHICS WITH A SMALL INVERSE"
1690 HTAB 1: VTAB 11: PRINT "PICTURE TO A PRINTER LOCATED IN SLOT 1"
1700 PRINT "CURRENT PARAMETERS ARE USR('A:B:C;1)"
1710 HTAB 1: VTAB 14: PRINT "HIT (CR) TO ACCEPT CURRENT PARAMETERS OR ENTER VALUE FOR A"
1720 INPUT "A";A%
1730 IF A% = "" GOTO 1910
1731 A = VAL (A%)
1732 IF A (0 OR A) 1 GOTO 1710
1735 IF A ( ) 1 THEN HTAB 14: PRINT "PICTURE ON PAGE 2 OF GRAPHICS-DO YOU WISH TO CONTINUE "; INPUT UY%: IF LEFT% (UY%,1) = "N" THEN A = 1
1740 HTAB 1: VTAB 16: PRINT "ENTER VALUE FOR B": INPUT B
1750 IF B (0 OR B) 1 GOTO 1740
1760 HTAB 1: VTAB 17: PRINT "ENTER VALUE FOR C": INPUT C
1770 IF C (0 OR C) 1 GOTO 1760
1775 POK% 10,76: POK% 11,00: POK% 12,96
1800 IF A = 0 AND B = 0 AND C = 0 THEN PRINT USR (0001)
1810 IF A = 0 AND B = 0 AND C = 1 THEN PRINT USR (0011)
1820 IF A = 0 AND B = 1 AND C = 1 THEN PRINT USR (0111)
1830 IF A = 0 AND B = 1 AND C = 0 THEN PRINT USR (1011)
1840 IF A = 1 AND B = 0 AND C = 0 THEN PRINT USR (1001)
1850 IF A = 1 AND B = 0 AND C = 1 THEN PRINT USR (1101)
1860 IF A = 1 AND B = 1 AND C = 1 THEN PRINT USR (1111)
1870 IF A = 1 AND B = 1 AND C = 0 THEN PRINT USR (1101)
1900 GOTO 2580
1910 POK% 10,76: POK% 11,00: POK% 12,96: PRINT USR (1001)
2580 FOR I = 1 TO 13
2590 A(I) = 0.0: NEXT I

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3180 DIM MDC(2),C(30),CRT(30),MFT(15),MCRET(15),R(13),R(7,B),T(8),RC(1),SEER(1),DX(1)
3190 L0X(1) = 140:L0X(2) = 254:L2X(1) = 145:L2X(2) = 260:L4X(1) = 276:L4X(2) = 308:L6X(1) = 324:L6X(2) = 200:L8X(1) = 200:L8X(2) = 102:L9X(1) = 280
3200 IF O0X = 4 THEN GOSUB 650
3210 IF O0X = 1 OR O0X = 2 OR O0X = 3 THEN GOSUB 65
3220 GOTO 2740
3225 O% = CHR$(4)
3230 REM PRINTO%,"CLOSE",I%
3235 REM PRINTO%,"LOCK",I%
3240 END
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2216 DIM ACRTX(N),PMAIX(G),REIX(G),YIYX(G),LOC(G),P(G),IRECX(G)
2218 PRINT "HOW MANY SIDES OF DISK ARE USED FOR DATA?": INPUT AMX
2219 IF AMX < 1 OR AMX > 6 GOTO 2218
2220 FOR IU = 1 TO AMX
2221 PRINT "ENTER LAST TRANSIENT # ON SIDE":IU
2222 INPUT ISIDEX(IU): IF ISIDEX(IU) < 1 OR ISIDEX(IU) > 6 THEN GOTO 2221
2223 NEXT IU: IF AMX = 2 THEN GOTO 2225
2224 GOSUB 200: GOTO 3000
2225 PRINT "DO YOU WISH TO GET A REPORT OF THESE VALUES?": INPUT YTR
2226 IF RIGHT$(YTR,1) < "Y" THEN GOTO 2600
2227 PRINT "HOW MANY RECORDS NEED TO BE RECALLED?": INPUT NMRX
2228 IF NMRX < 0 OR NMRX > 6 THEN GOTO 2227
2229 FOR IIX = 1 TO NMRX
2231 PRINT "RECORD #":IIX: INPUT IRECX(IIX)
2233 IF IRECX(IIX) < 1 OR IRECX(IIX) > 6 THEN GOTO 2231
2235 NEXT IIX
2236 FOR KIX = 1 TO 6
2237 PRINT D$: "M",C,I,"0"
2239 FOR IU = 1 TO AMX
2240 IF KIX = (ISIDEX(IU) + 1) THEN PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)": INPUT TR$: GOTO 2244
2242 NEXT IU
2244 FOR IIX = 1 TO NMRX
2245 IF KIX < ) IRECX(IIX) THEN GOTO 2256
2248 PRINT D$: "OPEN";IIX,"L";RI
2250 PRINT D$: "READ";IIX,"R": INPUT P(IIRECX(IIX)): INPUT PMAIX(IIRECX(IIX)): INPUT LOC(IIRECX(IIX))
2253 PRINT D$: "CLOSE";IIX
2256 NEXT IIX
2260 NEXT KIX
2500 REM
2530 POKE 33,33: PR# 1: PRINT CHR$(15)
2535 PRINT TAB(2): "TRAY ID": TAB(20): "PEAK VAL.": TAB(35): "PEAK LOCATION"
2560 FOR IIX = 1 TO NMRX
2570 PRINT TAB(2): P(IIRECX(IIX)): TAB(20): PMAIX(IIRECX(IIX)): TAB(35): LOC(IIRECX(IIX))
2580 NEXT IIX
2590 PR# 0
2600 PRINT "WOULD YOU LIKE TO OVERWRITE ANY OF THE VALUES?": INPUT RTX
2603 IF RIGHT$(RTX,1) < "Y" THEN GOTO 3000
2605 PRINT "ENTER TYPE OF CHANGE DESIRED"
2606 PRINT "(1) TRAY POSITION"
2607 PRINT "(2) DISCLOSE RECORD"
2608 PRINT "(3) BOTH": INPUT RTX
2610 IF RTX < 1 OR RTX > 3 THEN GOTO 2605
2614 FOR IC = 1 TO 2
2615 IF RTX = 1 AND IC = 2 GOTO 2763
2616 IF RTX = 2 AND IC = 1 GOTO 2763
2620 PRINT "ENTER # OF RECORDS YOU WOULD LIKE TO OVERWRITE FOR OPTION";IC: INPUT NMRX
2630 IF NMRX < 1 OR NMRX > 6 THEN GOTO 2620
2640 FOR IJ = 1 TO NMRX
2650 PRINT "ENTER RECORD #":IJ: INPUT IRECX(IJ)
2660 IF IRECX(IJ) < 1 OR IRECX(IJ) > 6 THEN GOTO 2650
2662 IF IC = 1 THEN PRINT "ENTER NEW VALUE FOR TRAY POSITION": INPUT P(IIRECX(IJ))
2670 NEXT IJ
2680 FOR KI = 1 TO 6
2710 FOR IJ = 1 TO AMX
2720 IF KI = (ISIDEX(IJ) + 1) THEN PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)": INPUT TR$: GOTO 2740
2730 NEXT IJ
2740 FOR IJ = 1 TO NMRX
2741 IF KI < ) IRECX(IJ) GOTO 2760
2743 PRINT D$: "OPEN";IIX,"L";RI
2745 IF IC = 2 THEN PRINT D$: "WRITE";IIX,"R": IRECX(IJ): "BLSA": PRINT "*"

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2748 IF IC = 1 THEN PRINT D$; "READ"; Z9$; "R"; I$; RECK(IJ); "B1"; INPUT PAX; INPUT PABX(I$RECK(IJ)); INPUT LOC(I$RECK(IJ))
2750 IF IC = 1 THEN PRINT D$; "WRITE"; Z9$; "R"; I$; RECK(IJ); "B1"; PRINT P(I$RECK(IJ)); PRINT PABX(I$RECK(IJ)); PRINT LOC(I$RECK(IJ))
2755 PRINT D$; "CLOSE"; Z9$
2760 NEXT IJ
2761 NEXT KI
2763 NEXT IC
2765 NURS = KNURS
2770 REM BOT2500
3000 FOR IU = 1 TO 3000: NEXT IU: RETURN
3820 TEXT : HOME : PRINT "MENU OPTIONS": CLEAR :DS = CHR$(4)
3830 HTAB 1: VTAB 5: PRINT "(1) PRINT RESULTS"
3850 HTAB 1: VTAB 6: PRINT "(2) PRINT RAW DATA INFORMATION"
3860 HTAB 1: VTAB 7: PRINT "(3) FORMAT ERROR CODE IN EACH RECORD"
3862 HTAB 1: VTAB 8: PRINT "(4) PRINT RESULTS/LABELS"
3864 HTAB 1: VTAB 9: PRINT "(5) PRINT RESULTS WITH CONCENTRATION"
3870 HTAB 1: VTAB 10: PRINT "(6) QUIT"
3890 INPUT Q8$
3900 IF Q8$ (1 OR Q8$) 6 GOTO 3890
3910 IF Q8$ = 6 GOTO 4020
3920 PRINT "CATALOG TO LOCATE FILE ?(Y/N)": INPUT Y$
3930 IF (LEFT$(Y$,1)) = "Y" THEN PRINT "DRIVER ?": INPUT R$: IF R$ = 1 OR R$ = 2 THEN PRINT D$; "CATALOG"; D$; R$:
3940 PRINT "ENTER FILENAME AND DRIVE # (SEPARATE RESOURCES BY COMMA)": INPUT Z9$, R2$
3950 IF R2$ (1 OR R2$) 2 THEN GOTO 3940
3960 IF ASC (LEFT$(Z9$,1)) (65 OR ASC (LEFT$(Z9$,1))) 90 GOTO 3940
3965 PRINT "ENTER VARC RUN #": INPUT Z1$
3970 PRINT "ENTER DISC BACKUP NUMBER": INPUT Z1$
3980 IF Q8$ = 1 OR Q8$ = 4 OR Q8$ = 5 THEN GOSUB 720
3985 IF Q8$ = 2 OR Q8$ = 3 THEN GOSUB 2150
3990 GOTO 3820
4020 END

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