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Automated Data Acquisition for Analysis of Fly Ash by Graphite Furnace Atomic Absorption Spectrophotometry

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

A THESIS

PRESENTED TO

The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements for the Degree of
Master of Arts

by

Eileen Dowds

1989

APPROVAL SHEET

This thesis is submitted in partial fulfillment of
the requirement for the degree of

Master of Arts

Eileen Dowds

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Dedicated to

my mother, Kathleen Dowds

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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.

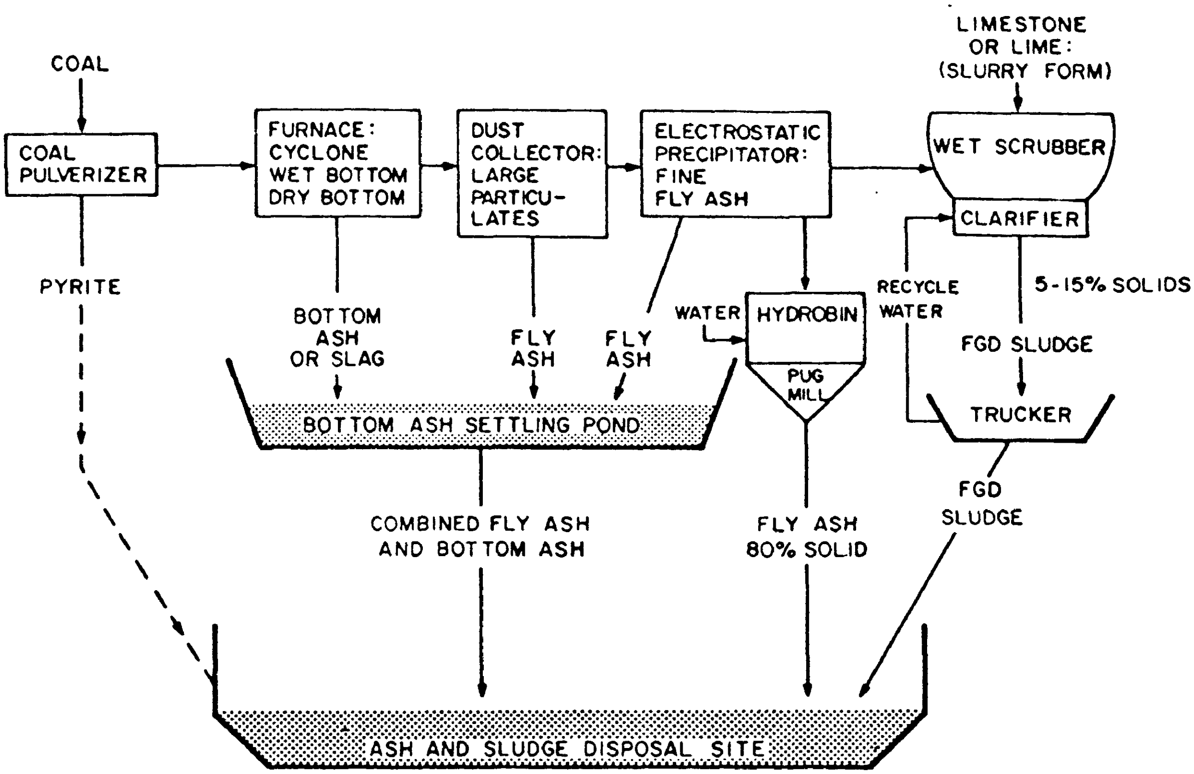
Various stages of ash production are shown along with the stages of processing. Fly ash is a type of fine residual ash captured in emission control devices. As the name implies, this type of ash is airborne and can escape into the atmosphere if not caught by electrostatic precipitators. Bottom ash is 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



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* 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	–

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* Source: ref. 7,12

Table 3 *

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

Element	Fly Ash (µg/ml) Water Soluble Before pH Adjustment (pH 12.5)	Water Soluble After pH Adjustment (pH 6.5)	Concentration in Soil Saturation Extracts (µg/ml)	
			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	–	–

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* 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).

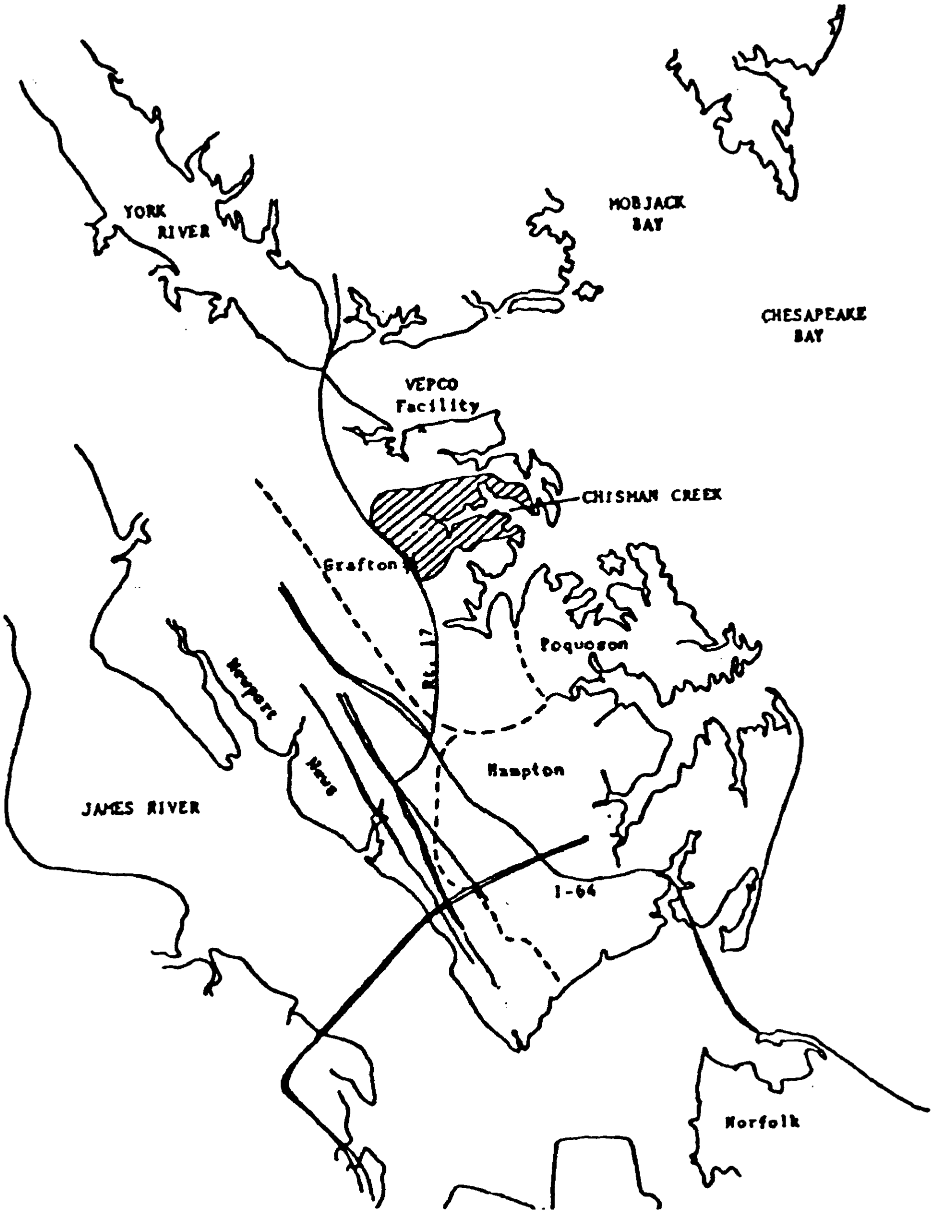
Since vanadium existed at relatively high levels in all samples analyzed in this study, a more in-depth future study of vanadium and its patterns seemed appropriate. Rather than taking samples from materials contaminated within Chisman Creek, fly ash would be taken back to the laboratory and subject 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*

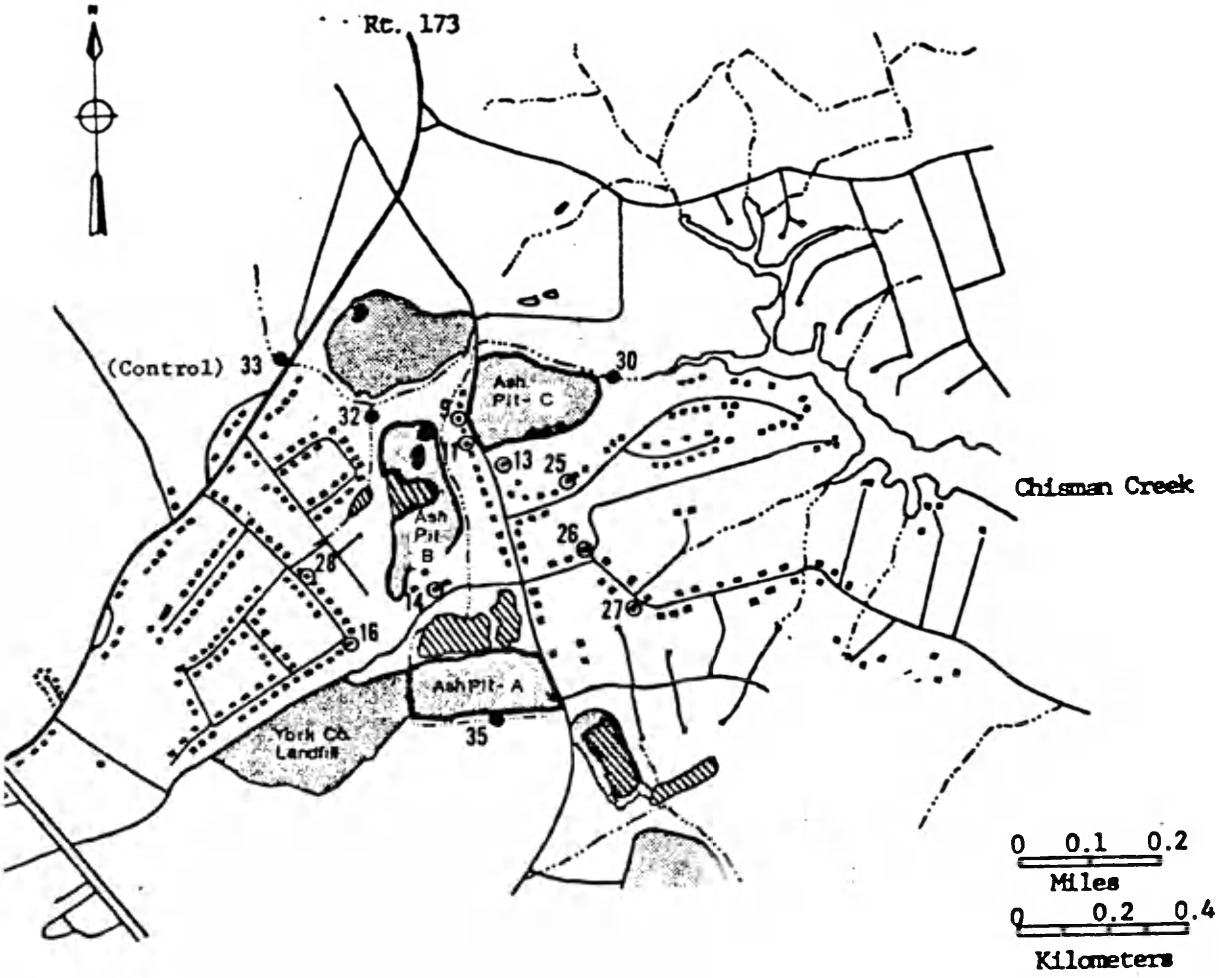
Chisman Creek study area and VEPCO facility in Grafton, Virginia



*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 reenlisted 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 µm 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

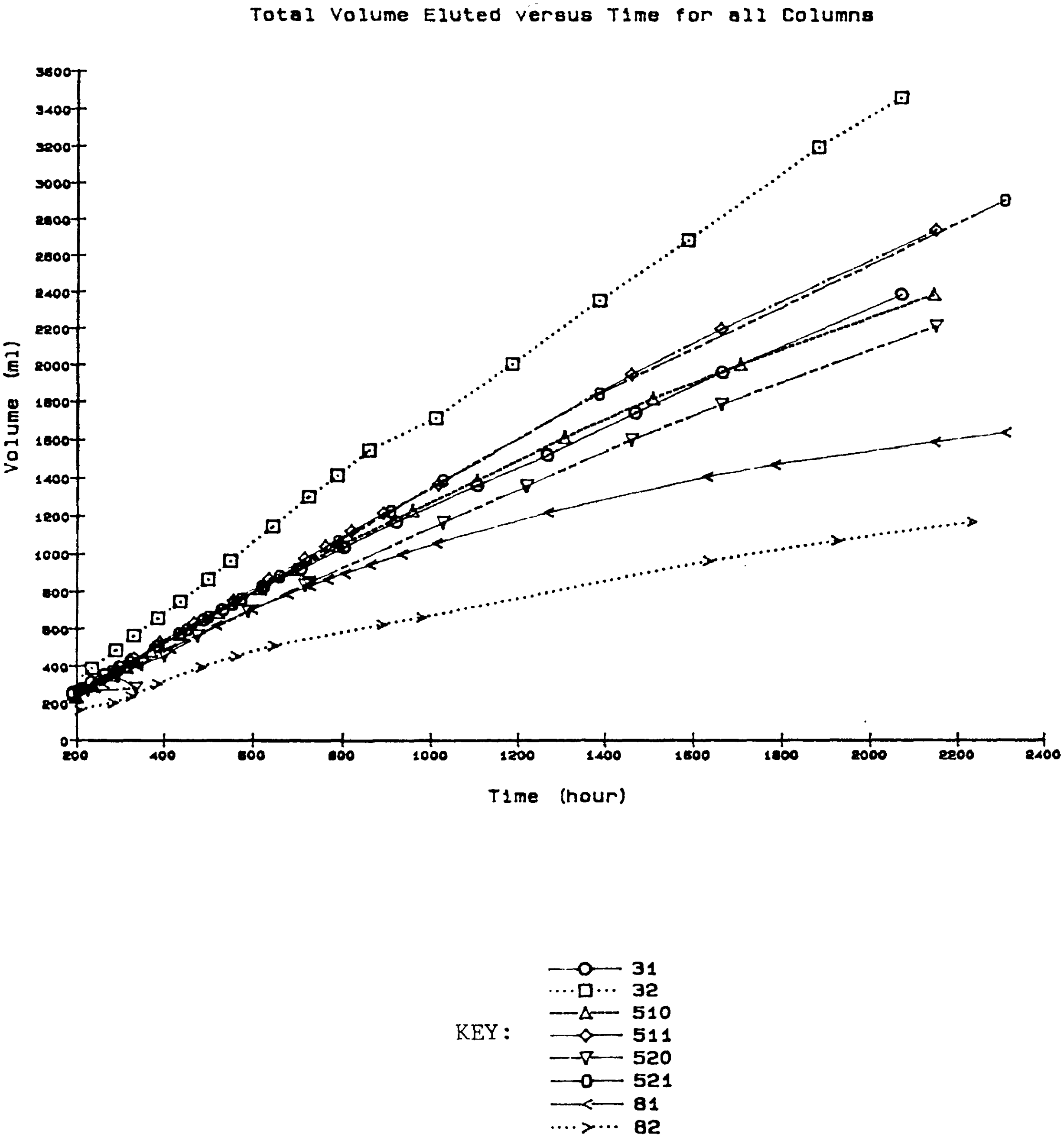
pH	Ionic Strength	Conjugate Base/Acid	Molarity	Acid/Base	Molarity
pH 3	0.10	$ClCH_2COO^-Na^+$	0.0960	$ClCH_2COOH$	0.0680
pH 5	0.01	$CH_3COO^-Na^+$	0.0096	CH_3COOH	0.0054
pH 5	0.10	$CH_3COO^-Na^+$	0.0960	CH_3COOH	0.0540
pH 8	0.01	$(CH_2OH)_3CNH_2(H)^+$	0.0096	$(CH_2OH)_3CNH_2$	0.0120

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 $ClCH_2COO^-Na^+$ 0.6800 M $ClCH_2COOH$	3.5	2.1	<1.1	52.0	2.2	5.1
Concentrated sodium carbonate solution 0.4850 M Na_2CO_3	<0.20	<0.08	<0.04	<0.07	<0.40	<0.04
Concentrated sodium acetate solution 0.8270 M $CH_3COO^-Na^+$	<0.13	<0.05	<0.04	<0.07	<0.30	<0.07
Regular pH 8 buffer 0.0096 M $(CH_2OH)_3CNH_2(H)^+$ 0.0120 M $(CH_2OH)_3CNH_2$	<0.06	<0.30	0.027	<0.02	<0.06	0.016
THAM solid sample 0.00874 g $(CH_2OH)_3CNH_2$	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


Total Volume Eluted versus Time for all 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 x 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 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 msecs 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), BG0 (background signal - reference beam), and I0 (hollow cathode signal - reference beam). Each set of signals was acquired every 16.67 msecs (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 msecs after the instrument had updated the hollow cathode sample beam signal (I) and 2.90 msecs 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, BGO, and IO 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 (IO), even when the energy of the deuterium lamp changes (BGO). 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 BGO and IO 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 IO/I, A(t), represents the absorbance of radiation from the hollow cathode lamp; IO and I are the lamp intensities after passing through the reference and sample paths, respectively. Average values of IO 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 I0' 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 I0' and I0 should be equal. This principle applies to calculating the deuterium lamp absorbance, A(BG) in equation G. The final corrected absorbance, Acorr 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 BG0, I0, 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 msecs), 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 I0. 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, I0, 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.

<u>Within-run Calculations</u>: 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

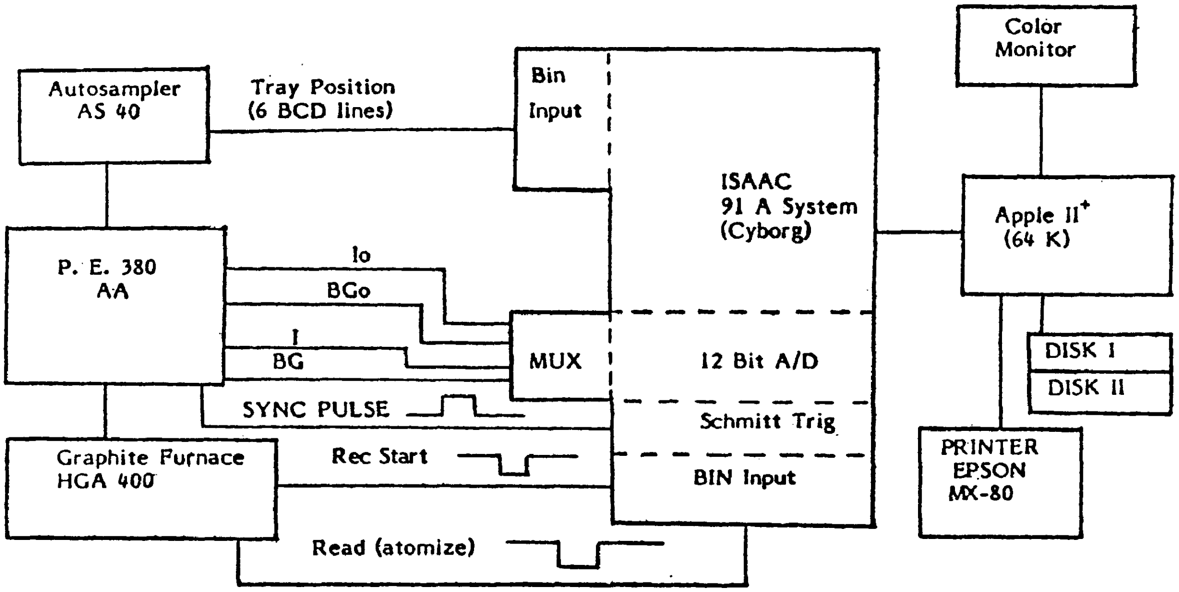


Figure 6

PE 380 timing diagram (60 Hz)

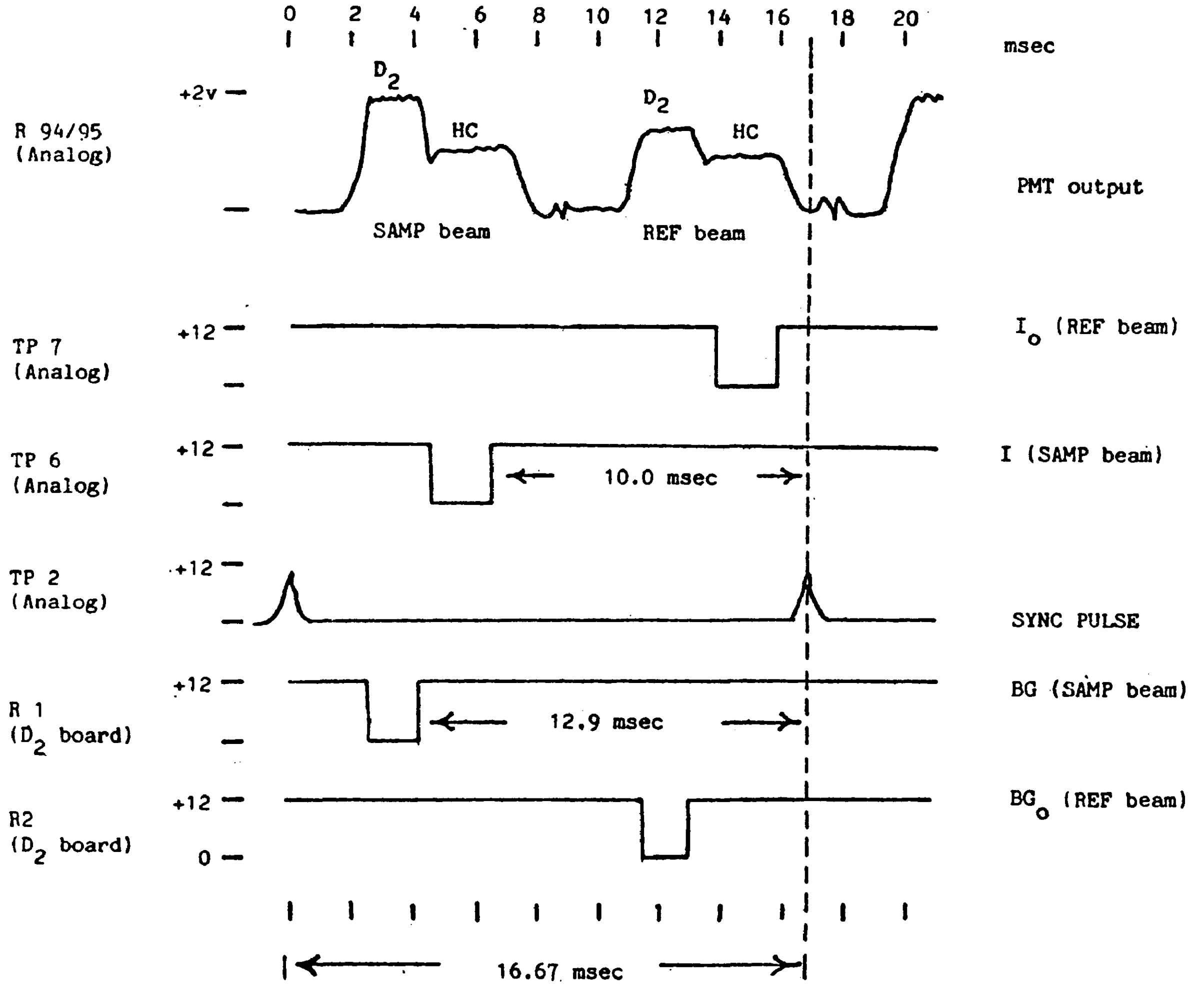


Figure 7

Data acquisition program flow chart

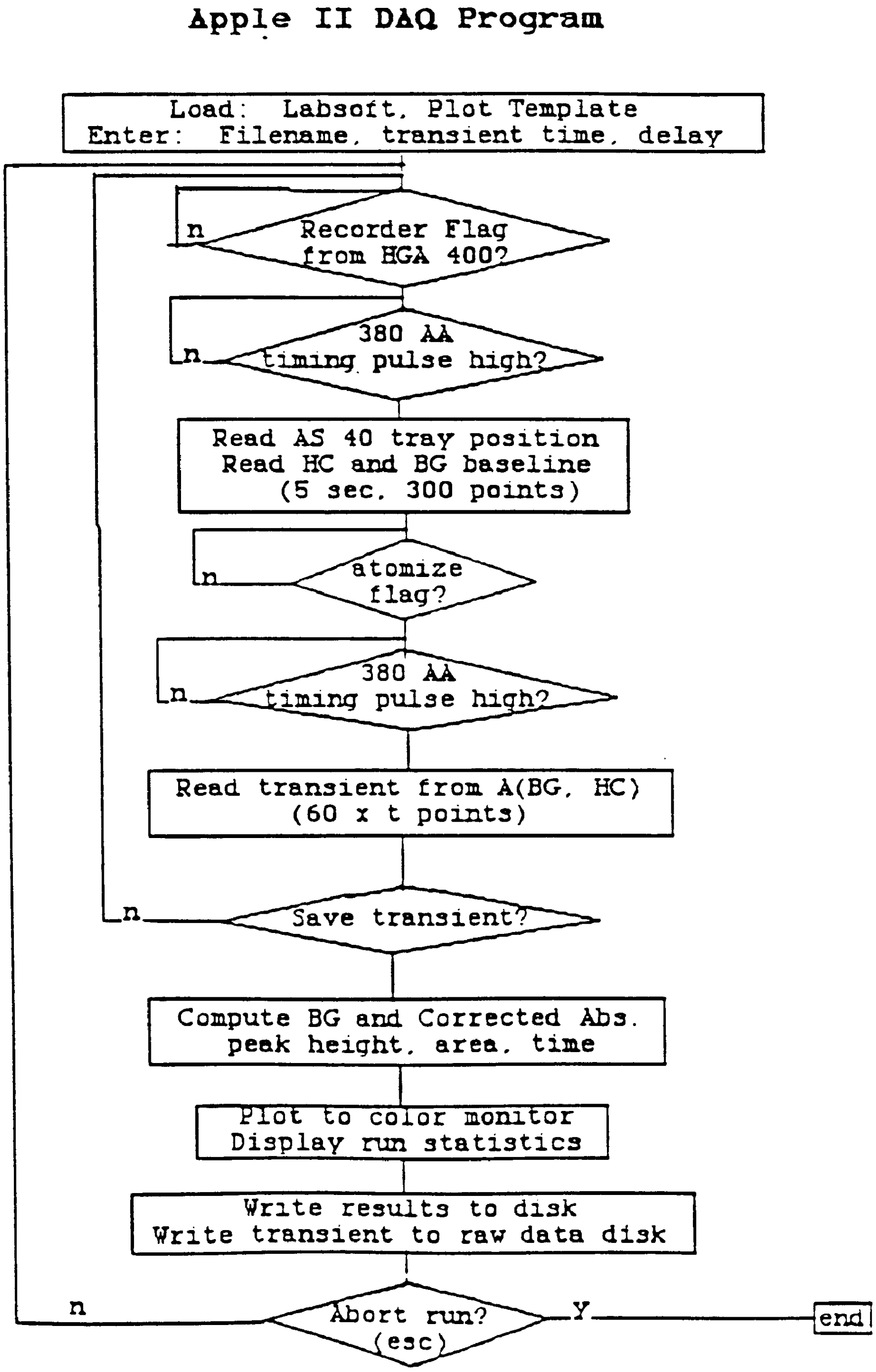


Figure 8

Transients produced during atomization as recorded by data acquisition system

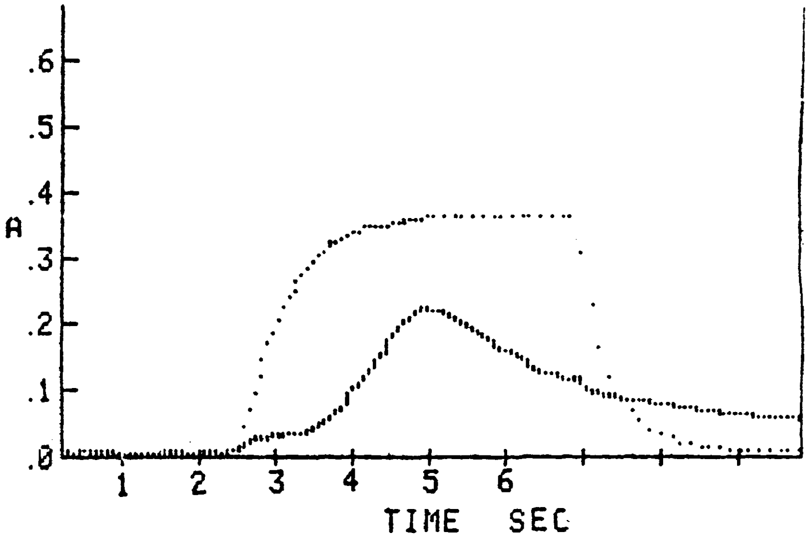


Figure 9

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

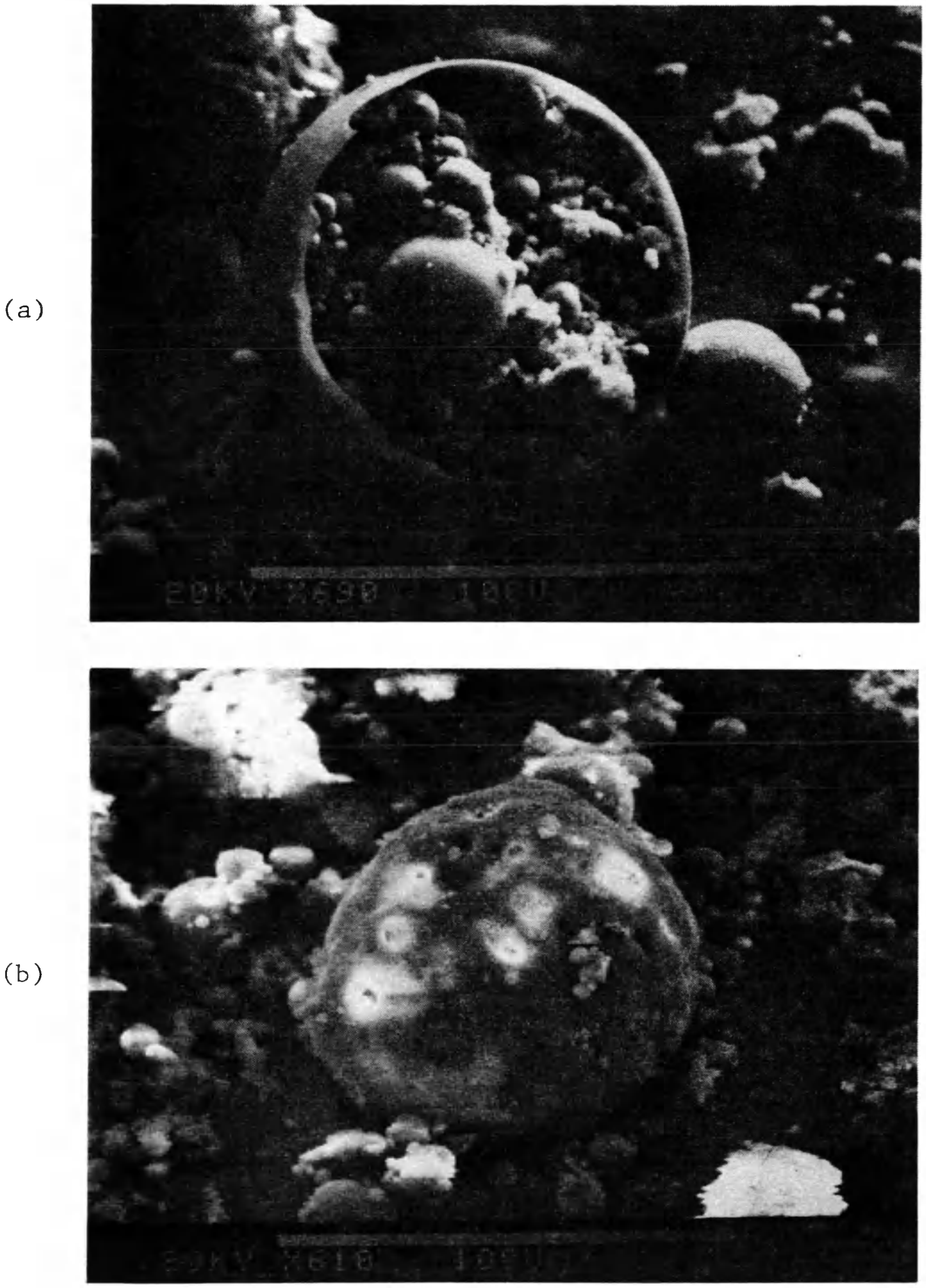


Table 5

Trace element analysis results generated by PDP-11 computer

```
AA RESULTS FOR V   410-5174   FLYASH LEACHATE           ED
DATE ANALYZED    DIL.VOL.SUB.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=P0+P1*A+P2*(A**2)
 1    2    3  4    5      6    7     8     9    10      11   12   13    14  15
       SAMPLE ID    DILTN SOLTN 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
MTX  15130 31   1  1.000.000207  94  1.619  94  1.000 Less Than .000391 MTX
TEGC 38904  1   1  9.000.001509  21  11.76  21      0.001509  21.000312 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  133.8 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.   REPS
             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 410-5174 Sample FLYASH LEACHATE	Date 6/23/85
RAMP TIME (s)	10	10	0	1		Element V	[✓ ABS]/CONC
HOLD TIME (s)	60	20	2	3		Wavelength 318.4 nm	Filter: IN/[✓ OUT]
RECORD		24				Slit(ALT) .7 nm	D_2: [✓ ON]/OFF
READ		24	-5			Lamp 15 ma	MODE: TC INT [✓ PEAK]
BASELINE						Samp Volume 50 μl	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) $A = A(t) - A'$ $\quad (A' = \log (Io'/I')$ and $A(t) = \log (Io/I))$

B) $A = \log (Io/I) - \log (Io'/I')$

C) $A = \log (Io/I) + \log (I'/Io')$

D) $A = \log (Io/I * I'/Io')$

E) $A = \log (I'/I * Io/Io')$

F) $A = \log (I'/I)$ $\quad$ (since $Io' = Io$, autogain circuit)

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

G) $A(BG) = \log (BG'/BG)$

H) $Acorr = A - A(BG)$

Table 8

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

Copper lamp current/ absorbance conditions	BGO	BG	IO	I	^{a}A	$^{b}A_{(BG)}$
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) I′ represents balance conditions

$^{b}A_{(BG)}$ = log (BG′/BG) BG′ 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 <u>future</u> 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 µm and larger, are composed chiefly of anhydrite ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$) (29,28). Calcium is probably chiefly present from intrusions of $CaCO_3$. The larger crystals contain H_2SO_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 Al_2O_3, SiO_2, CaO, FeO, and 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 ($Ca_3(PO_4)_2$) (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.

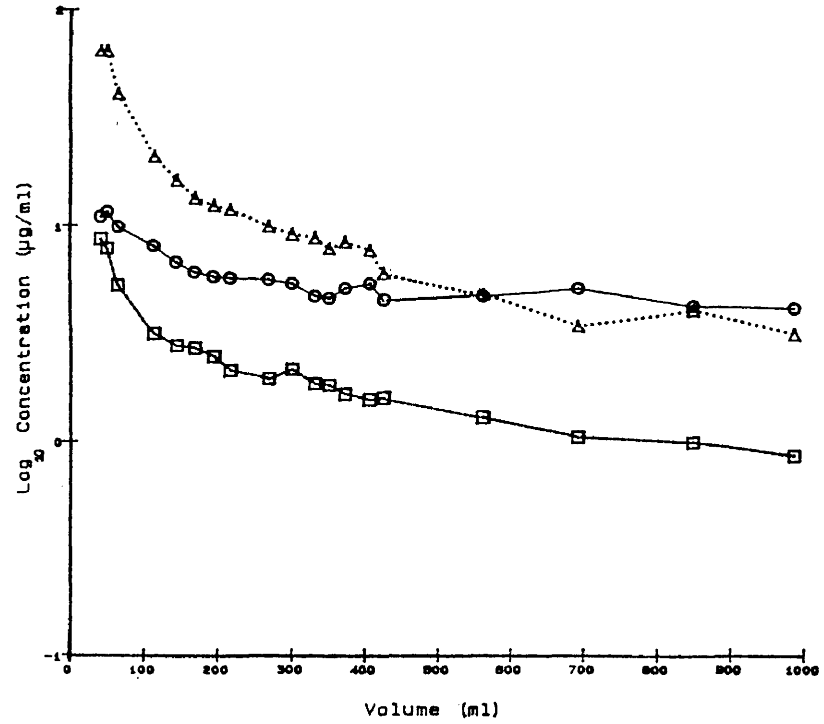
It is a well-known fact that many transition elements are more soluble at acidic pHs than neutral pHs (41,42). Transition metal behavior is unpredictable at high pHs due to the possible formation of anions. These anions are soluble at high pHs when the corresponding metallic cation would precipitate 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

Element Concentration versus Volume Eluted from Column 31



Element Concentration versus Volume Eluted from Column 32

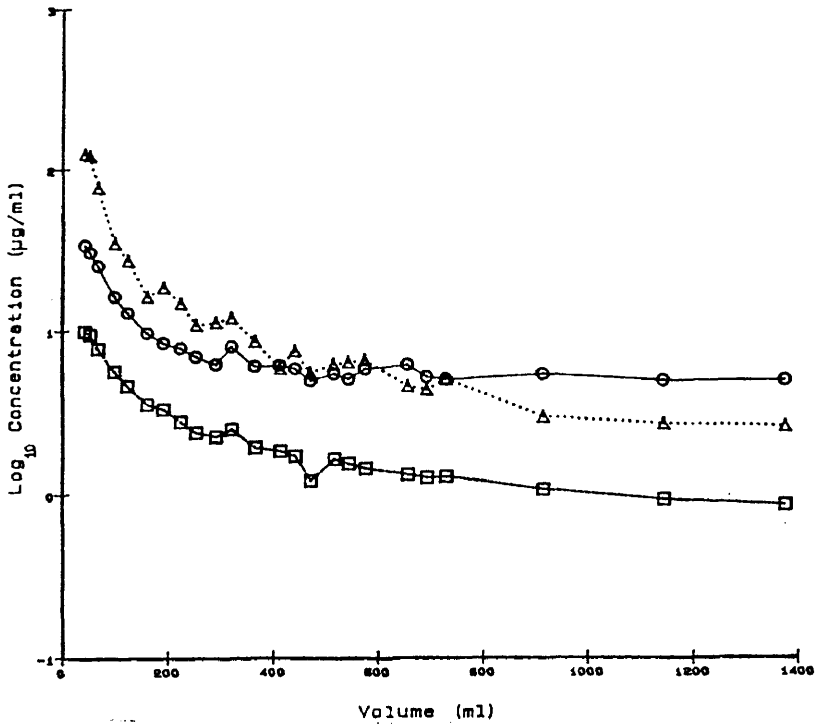
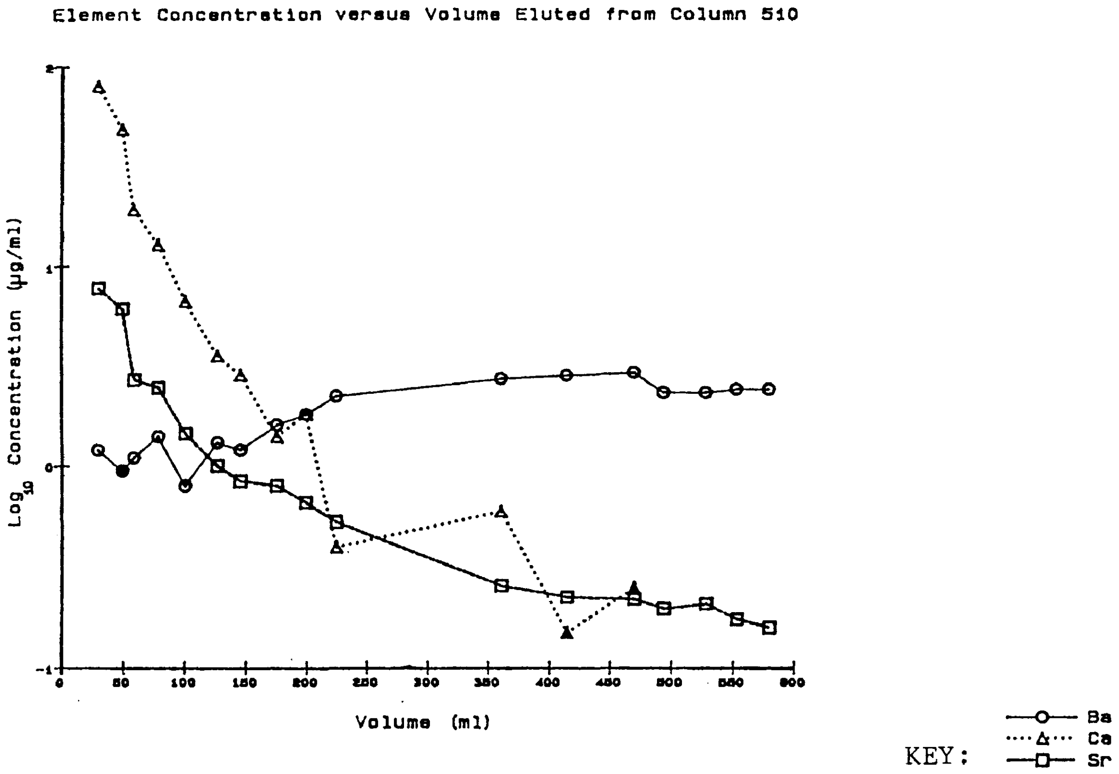


Figure 10b

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


Element Concentration versus Volume Eluted from Column 510

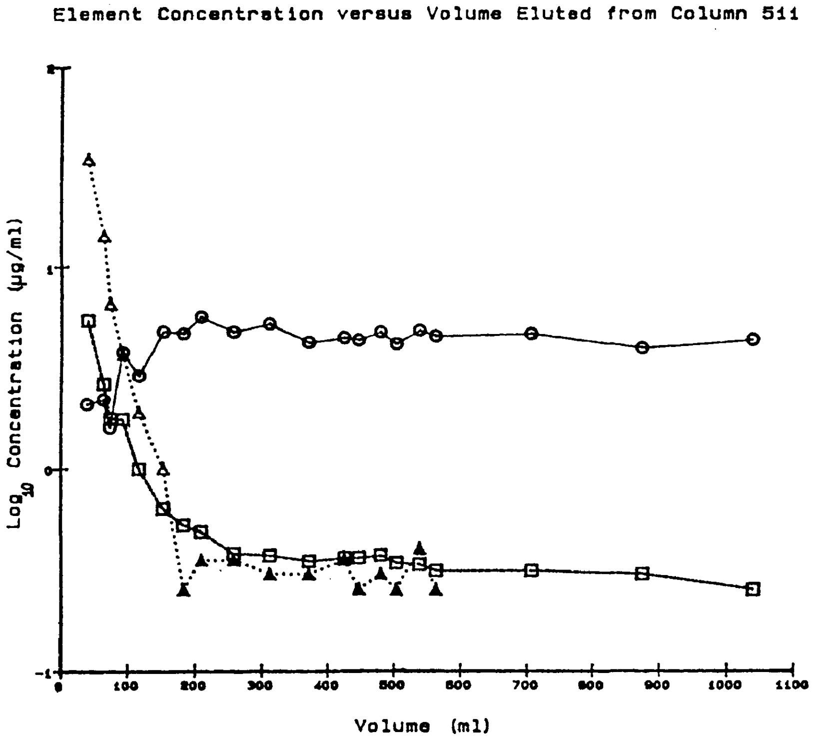
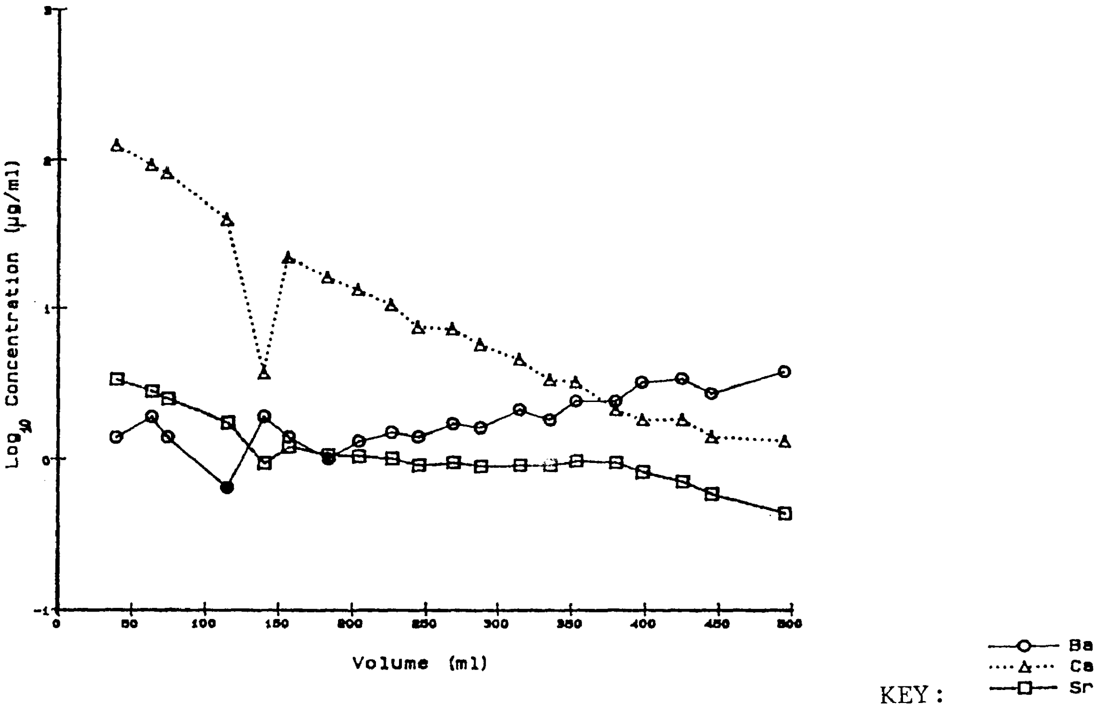

Element Concentration versus Volume Eluted from Column 511

Figure 10c

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

Element Concentration versus Volume Eluted from Column 520



Element Concentration versus Volume Eluted from Column 521

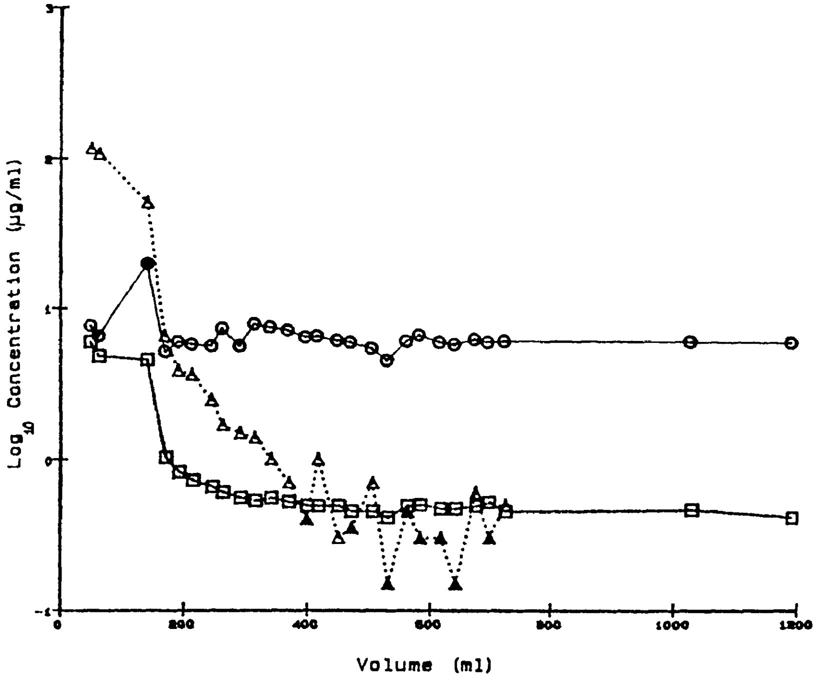
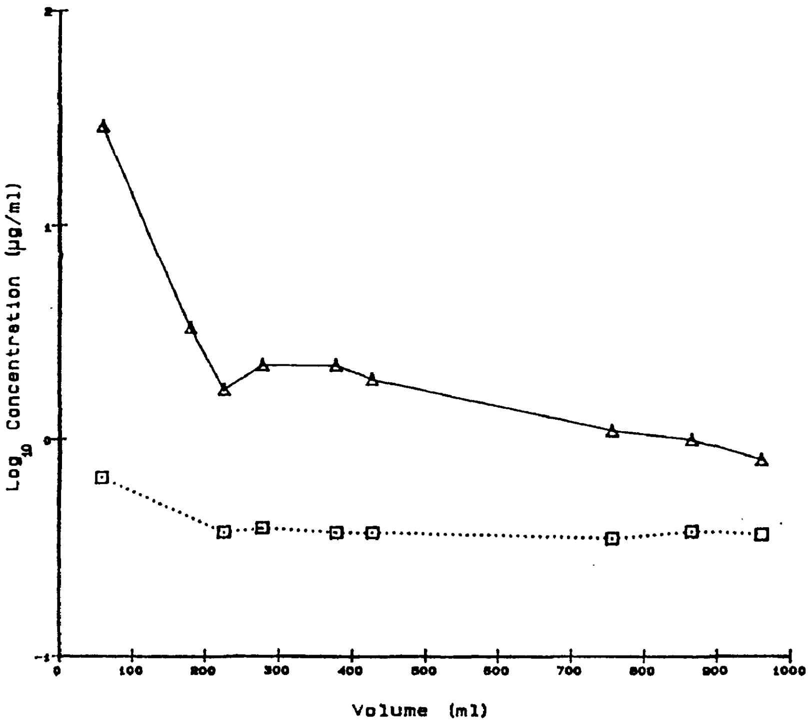


Figure 10d

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

Element Concentration versus Volume Eluted from Column 81



KEY: —△— Ca
····□···· Sr

Element Concentration versus Volume Eluted from Column 82

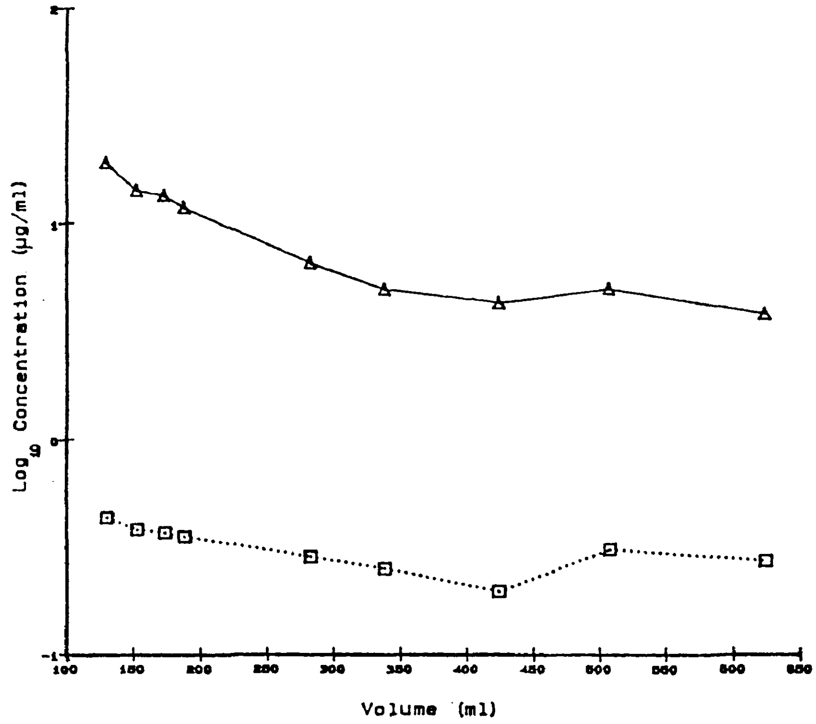
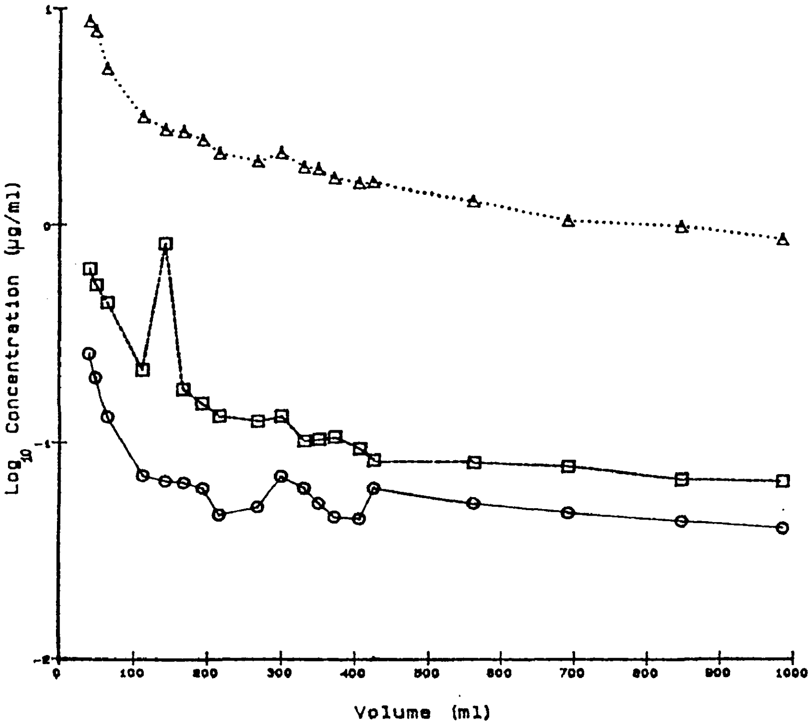


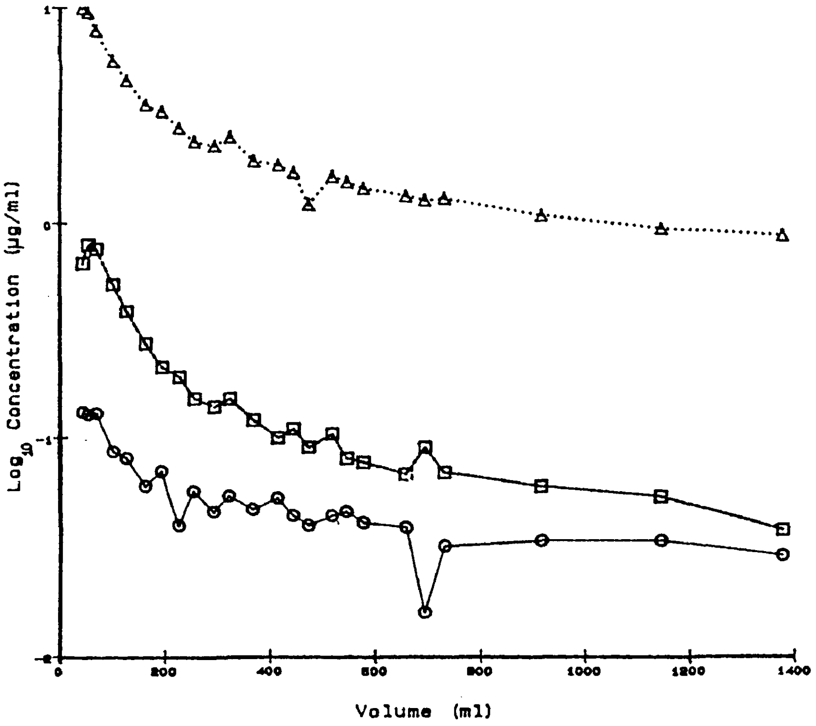
Figure 11a

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

Element Concentration versus Volume Eluted from Column 31



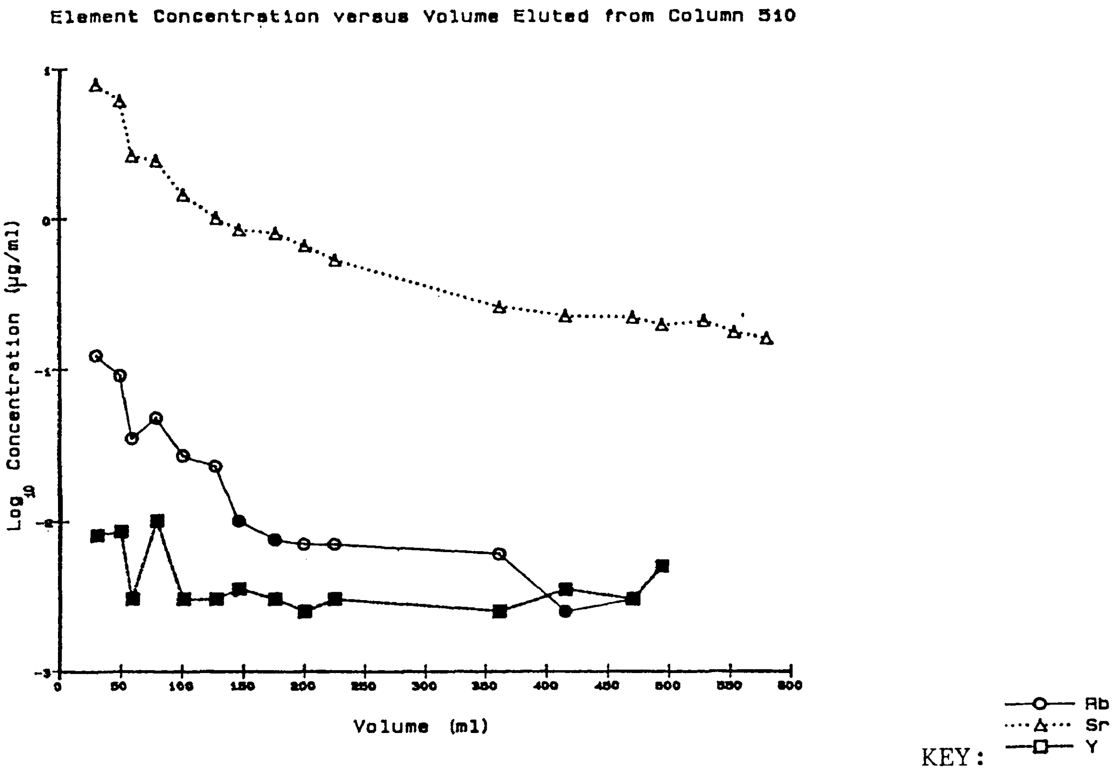
Element Concentration versus Volume Eluted from Column 32



KEY:
—○— Rb
···△··· Sr
—□— Y

Figure 11b

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



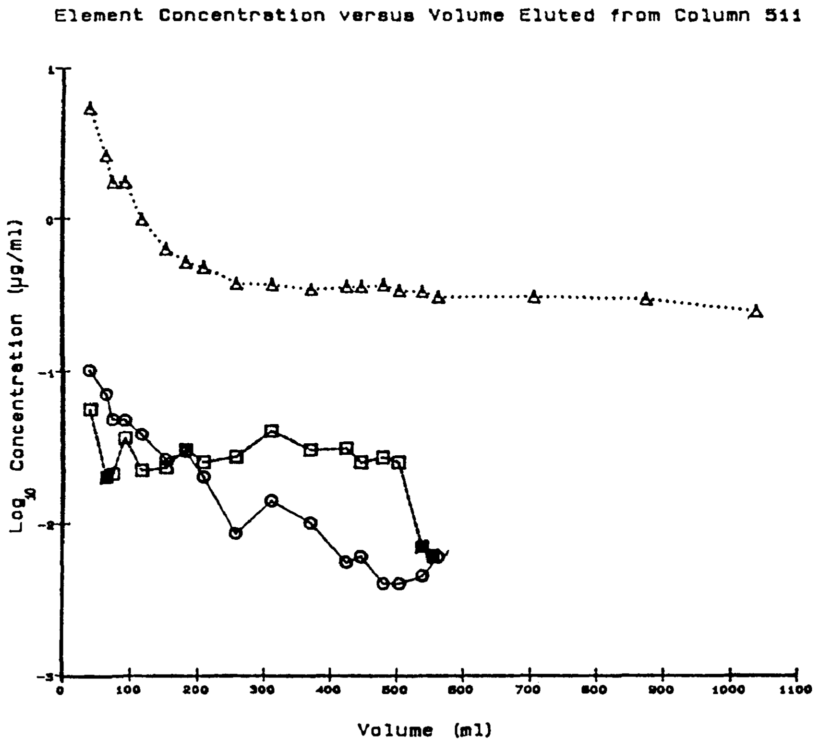
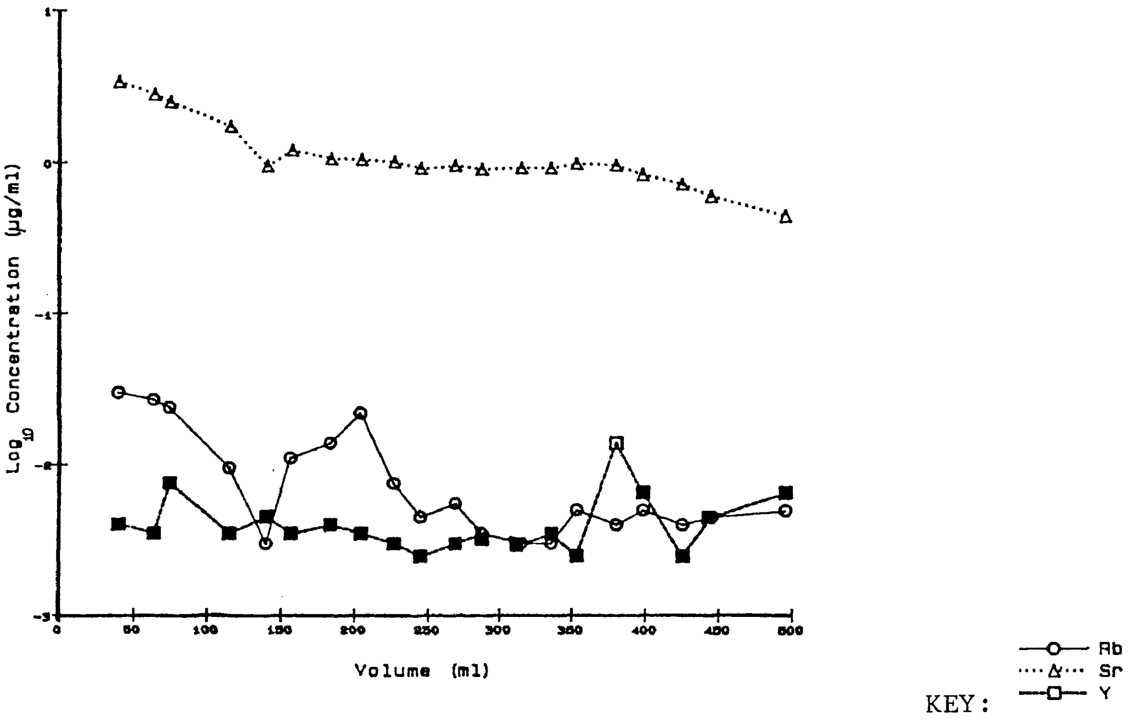


Figure 11c

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

Element Concentration versus Volume Eluted from Column 520



Element Concentration versus Volume Eluted from Column 521

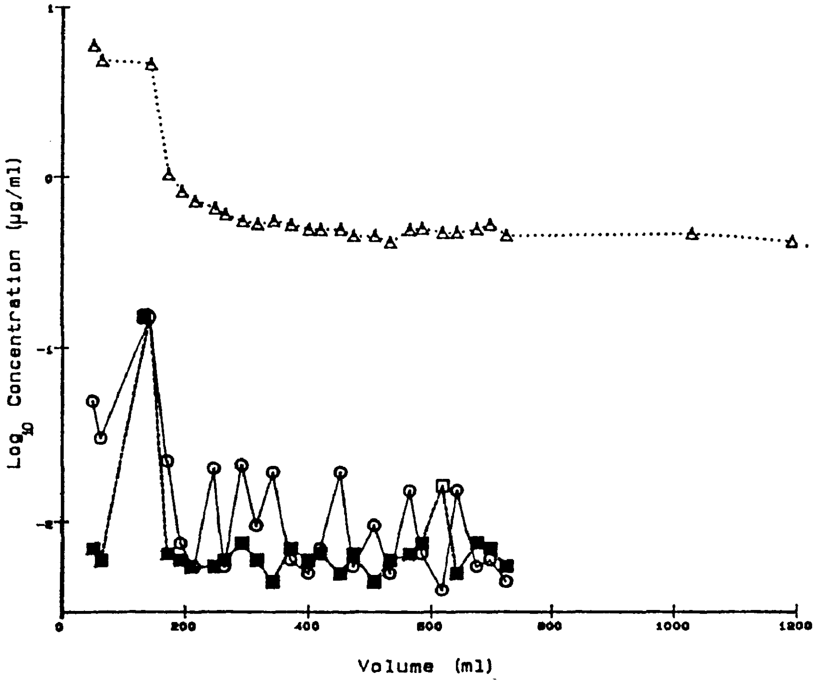
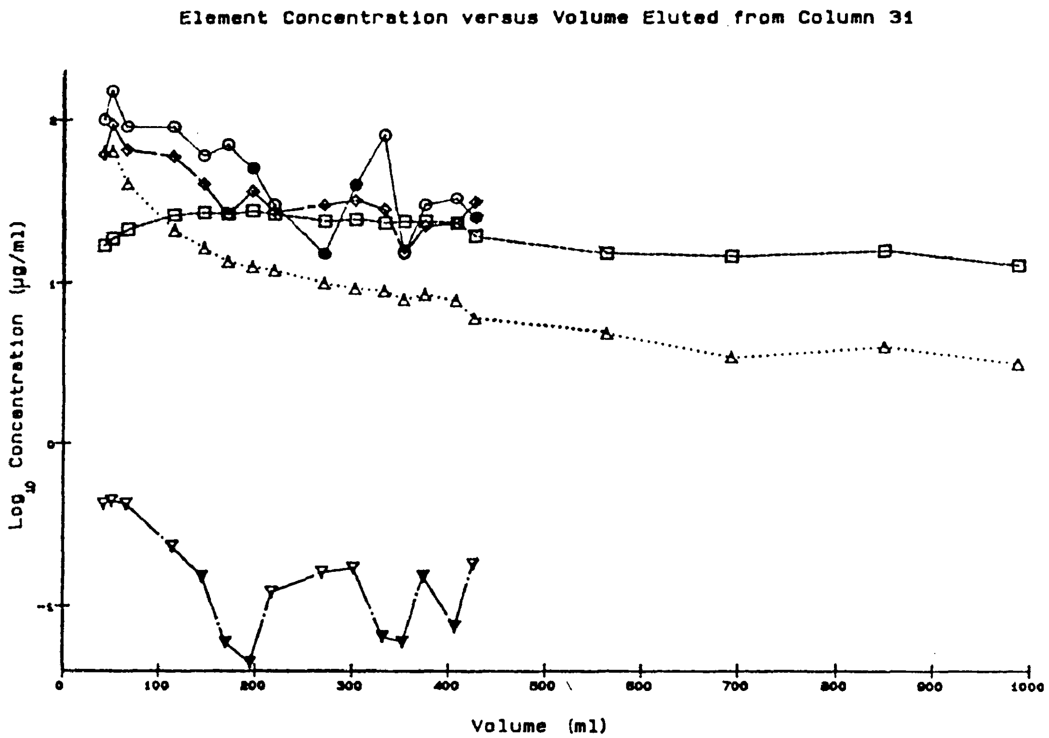


Figure 12a

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

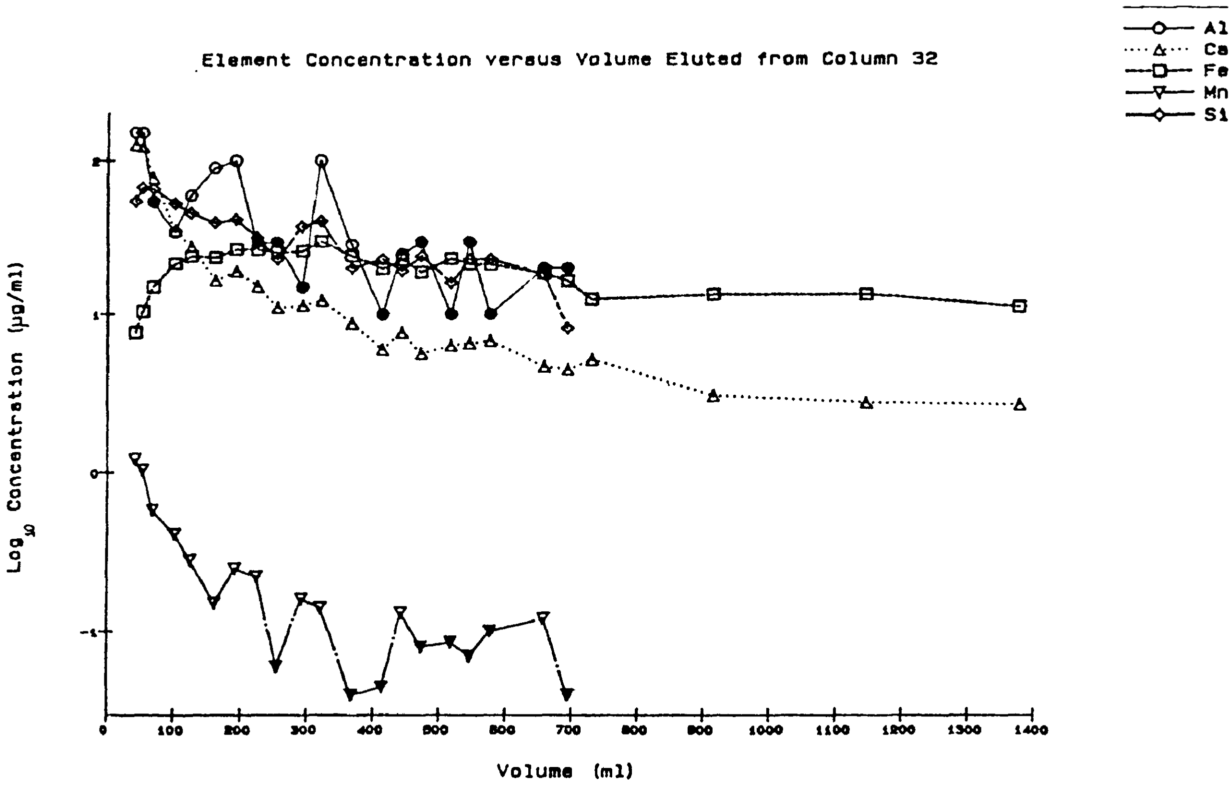
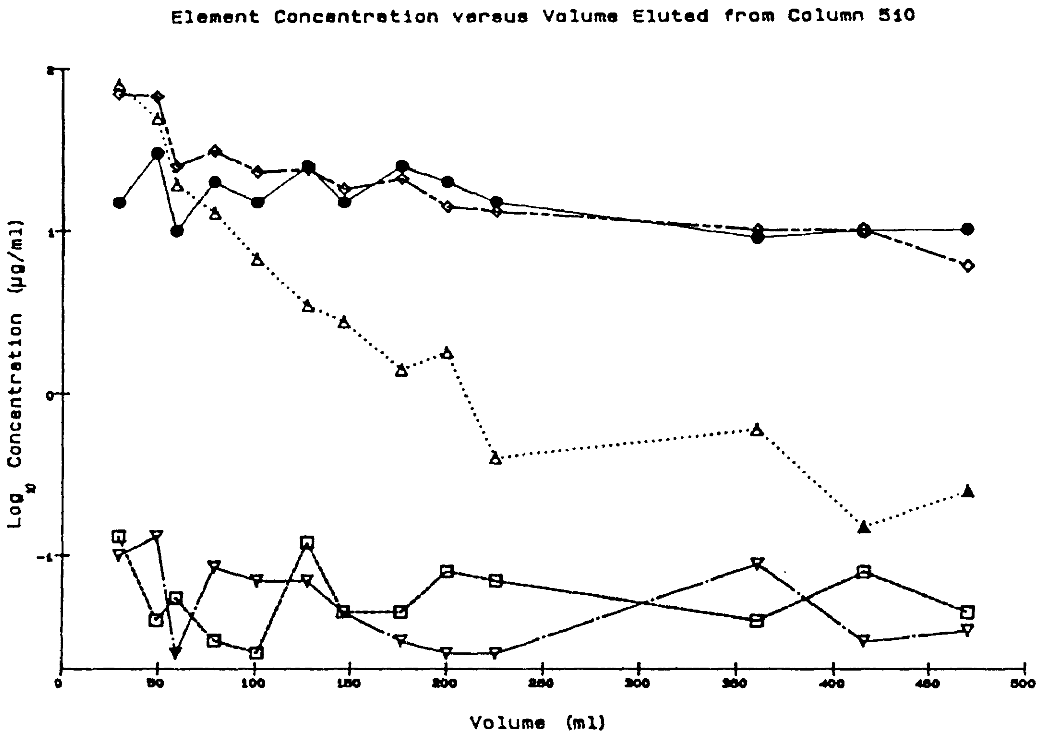
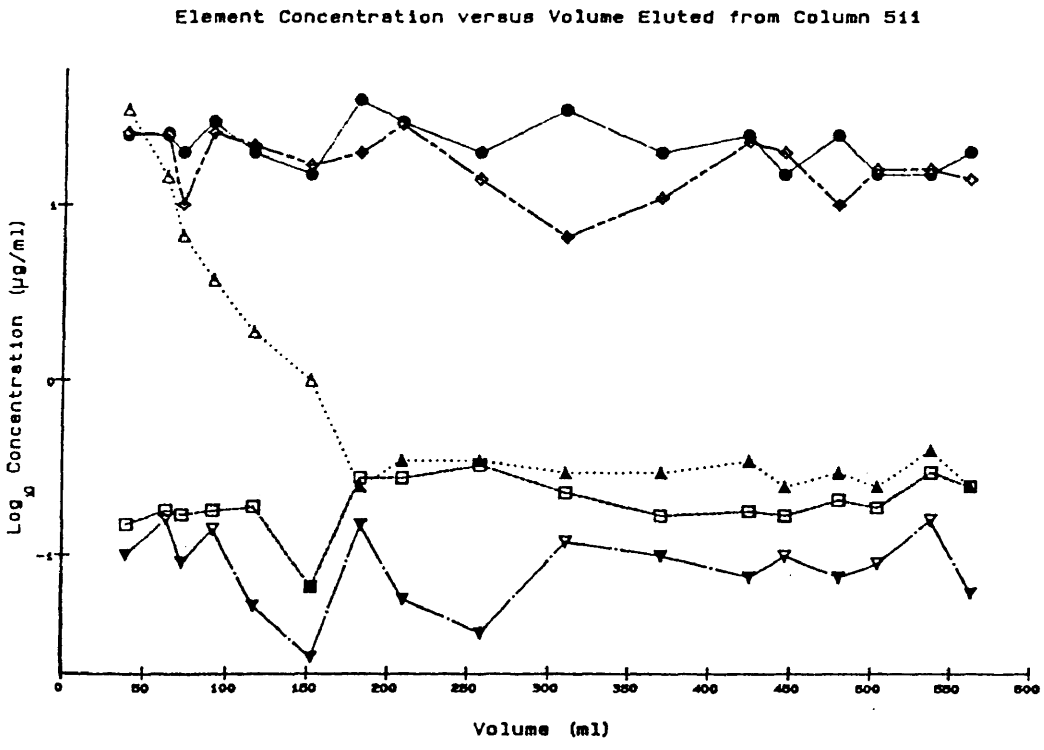

Element Concentration versus Volume Eluted from Column 32

Figure 12b

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

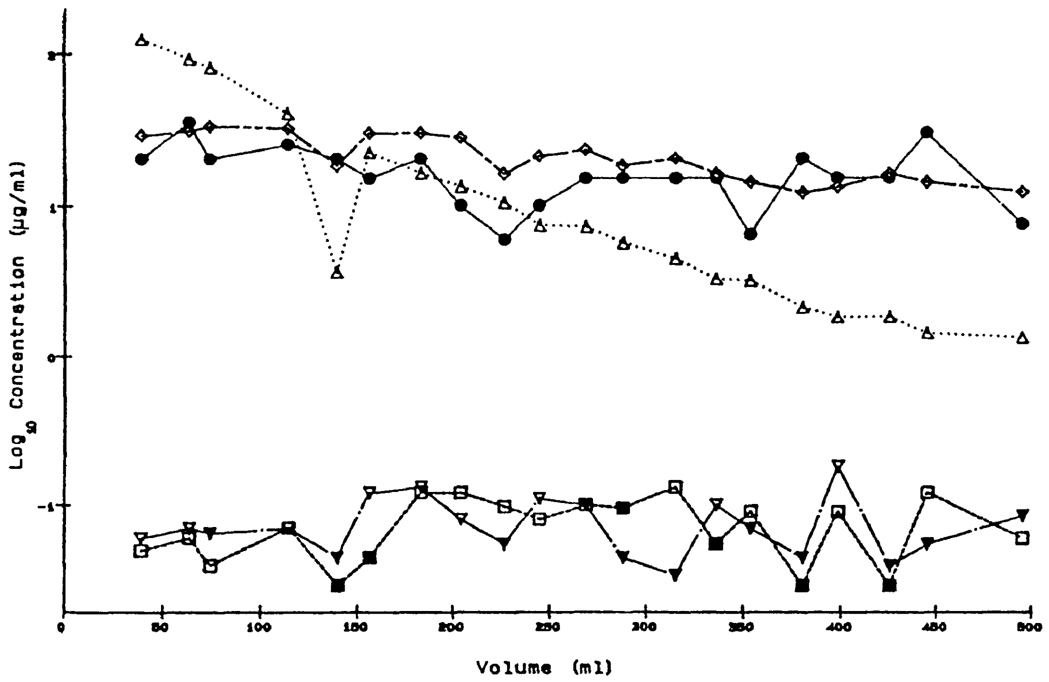

Element Concentration versus Volume Eluted from Column 510


Element Concentration versus Volume Eluted from Column 511

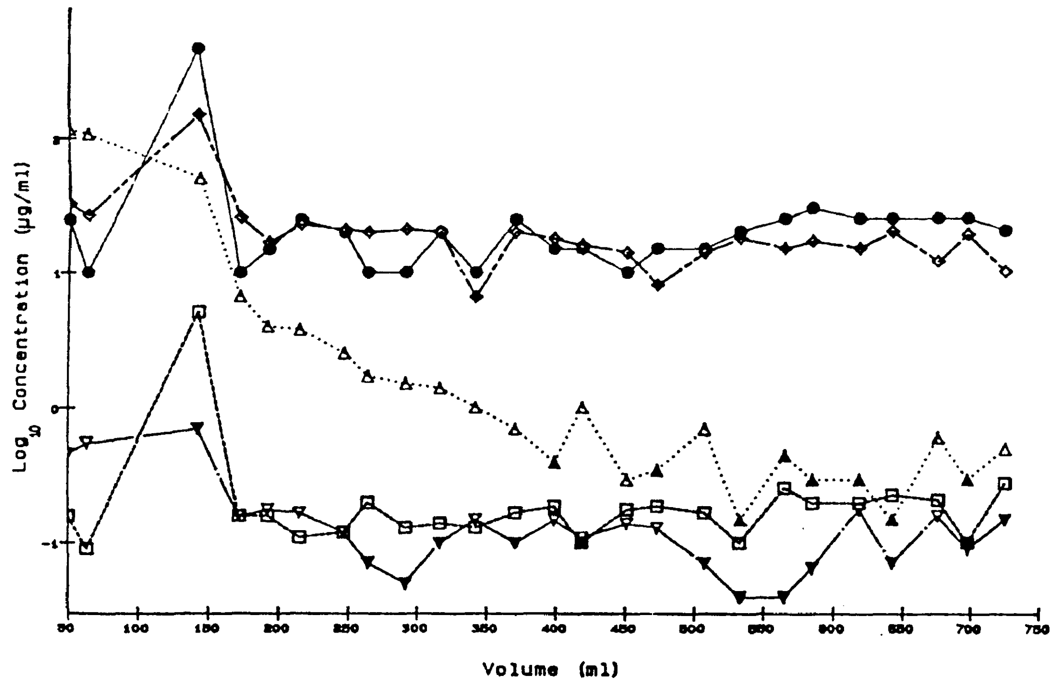
KEY
—○— Al
···△··· Ca
—□— Fe
—▽— Mn
—◇— Si

Figure 12c

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 520



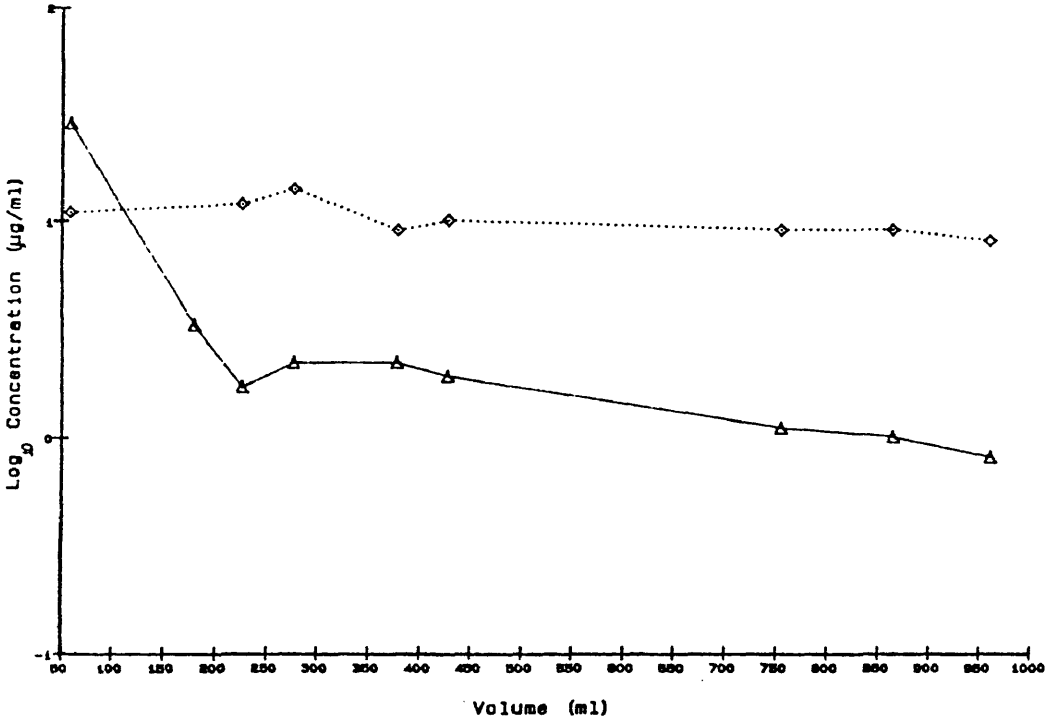
Element Concentration versus Volume Eluted from Column 521

KEY
- —○— Al
- ···△··· Ca
- —□— Fe
- —▽— Mn
- —◇— Si

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

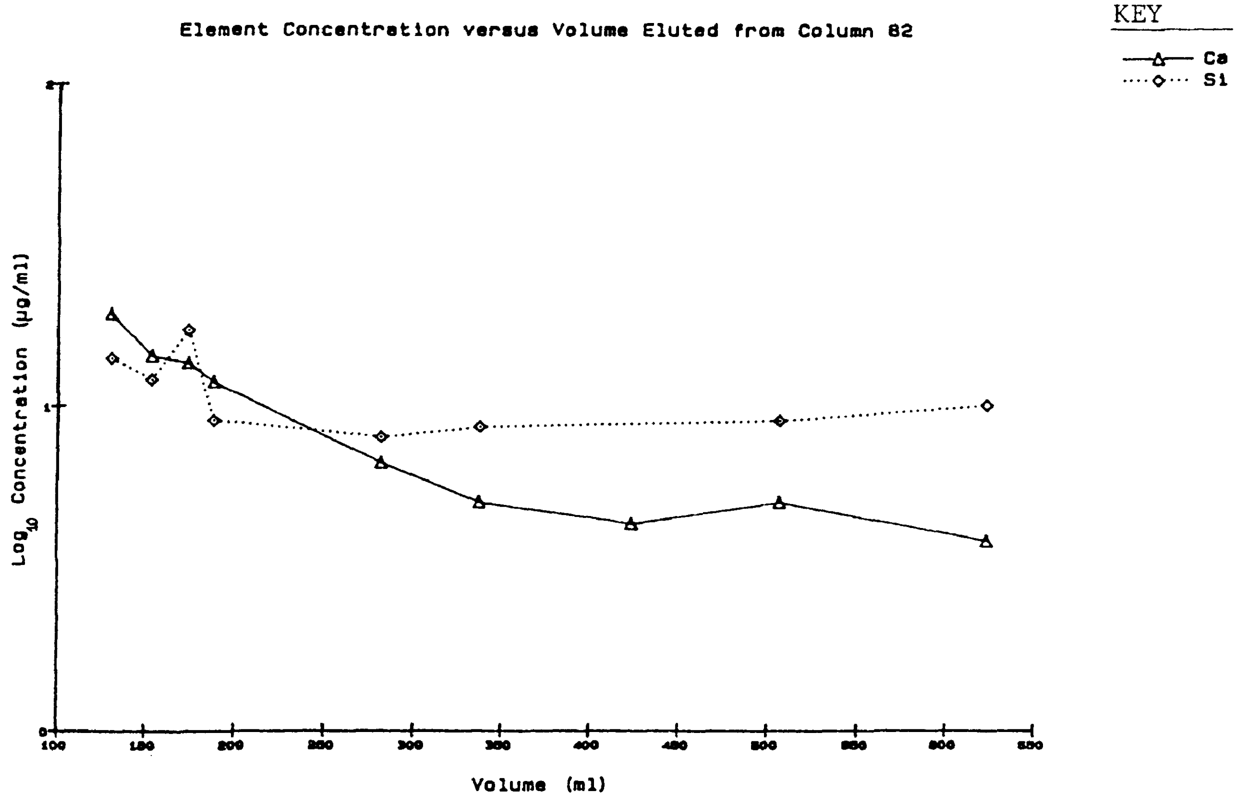


Figure 13a

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

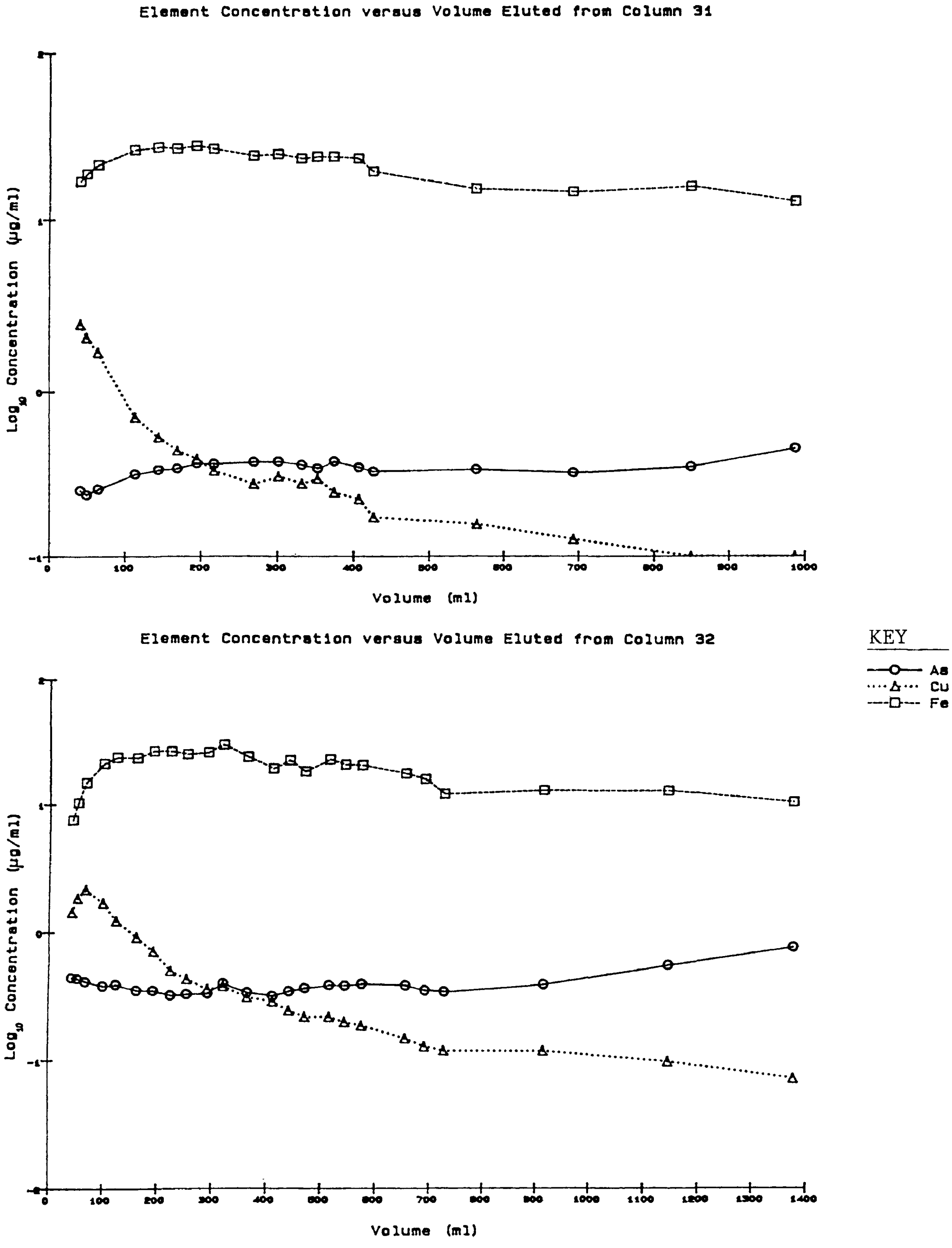
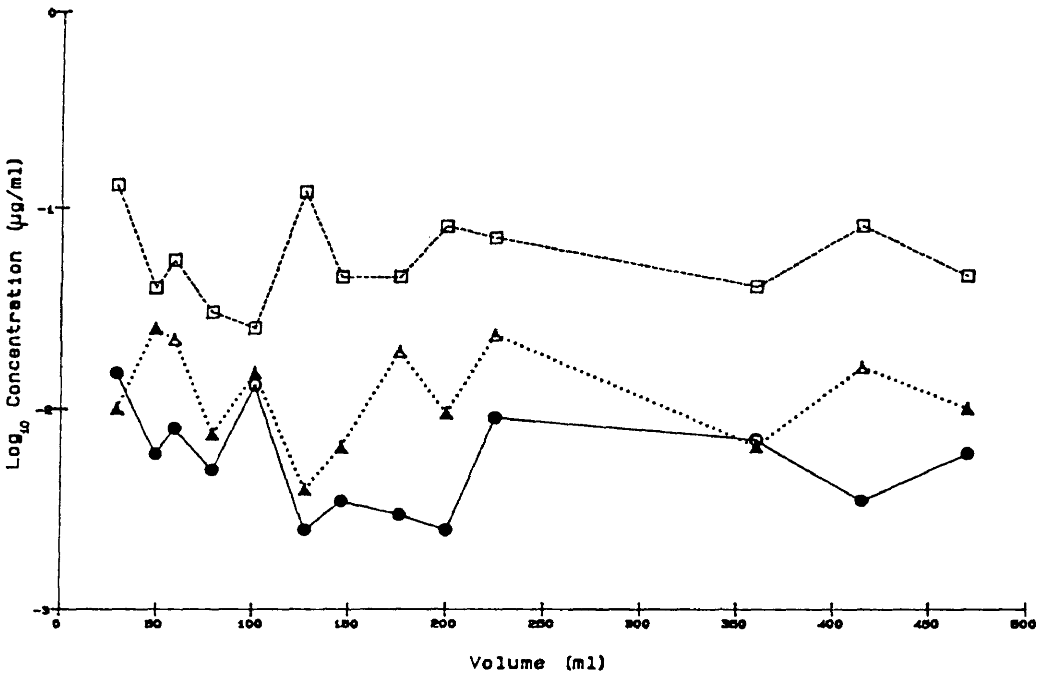


Figure 13b

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

Element Concentration versus Volume Eluted from Column 510



Element Concentration versus Volume Eluted from Column 511

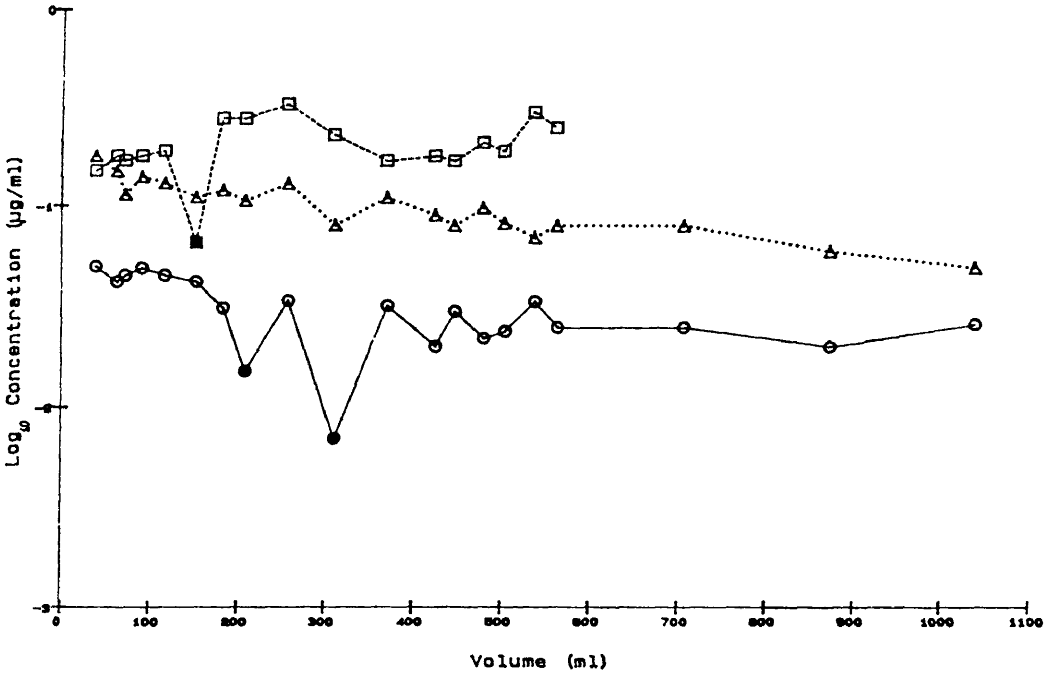
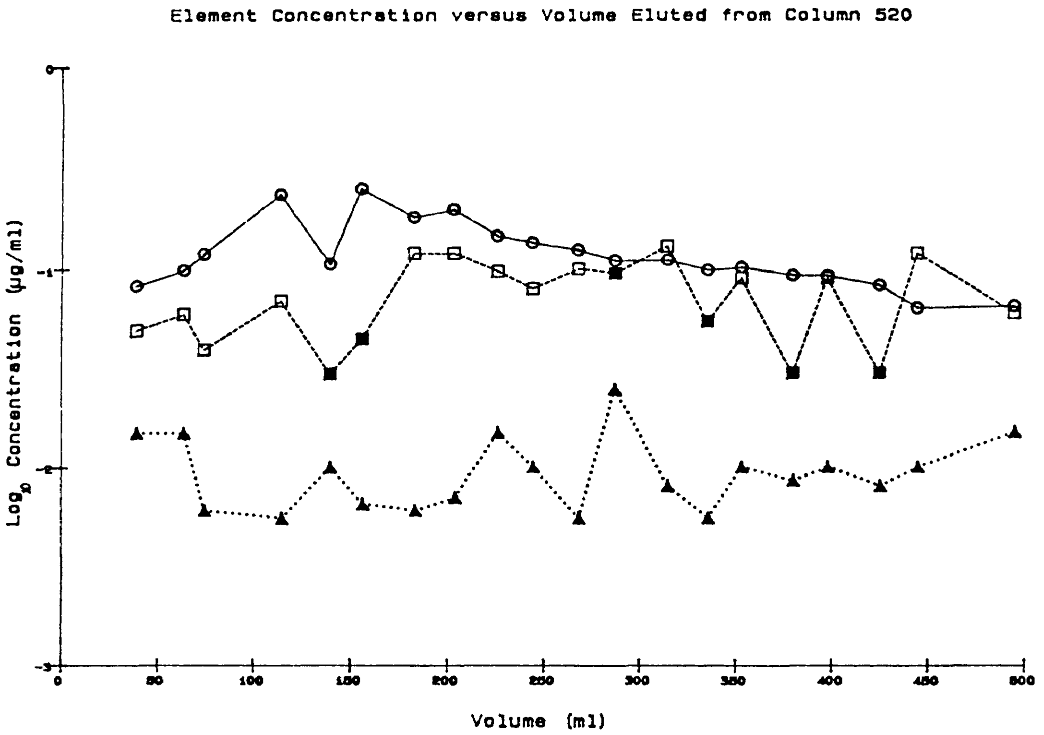


Figure 13c

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



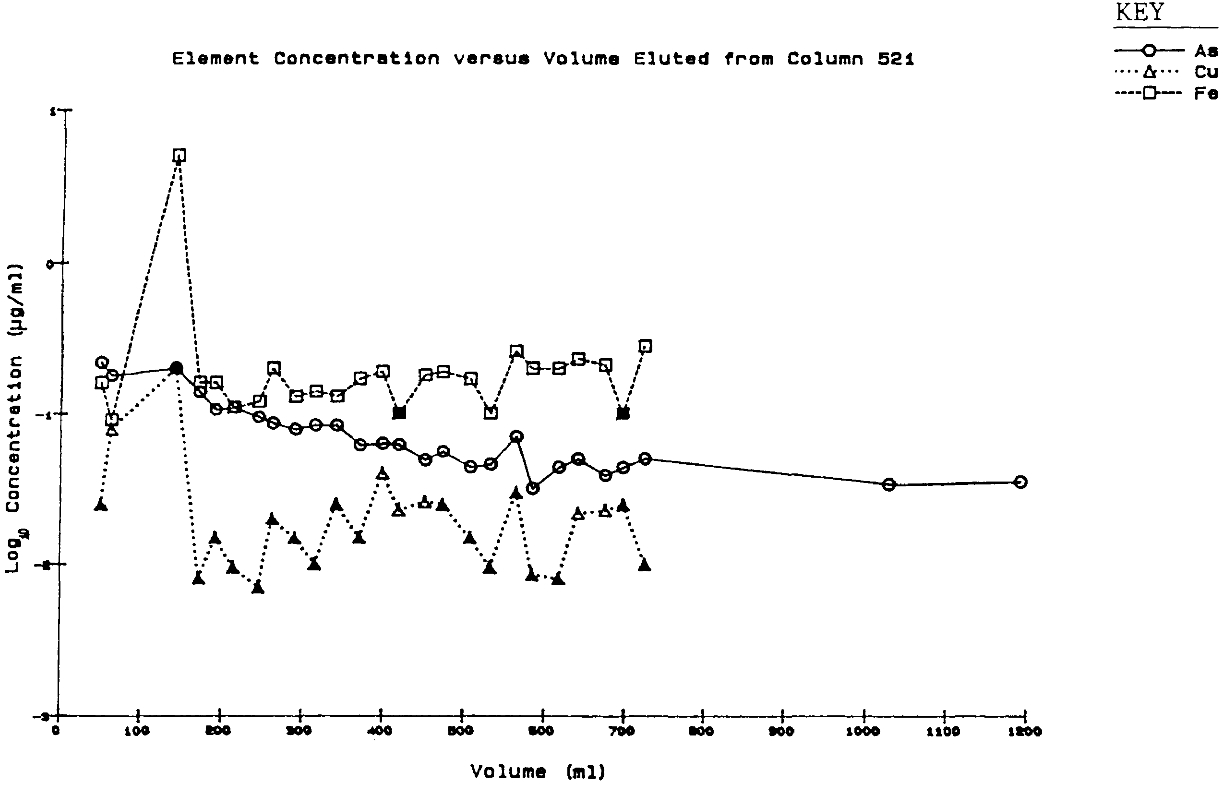
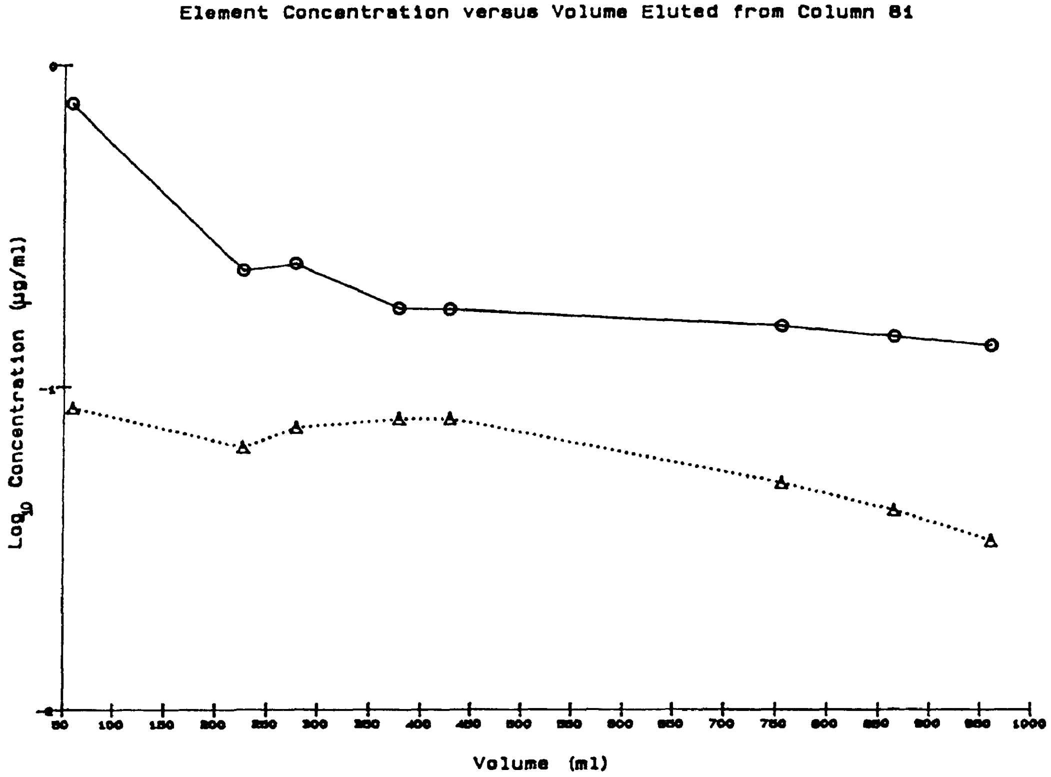


Figure 13d

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



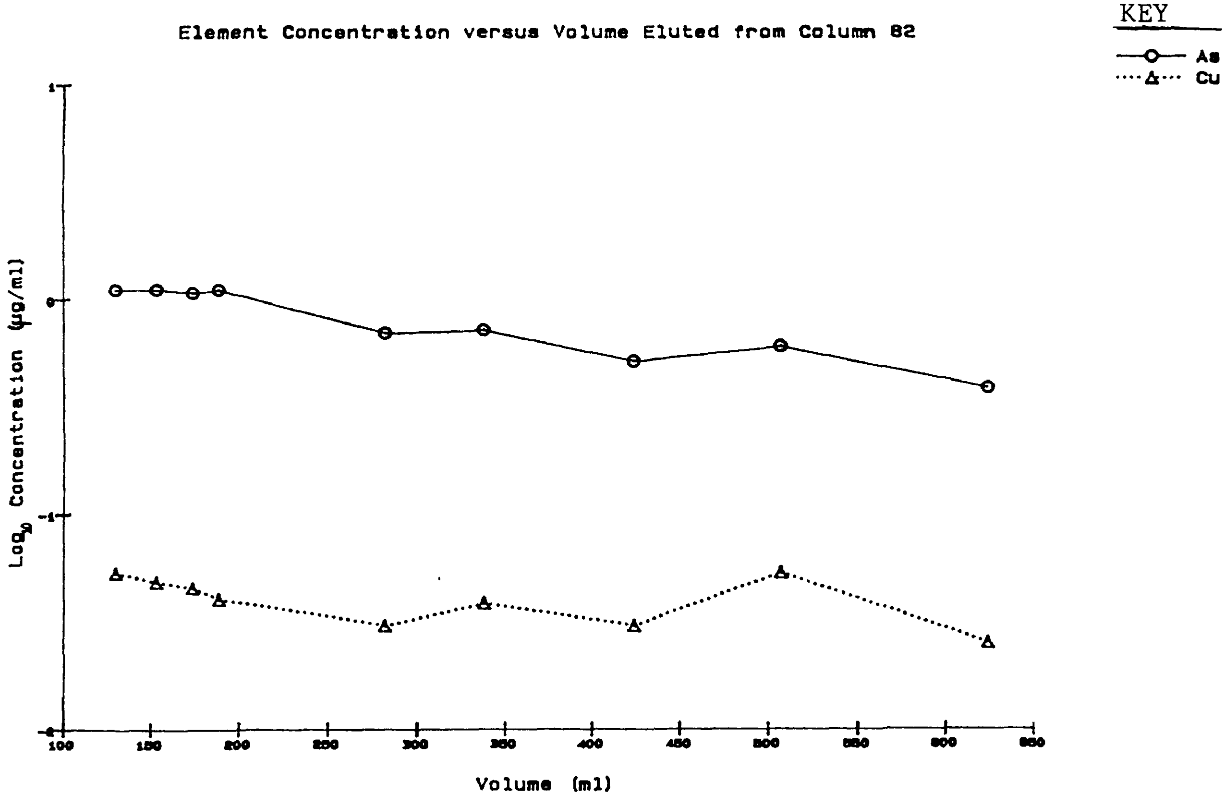
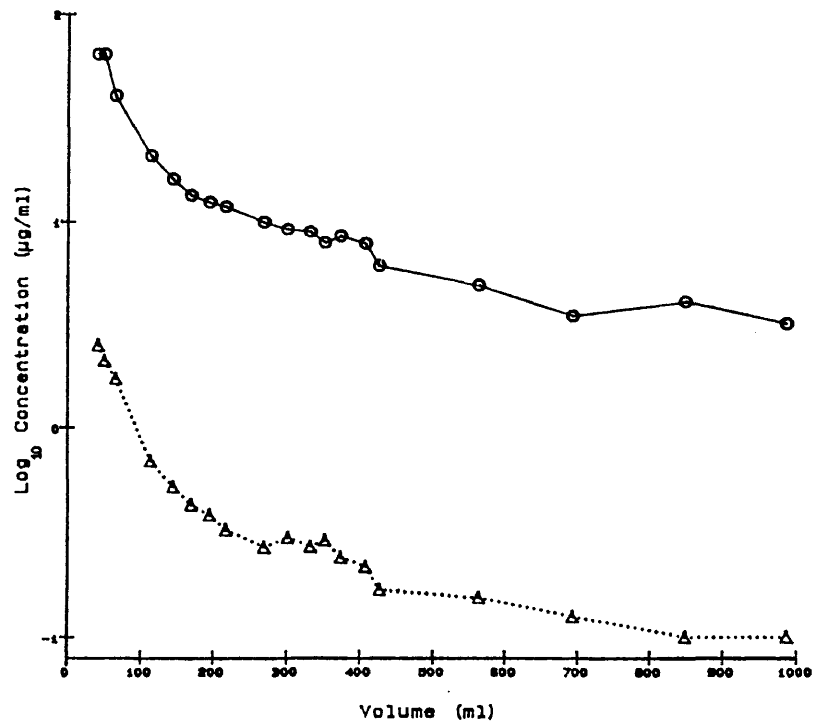


Figure 14a

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

Element Concentration versus Volume Eluted from Column 31



KEY: —○— Ca ···△··· Cu

Element Concentration versus Volume Eluted from Column 32

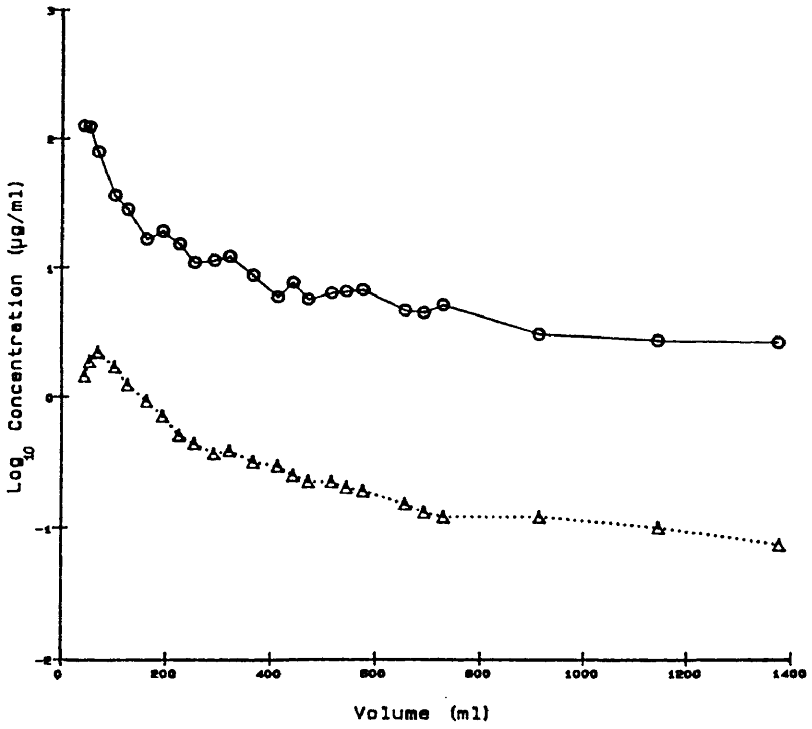
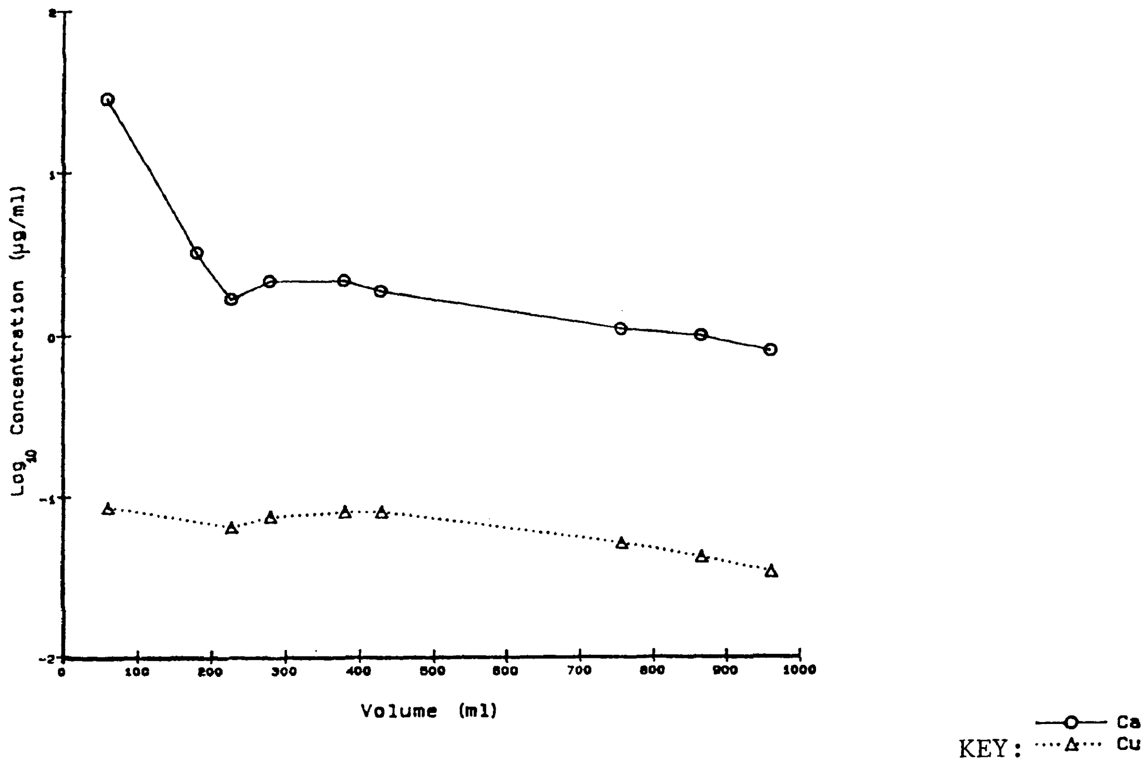


Figure 14b

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

Element Concentration versus Volume Eluted from Column 81



Element Concentration versus Volume Eluted from Column 82

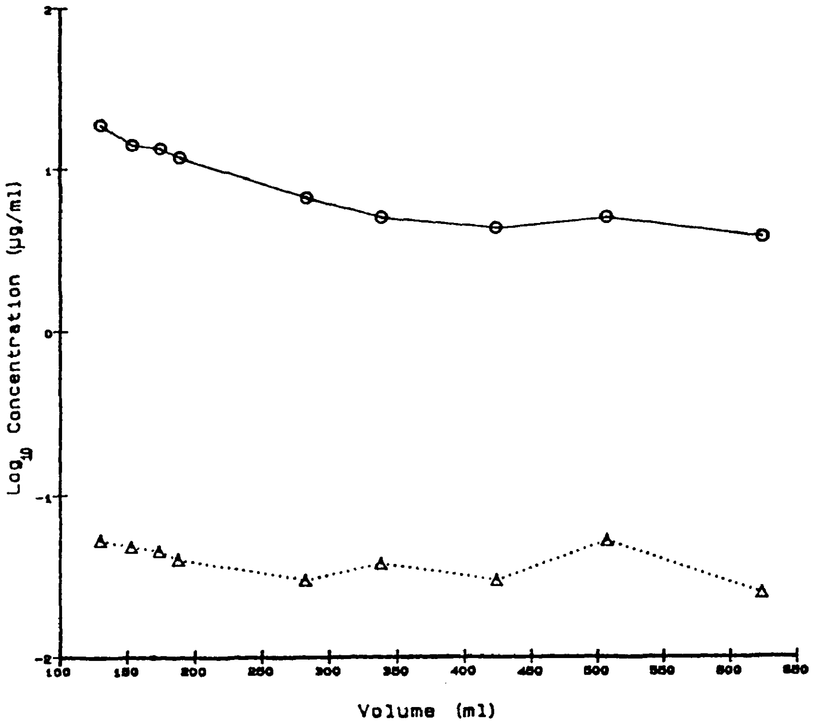
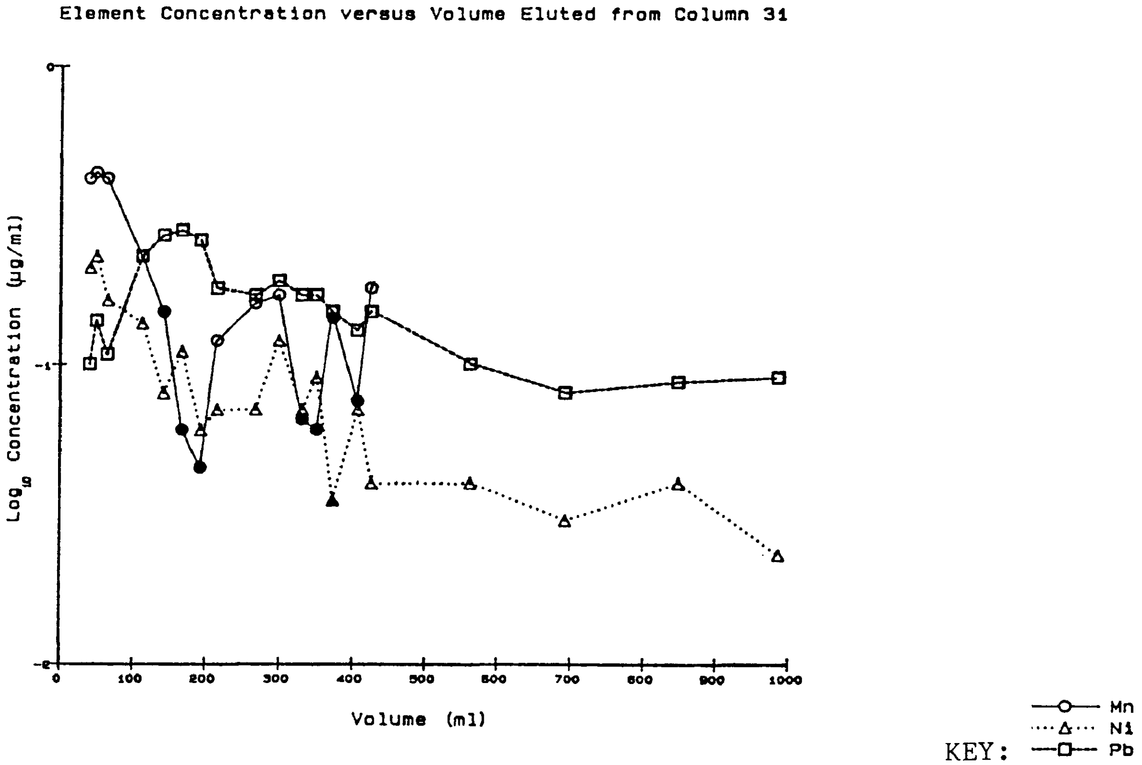


Figure 15

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


Element Concentration versus Volume Eluted from Column 31

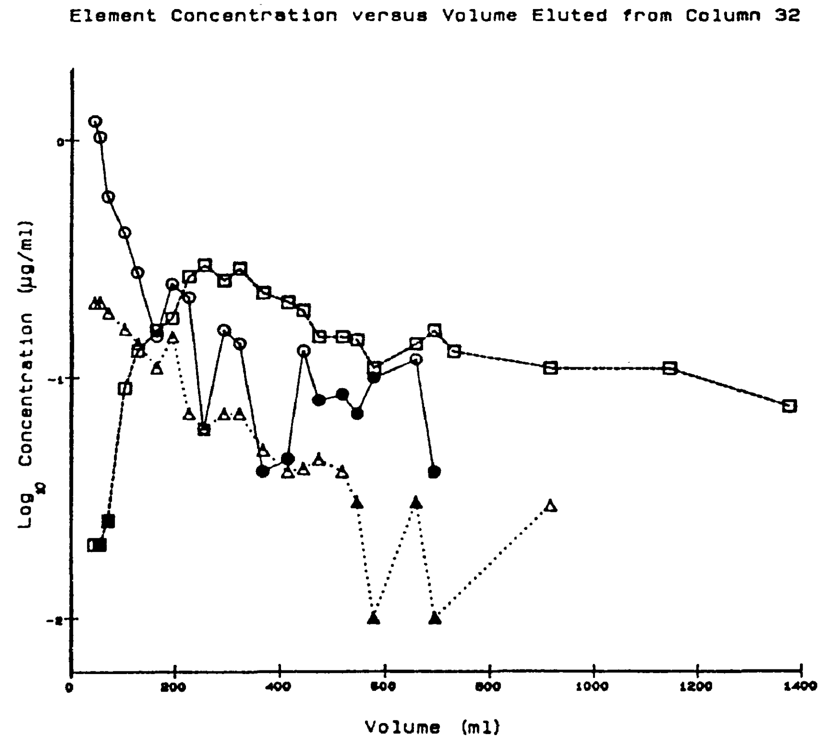
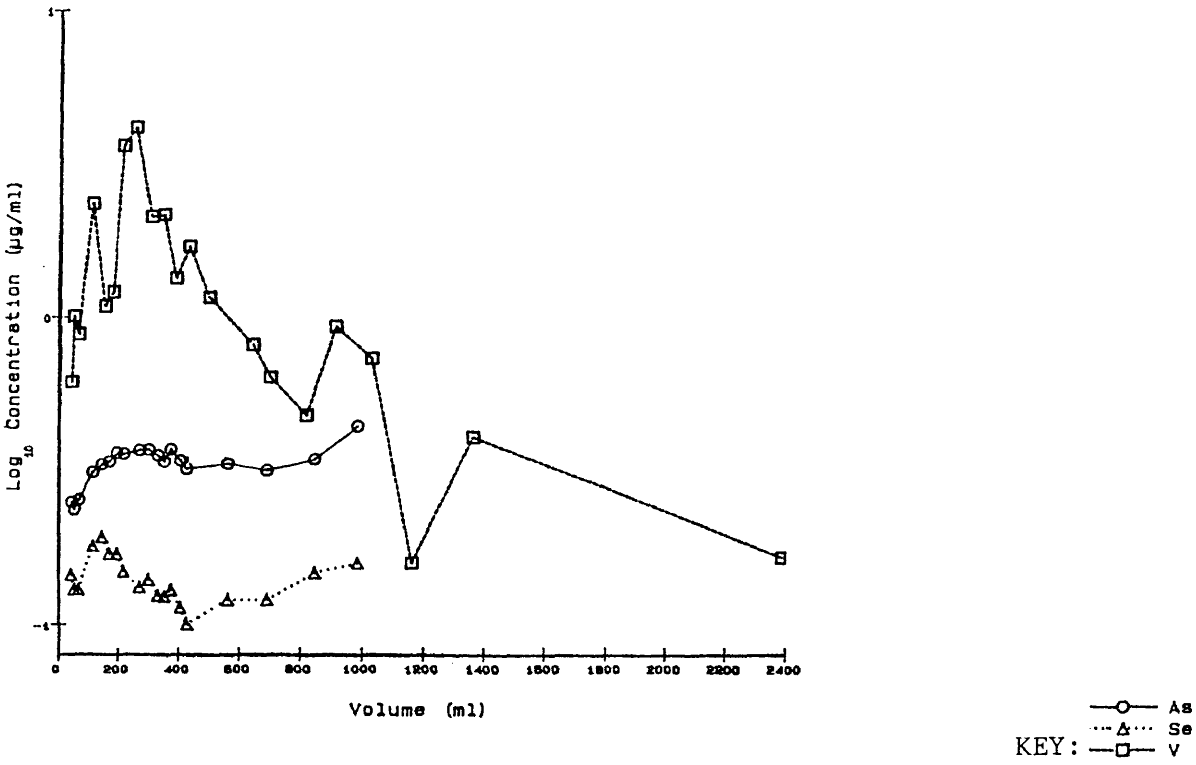
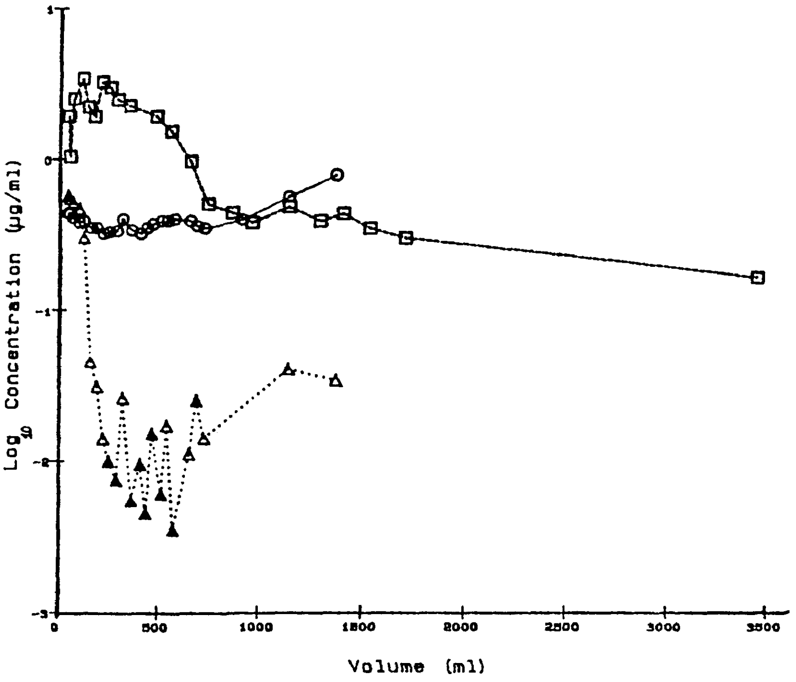

Element Concentration versus Volume Eluted from Column 32

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

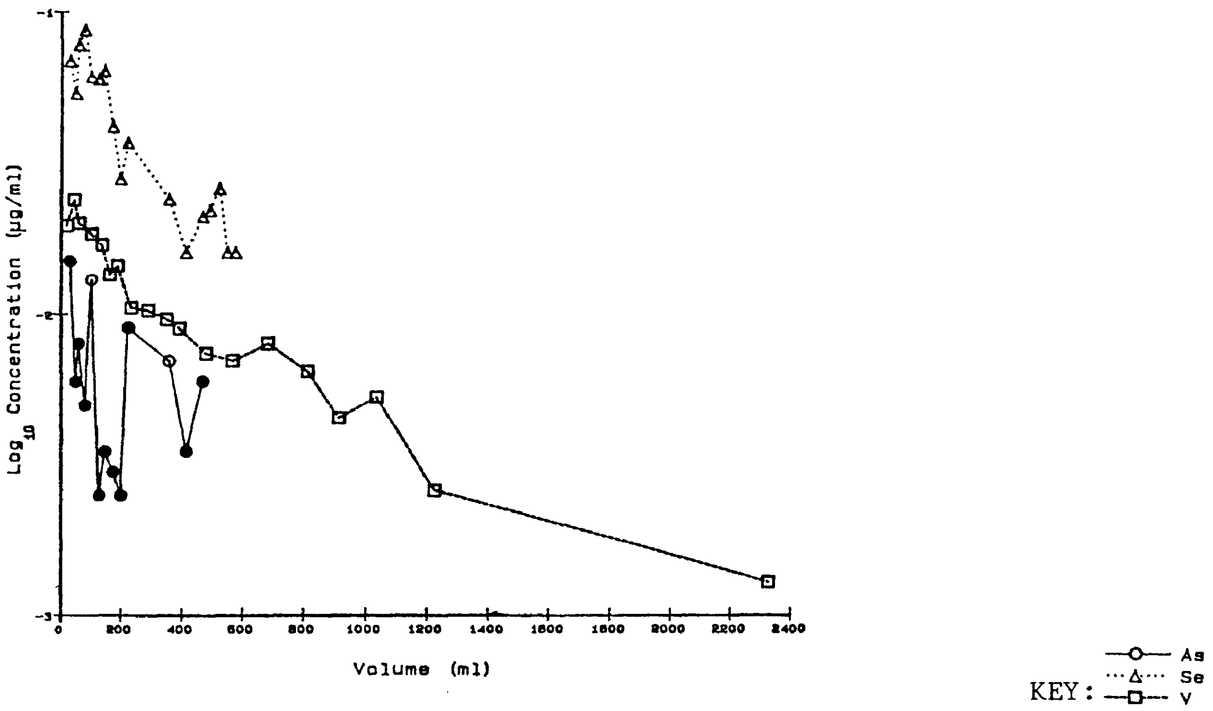


Element Concentration versus Volume Eluted from Column 32

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



Element Concentration versus Volume Eluted from Column 511

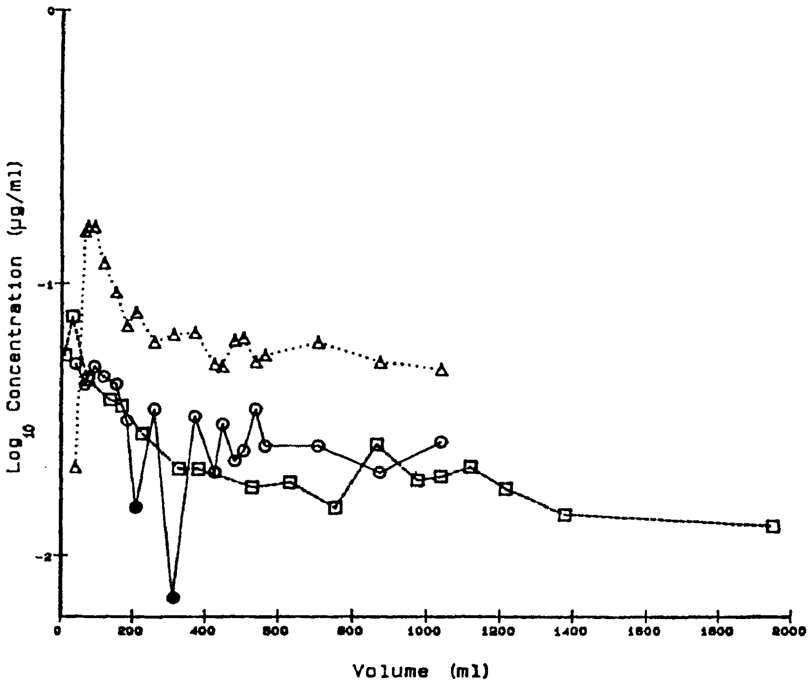
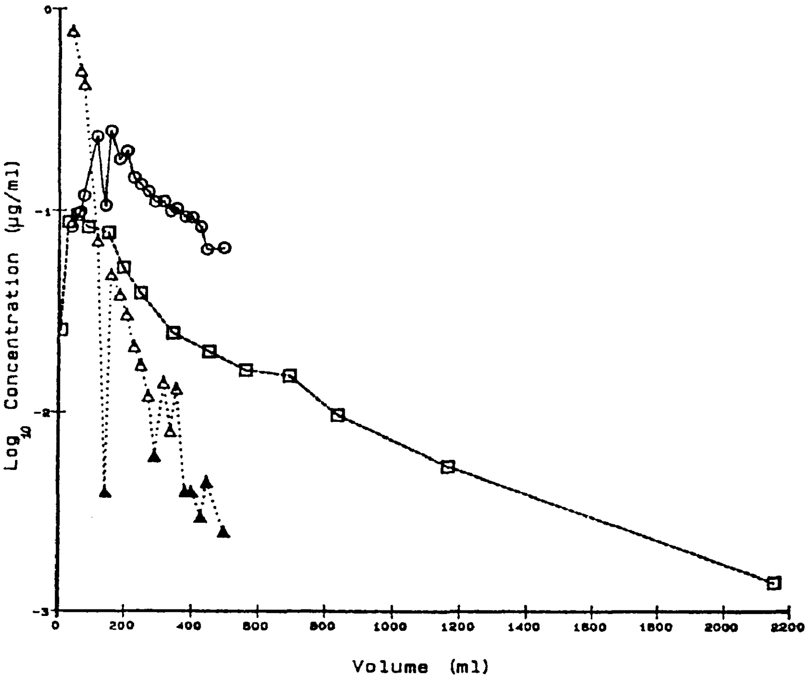


Figure 16c

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

Element Concentration versus Volume Eluted from Column 520



KEY: —○— As
···△··· Se
—□— V

Element Concentration versus Volume Eluted from Column 521

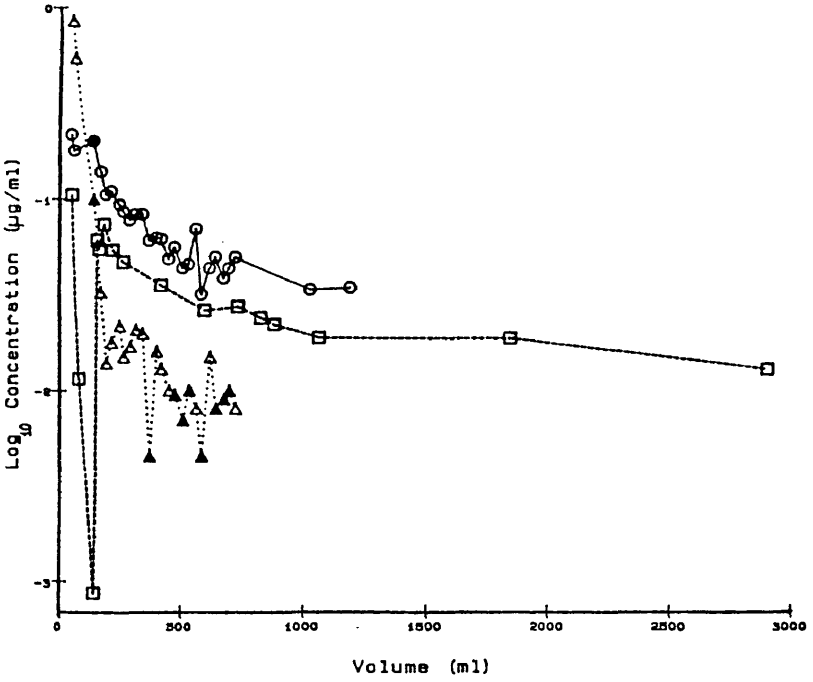
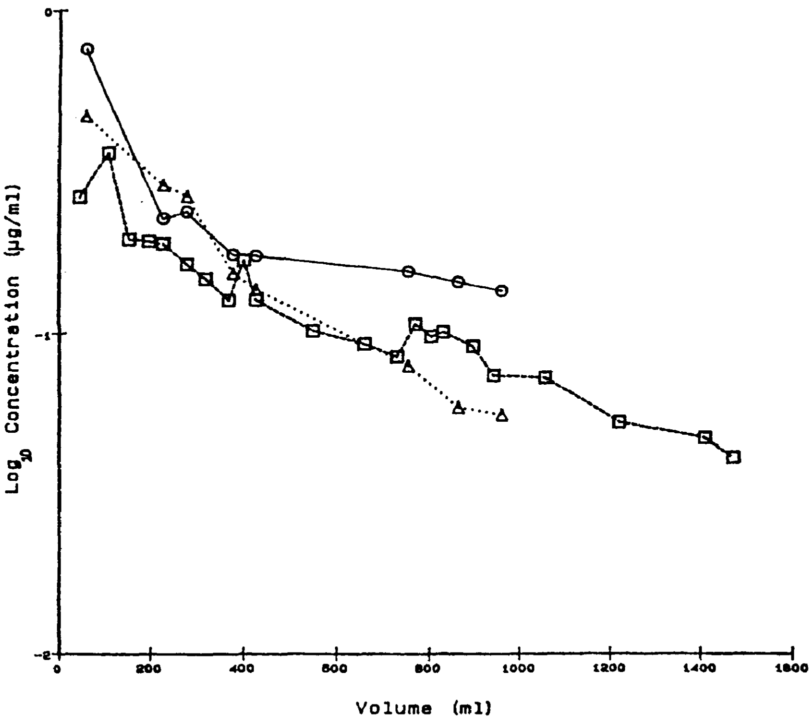


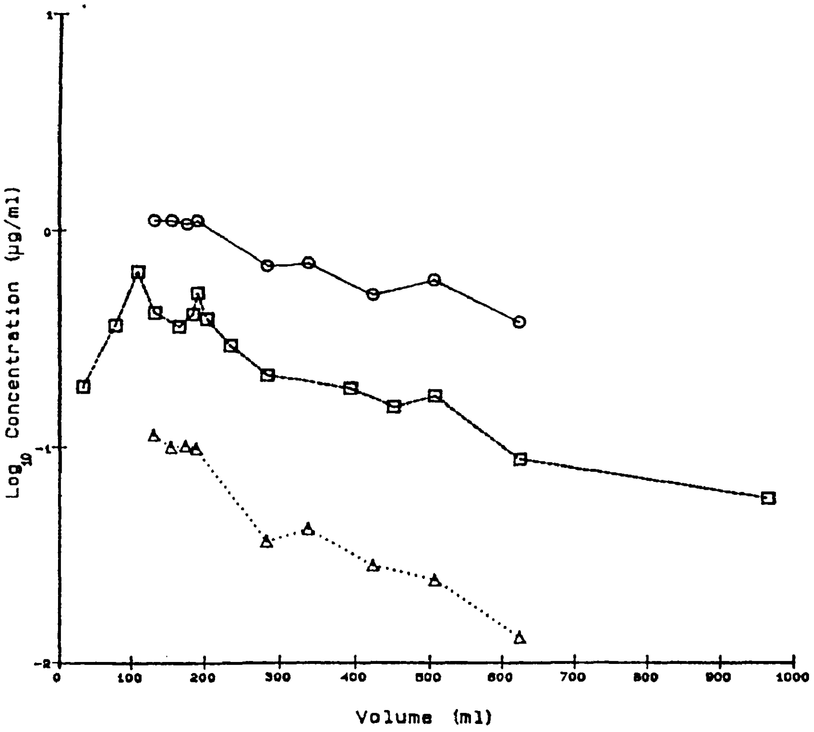
Figure 16d

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



KEY:
—○— 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 µg/ml range. Arsenic, selenium, and nickel were found to exist in the .1-1 µg/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, S0, 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, S1. 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 (D2) 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, S2. 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) $S0 = \Sigma\ (S\%(0,i))/n_1$* average deuterium signal -sample beam (BG)
2) $S1 = \Sigma\ (S\%(1,i))/n_1$ average hollow cathode signal -sample beam (I)
3) $S2 = \Sigma\ (S\%(2,i))/n_1$ average deuterium signal -reference beam (BG0)
4) $S3 = \Sigma\ (S\%(3,i))/n_1$ 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) $ACRRT\%(ii) = AHC\%(ii) - ABG\%(ii)$
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 = G + 2: GOTO 4004
5  TEXT
10 D$ =  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 Q%
22  IF Q% ( 1 OR Q% ) 3 THEN  GOTO 20
25  IF Q% = 1 THEN  GOTO 4770
27  IF Q% = 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 "INTERRUPTING": GOTO 20
40  RETURN
44  HOME : HTAB 1: VTAB 22: PRINT "STORING RAW DATA"
45  PRINT D$;"OPEN";Z9$;",L";R1;",D";R2%
47  PRINT D$;"WRITE";Z9$;",R";G;",B0": PRINT ":":P1 = G + 1:Y7 = 0
51  FOR PP = 1 TO 2
53  PRINT D$;"WRITE";Z9$;",R";P1
55  FOR K = 0 TO 1
56 N9 = K + Y7
57  FOR I = ED TO F STEP 2
58  PRINT S%(N9,I)
61  NEXT I
71  NEXT K
74 P1 = P1 + 1:Y7 = 2
77  NEXT PP
80  PRINT D$;"CLOSE";Z9$
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 "S%(0,";I;")=";S%(0,I);"  S%(1,";I;")=";S%(1,I);"  S%(2,";I;")=";S%(2,I);"  S%(3,";I;")=";S%(3,I)
92  NEXT I
94  PR# 0
98  POKE 33,40: RETURN
100  FOR I = ED TO F - 4:D = 0.0:E = 0.0
110  FOR K = I TO I + 4
120 D = D + S%(0,K):E = E + S%(1,K)
130  NEXT K
140 S%(0,I + 2) = D / 5.0:S%(1,I + 2) = E / 5.0
150  IF I = ED THEN BB = 0: GOSUB 190
160  IF I = F - 4 THEN BB = F - 1: GOSUB 190
170  NEXT I
180  RETURN
190  FOR M = BB TO BB + 1
200 S%(0,M) = D / 5.0:S%(1,M) = E / 5.0
210  NEXT M
220  RETURN
300 PMAX = 0:RE% = 0
480  FOR I = 0 TO NN
485  IF ACRRT%(I) ) PMAX THEN PMAX = ACRRT%(I):LOC = I
490  NEXT I
495  HOME
500  HTAB 24: VTAB 23: PRINT "HT=";PMAX: HTAB 33: VTAB 23: PRINT "N=";LOC: HTAB 26: VTAB 24: PRINT "TRANSIENT#";G
505  RETURN
890  PRINT D$;"BLOAD  PIC,A16384,D1"
891  PRINT D$;"BLOAD FREECAT.OBJ,A38350"
892  PRINT D$;"BLOAD FFFF,A36847": POKE 233, INT (36847 / 256): POKE 232,((36847 / 256) -  INT (36847 / 256)) * 256: HIMEM: 36846
895  PRINT D$;"BLOAD WORKING2.OBJ,A7800": LOMEM: 24576
897 D$ =  CHR$ (4):G = 0
```

```
900  PRINT "ENTER NAME OF FILE AND DRIVE # FOR DATA STORAGE (SEPARATE RESPONSES BY A COMMA)": INPUT Z9$,R2%
902  IF R2% ( 1 OR R2% ) 2 THEN  GOTO 900
904  PRINT "ENTER ELEMENT NAME, # OF SECONDS FOR TRANSIENT (SEPARATE RESPONSES BY COMMA AND ONLY INTEGERS FOR TIME": INPUT SY$,N:UN = N:N = N * 60:L = 300 - 8:IL = L + 1 + N:F = IL:ED = L + 1
906 RI =  INT ((65.0 / 12.0) * N) + 33
907 RP =  INT ((N / 3.0) * 4.0) + 2 * N + 29:Z9$ = Z9$ +  STR$ (RI)
909  PRINT D$;"OPEN";Z9$;",L";RI;",D";R2%
910  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE";Z9$: GOTO 930
915  PRINT D$;"CLOSE";Z9$
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 D$;"DELETE";Z9$
930  NORMAL
935  POKE  PEEK (966) +  PEEK (967) * 256,0:ADR = 7800
940  DIM A%(3),S%(3,IL),ABG%(N),ACRRT%(N),LD(9),D2(9),S(N),AHC%(N)
955 Z = .826:Y = .174:X = 2.3025851:W = 1.0 / 5.0:V = .200:U = 258.9 / (N * 1.000001):T = 1000
956  HOME :S0 = 0:S1 = 0:S2 = 0:S3 = 0:S = 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  & BIN, (TV) = Q, (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 Q (  ) 0 THEN  GOTO 1000
1020  FOR I = 0 TO L
1030  CALL ADR,A%,0,0,1
1040  NEXT I
1045  & BCDIN, (TV) = P, (AM) = 63:P = P - 4
1050  & BIN, (TV) = Q, (AM) = 256
1055  HTAB 1: VTAB 21: PRINT "WAITING FOR ATOMIZE
1060  IF Q (  ) 0 THEN  GOTO 1050
1067  HOME
1070  FOR K = ED TO F
1080  CALL ADR,A%,0,0,1
1090  NEXT K:G = G + 1
1091  IF Y5 = 177 OR Y5 = 178 THEN Y3 = Y5: GOTO 1094
1092 Y3 =  PEEK ( - 16384): POKE  - 16368,0
1094  IF Y3 = 177 OR Y3 = 178 THEN  NORMAL : GOSUB 44
1096  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           ": NORMAL : GOSUB 100
1100  FOR I = 0 TO L
1105  REM RINT "I";I;" S0";S%(0,I);" S1";S%(1,I);" S2";S%(2,I);" S3";S%(3,I)
1120 S1 = S1 + S%(1,I):S2 = S2 + S%(2,I):S3 = S3 + S%(3,I):S0 = S0 + S%(0,I)
1150  NEXT I
1170 S0 = S0 / I:S1 = S1 / I:S2 = S2 / I:S3 = S3 / I
1175  REM RINT "AVG: 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 ABG%(NN) =  INT (T * ( LOG (S0 / S(NN)) / X))
1230 AHC%(NN) =  INT (T * ( LOG (S1 / S%(1,K)) / X))
1250 ACRRT%(NN) = AHC%(NN) - ABG%(NN)
1265  REM RINT "S(NN)";S(NN);" S1";S%(1,K);" S2";S%(2,K);" S3";S%(3,K);" ABG";ABG%(NN);" AC";ACRRT%(NN)
1270  IF K = F THEN  GOTO 1280
1275 NN = NN + 1
1280  NEXT K
1295  GOSUB 300: REM   AREA SUBROUTINE
```

```
1296  CALL  - 182: POKE 71,0: CALL  - 193: HGR : ROT= 0: SCALE= 1
1297  POKE 60,0: POKE 61,64: POKE 62,255: POKE 63,95: POKE 66,0: POKE 67,32
1298  CALL  - 468
1299  HCOLOR= 3
1300 UN$ =  STR$ ( INT (UN));U2$ = ( LEFT$ ( STR$ (UN / 2.0),3));X5 = 142
1301  FOR I = 1 TO  LEN (U2$)
1302  DRAW ( ASC ( MID$ (U2$,I,1)) - 31) AT X5,150
1303 X5 = X5 + 5
1304  NEXT I
1307  DRAW ( ASC (UN$) - 31) AT 274,150
1308  HCOLOR= 2
1309  FOR I = 0 TO NN STEP 2
1310  IF ABG%(I) ) 699 OR ABG%(I) (  - 99 THEN  GOTO 1320
1312  HPLOT  INT (I * U) + 20, INT (136 - (ABG%(I) * V))
1320  NEXT I
1330  HCOLOR= 6
1340  FOR I = 0 TO NN STEP 2
1342  IF ACRRT%(I) ) 699 OR ACRRT%(I) (  - 99 THEN  GOTO 1352
1350  HPLOT  INT (I * U) + 20, INT (136 - (ACRRT%(I) * V))
1352  NEXT I
1353  HCOLOR= 1
1354  FOR I = 0 TO NN STEP 4
1355  IF AHC%(I) ) 699 OR AHC%(I) (  - 99 THEN  GOTO 1360
1358  HPLOT  INT (I * U) + 19, INT (136 - (AHC%(I) * V))
1360  NEXT I
1361 X4 =  PEEK ( - 16384): POKE  - 16368,0
1362  IF X4 = 155 THEN G = G - 1: GOTO 4000
1363  IF X4 = 141 THEN RE% = 1
1365  PRINT  CHR$ (4):D$ =  CHR$ (4)
1368  PRINT D$;"OPEN";Z9$;",L";R1;",D";R2%
1369  PRINT D$;"WRITE";Z9$;",R";G;",B0": PRINT RE%
1370  PRINT D$;"WRITE";Z9$;",R";G;",B2"
1375  PRINT P: PRINT PMAX: PRINT LOC
1380  PRINT D$;"WRITE";Z9$;",R";G;",B14"
1384 II = 0
1385  FOR I = 0 TO NN STEP 31
1387 D2(II) = S * ( ABS (S2 - S%(2,I)) / S2):DSUM = DSUM + D2(II)
1389 LD(II) = S * ( ABS (S3 - S%(3,I)) / 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 D$;"WRITE";Z9$;",R";G;",B25"
2015 NO = NN / 2:MO = (NN / 2) + 1
2020  FOR I = 0 TO NN
2030  PRINT ACRRT%(I)
2040  NEXT I
2050  PRINT D$;"WRITE";Z9$;",R";G;",B";RP
2060  FOR I = 0 TO NO
2070  PRINT ABG%(I)
2072  NEXT I
2074  FOR I = MO TO NN STEP 4
2076  PRINT ABG%(I)
2080  NEXT I
2095  PRINT D$;"CLOSE";Z9$
3000  CALL 38350
3010  IF ( PEEK (38349) * 256 +  PEEK (38348)) )  =  INT (((R1 * 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 HG%
3014  IF HG% ( 1 OR HG% ) 2 THEN  PRINT  CHR$ (7): GOTO 3012
```

```
3016  & BUZZ STOP : IF H6% = 2 GOSUB 20
3018  PRINT "HIT ANY KEY AFTER NEW DISK IS INSERTED": INPUT "";KEY$: HOME
4000  IF Y3 = 177 OR Y3 = 178 THEN G = G + 2
4004  GOTO 956
4770  PRINT D$;"OPEN";Z9$;",L";RI;",D";R2%
4772  PRINT D$;"WRITE";Z9$;",RO": PRINT G: PRINT SY$: PRINT N: PRINT RI: PRINT RP
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:

$$A/C = P0 + P1 \times A + P2 \times A^2 \quad \text{(Routh, 1981)}$$

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, SCERR(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
--------------------------------------------------------------------------

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
--------------------------------------------------------------------------

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) $A/C = P0 + P1 \times A + P2 \times A^{2*}$
general form of non-linear regression equation.

B) $C(i) = A(i) / (P0 + P1 \times A(i) + P2 \times A(i)^{2})$
concentration not corrected for instrument sensitivity changes.

C) $\mathrm{CORR}(i) = C(i) / \mathrm{SOLNC}(i)^{**}$
instrument sensitivity correction factor.

D) $\mathrm{AVGCORR}(i) = \sum (\mathrm{CORR}(i)) / \mathrm{NSTDS}^{***}$
average instrument sensitivity correction factor.

E) $\mathrm{AVGCORR2}(i) = (\mathrm{AVGCORR}(i-1) + \mathrm{AVGCORR}(i)) / 2.0^{****}$
block averaged instrument sensitivity correction factor.

F) $\mathrm{CONC}(i) = (A(i) / \mathrm{AVGCORR2}(j)) / \mathrm{DIL}(i)$
sample concentration corrected for average instrument sensitivity change and dilution factor (DIL(i)).

G) $\mathrm{CONC}(i) = \mathrm{ADJWT}(i) \times \mathrm{CONC}(i)$
sample concentration corrected for adjusted sample weight (ADJWT(i))

H) $\mathrm{MRSD} = (\sqrt{(\sum(\mathrm{SD}(i) / A(i))^{2}) / N}) \times 100.0^{*****}$
mean relative standard deviation.

I) $\mathrm{RMSD} = \sqrt{(\sum (1 - \mathrm{CORR}(i))^{2}) / N}^{******}$
relative mean standard deviation.

J) $\mathrm{SCERR}(i) = \sqrt{(((\mathrm{SD}(i)^{2}) / (P0+P1\times A(i)+P2\times A(i)^{2})) + ((\mathrm{RMSD}\times C(i))^{2}))}$
sample solution concentration error.

* in the regression equation, X is absorbance (A) and Y is absorbance divided by solution concentration (C); P0, P1, and P2 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 :D$ =  CHR$ (4): GOTO 3820
10  HOME : IF AJW$ (  ) "*" THEN  PRINT "SAMPLE WTS/LABELS PRESENT- DO YOU WISH TO REDO": INPUT Y$: IF  LEFT$ (Y$,1) = "N" GOTO 499
15  DIM T1C$(Q1),T2C$(Q1),NNTX(18,15),NUMR$(18),NSTK$(18,15),NX%(18),MX$(18)
20 FM = 0:IO = 0
50  FOR I = 1 TO Q1
60  IF LBL1$(I) = "STD" THEN IO = IO + 1: GOTO 90
62  IF  LEFT$ (LBL1$(I),3) = "EPA" OR  LEFT$ (LBL1$(I),3) = "TEG" OR  LEFT$ (LBL1$(I),3) = "MTX" THEN IO = IO + 1: GOTO 90
63  IF FM = 1 GOTO 90
64 V9 = 0: SPEED= 80
65  FOR II = 1 TO  LEN (NMB1$(I))
70  IF  MID$ (NMB1$(I),II,1) = "-" THEN V9 = V9 + 1
75  IF V9 = 2 THEN NUMR$(1) =  LEFT$ (NMB1$(I),II - 1):NX%(1) = 1:TF = 1:TA = 1:NSTK$(TF,TA) = NMB1$(I):NNTX(TF,TA) = I:FM = 1: GOTO 90
80  NEXT II
90  NEXT I
94  FOR K = 1 TO Q1
100  FOR I = 1 TO Q1
110  IF LBL1$(I) = "STD" GOTO 200
115  IF  LEFT$ (LBL1$(I),3) = "EPA" OR  LEFT$ (LBL1$(I),3) = "TEG" OR  LEFT$ (LBL1$(I),3) = "MTX" GOTO 200
120  IF TA ) 0 GOTO 178
122 STR = 0
125  FOR II = 1 TO TF
130  IF  LEFT$ (NMB1$(I),( LEN (NUMR$(II)))) = NUMR$(II) THEN STR = STR + 1
135  NEXT II: IF STR (  ) 0 GOTO 200
140 TF = TF + 1
145 V9 = 0
150  FOR J = 1 TO  LEN (NMB1$(I))
155  IF  MID$ (NMB1$(I),J,1) = "-" THEN V9 = V9 + 1
160  IF V9 = 2 THEN NUMR$(TF) =  LEFT$ (NMB1$(I),J - 1):NX%(TF) = 1: GOTO 175
165  NEXT J:NUMR$(TF) = NMB1$(I):NX%(TF) = 1
175 TA = 1:NSTK$(TF,TA) = NMB1$(I)
176  GOTO 200
178  IF NMB1$(I) = NSTK$(1,1) GOTO 200
180  IF  LEFT$ (NMB1$(I),( LEN (NUMR$(TF)))) = NUMR$(TF) THEN TA = TA + 1:NSTK$(TF,TA) = NMB1$(I):NNTX(TF,TA) = I:NX%(TF) = TA
200  NEXT I
201 TA = 0:NSUM% = 0
202  FOR J = 1 TO TF
204 NSUM% = NSUM% + NX%(J)
205  NEXT J
207  IF (NSUM% + IO) )  = Q1 THEN  GOTO 220
210  NEXT K
220  PRINT "FILES TO BE READ"
230  PRINT "FILENAME AND # OF ENTRIES IN THAT SERIES"
235  FOR J = 1 TO TF
240  PRINT NUMR$(J);"  ";NX%(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$,1) (  ) "Y" GOTO 310
300  PRINT D$;"CATALOG,D1"
305  GOTO 280
310  PRINT D$;"MON,C,I,O"
311  PRINT D$;"OPEN BP ";NUMR$(J);",L70"
315  FOR BV = 1 TO NX%(J)
317 MX$(BV) = "0"
318  NEXT BV
320  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE BP ";NUMR$(J): GOTO 280
```

```
330  PRINT D$;"READ BP ";NUMR$(J);",R0": INPUT S:STR = 0:KCTR = 0
340  FOR JK = 1 TO S
350  PRINT D$;"READ BP ";NUMR$(J);",R";JK: INPUT SN$
360  FOR JL = 1 TO NX%(J)
370  IF MX$(JL) = "*" GOTO 400
375  IF SN$ (  ) NSTK$(J,JL) GOTO 400
380 KCTR = KCTR + 1
385  PRINT D$;"READ BP ";NUMR$(J);",R";JK: INPUT U1$: INPUT U2: INPUT U3$: INPUT U4: INPUT U5$: INPUT U6$
388 MX$(JL) = "*"
389 AJW1(NNT%(J,JL)) = U2
390 T1C$(NNT%(J,JL)) = U5$
392 T2C$(NNT%(J,JL)) = U6$
395  IF KCTR )  = NX%(J) THEN  PRINT D$;"CLOSE BP ";NUMR$(J): GOTO 430
398  GOTO 410
400  NEXT JL
410  NEXT JK: PRINT D$;"CLOSE BP ";NUMR$(J)
412  IF KCTR )  = NX%(J) GOTO 430
414  PRINT "SAMPLES IN BP ";NUMR$(J);" SERIES NOT SATISFIED"
416  PRINT "NUMBER IN SERIES ";NX%(J)
418  PRINT "NUMBER FOUND ";KCTR
419  FOR HP = 1 TO 3000: NEXT HP
430  NEXT J
440 X = Q1
498  PRINT "INSERT DISK WITH FILE";Z9$;" AND HIT ANY KEY TO CONTINUE": INPUT Y$:Y$ = "Z"
499  RETURN
500  FOR I = 1 TO 3000: NEXT I: GOTO 1490
510  PRINT "SUBROUTINE"
520 P4(R - 1) = ((P2) * 1.000001) / RE1%(R - 1):P4$(R - 1) =  STR$ (P4(R - 1))
540  REM IFYY = 0 THEN A4$(R - 1) = "0*": GOTO 560
550  REM VR=(A2 * 1.000001) / YY:A4$(R - 1) =  STR$ (VR):A4$(R - 1) =  LEFT$ (A4$(R - 1),7)
570 I1 = 0.000:I2 = 0.000:S1D(R - 1) = 0.000:S2D(R - 1) = 0.000:IKNT = 0
575  IF RE1%(R - 1) = 1 THEN S1D(R - 1) = 0.0: GOTO 610
578  IF P4(R - 1) = 0 THEN S1D(R - 1) = 0.0: GOTO 610
580  FOR I = 1 TO RE1%(R - 1)
590 I1 = I1 + ( ABS (P4(R - 1) - PMAX%(R - 1,I))) ^ 2
600  NEXT I:S1D(R - 1) = (( SQR (I1 / (RE1%(R - 1) - 1))) / P4(R - 1)) * 100.0
610  REM IFYY = 1 THEN S2D(R - 1) = 0.0
620  REM IFYY = 0 OR YY = 1 GOTO 690
625  REM  IF VAL (A4$(R-1))(1 THEN GOTO 690
630  FOR I = 1 TO YY
632  IF AEA$(R - 1,I) = "0*" GOTO 636
634 IKNT = IKNT + 1
636  NEXT I
638  IF IKNT = 0 THEN A4$(R - 1) = "0*": GOTO 690
642 VR = (A2 * 1.000001) / IKNT:A4$(R - 1) =  STR$ (VR):A4$(R - 1) =  LEFT$ (A4$(R - 1),7)
644  IF IKNT = 1 THEN S2D(R - 1) = 0.0: GOTO 690
646  IF ( VAL (A4$(R - 1))) = 0 THEN S2D(R - 1) = 0.0: GOTO 690
648  FOR I = 1 TO YY
650  IF AEA$(R - 1,I) = "0*" GOTO 670
660 I2 = I2 + ( ABS ( VAL (AEA$(R - 1,I)) -  VAL (A4$(R - 1)))) ^ 2
670  NEXT I
680 S2D(R - 1) = (( SQR (I2 / (IKNT - 1))) /  VAL (A4$(R - 1))) * 100.0
690 Y1Y%(R - 1) = YY
700 A2 = 0:P2 = 0:YY = 0:TP = P
705 ERE =  FRE (0)
710  RETURN
720  IF  RIGHT$ (Z9$,1) = "C" THEN  PRINT D$;"CLOSE";Z9$: PRINT "INCORRECT NAME FORMAT FOR READING RAW DATA FILE- DO NOT APPEND NAMES WITH A 'C'": GOTO 500
730  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE";Z9$: PRINT "FILE HAS NO RAW DATA": GOTO 500
770  PRINT D$;"CLOSE";Z9$
780  IF D ) 0 THEN  PRINT "AREA ALREADY CALCULATED- DO YOU WISH TO REDO?": INPUT Q0$: IF  LEFT$ (Q0$,1) (  ) "Y" GOTO 1490
```

```
790  PRINT D$;"READ";Z9$;",R0,B0": INPUT G: INPUT SY$: INPUT N: INPUT RI: INPUT RP: PRINT D$;"CLOSE";Z9$
800  DIM ACRRT%(N),PMAX%(G,9),P4(G),RE1%(G),AEA$(G,9),A4$(G),Y1Y%(G),AJW1(G),S1D(G),S2D(G),PMAX$(G,9),P4$(G)
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 ICZ%(IY)
815  IF ICZ%(IY) (  = 0 THEN  GOTO 814
816  NEXT IY
818 XS% = 0:EI% = 0:SI% = 0
820  FOR W = 1 TO 6
821  FOR IY = 1 TO IY%
822  IF W = (ICZ%(IY) + 1) THEN  PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)": INPUT ZZ$
825  NEXT IY
826  PRINT D$;"OPEN";Z9$;",L";RI
839 SUM = 0.0:AREA = 0.0:R1 = 0:CTR1 = 0:H1 = 0:LAG2 = 0:RR = 0
850  PRINT D$;"READ";Z9$;",R";W;",B1": INPUT P
860  IF W = 1 THEN TP = P;R = 1:PR = 1
865  PRINT D$;"READ";Z9$;",R";W;",B1654": INPUT FLZ$: IF FLZ$ = "*" THEN  PRINT D$;"CLOSE";Z9$: GOTO 1410
870  IF P (  ) TP THEN RE1%(R) = PR - 1:R = R + 1:PR = 1
878  IF R ) 5 AND XS% ) 0 THEN SI% = SI% / XS%:EI% = EI% / XS%:XS% = 0
880  PRINT D$;"READ";Z9$;",R";W;",B1": INPUT P: INPUT PMAX%(R,PR): INPUT LOC:PMAX$(R,PR) =  STR$ (PMAX%(R,PR))
890  PRINT D$;"READ";Z9$;",R";W;",B25"
900  FOR I = 0 TO N
910  INPUT ACRRT%(I)
920  NEXT I
930  PRINT D$;"CLOSE";Z9$
932  IF PMAX%(R,PR) ) 40 OR PMAX%(R,PR) (  = 10 GOTO 940
934  IF EI% = 0 GOTO 940
935  FOR I = SI% TO EI%
936 AREA = AREA + ACRRT%(I)
938  NEXT I: GOTO 1300
940  FOR I = 0 TO N
950  IF I = N AND PMAX%(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 ACRRT%(I) ( 0 GOTO 1050
980  IF CTR1 ) 0 GOTO 1010
990  IF (ACRRT%(I + 1) - ACRRT%(I)) ) 0 THEN RR = (ACRRT%(I + 1) - ACRRT%(I)):CTR1 = 1
1000  GOTO 1050
1010  IF (ACRRT%(I + 1) - ACRRT%(I)) )  = RR THEN CTR1 = CTR1 + 1:SUM = SUM + (ACRRT%(I + 1) - ACRRT%(I)): GOTO 1040
1020 CTR1 = 0
1030 SUM = 0.0
1040  IF CTR1 = 5 THEN RR = SUM / 5.0: GOTO 1060
1050  NEXT I
1060 CTR1 = 0
1070  IF (I - 9) ( 0 THEN AREA$ = "0*": GOTO 1320
1090  SPEED= 255
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 (ACRRT%(K) - ACRRT%(K + 1)) )  = RR THEN R1 = 0: GOTO 1160
1150 R1 = R1 + 1
1160  IF R1 = 3 THEN CTR1 = CTR1 - 2: GOTO 1190
1170 AREA = AREA + ACRRT%(K):CTR1 = CTR1 + 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 = PMAX%(R,PR) * .04
1220  FOR H = K - 2 TO N: REM PRIN"H=";H
1230 H1 = H1 + 1
```

```
1240  IF H = N - 1 THEN  GOTO 1300
1250  IF ACRRT%(H) ) RR GOTO 1270
1260  IF (((ACRRT%(H) + ACRRT%(H + 1) + ACRRT%(H + 2)) * 1.000001) / 3.0) (  = RR GOTO 1300
1270  IF H1 ) 2 THEN AREA = AREA + ACRRT%(H)
1280  NEXT H
1290  REM  THE ABOVE LOOP HAS ALL POINTS ENTERING WHICH EXCEED THE THRESHOLD ON THE SLOPE DOWNSWING- 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% + K:EI% = EI% + H
1340 A2 = A2 + AREA
1350 P2 = P2 + PMAX%(R,PR):AEA$(R,PR) = AREA$:YY = YY + 1
1370 PR = PR + 1
1380  PRINT D$;"MONC,I,O"
1400  SPEED= 255
1410  NEXT W:RE1%(R) = PR - 1:R = R + 1: GOSUB 510
1420 R = R - 1
1430  PRINT "PLACE SIDE 1 BACK IN DRIVE AND HIT ANY KEY AND (RTN)": INPUT ZZ$
1438  PRINT D$;"UNLOCK";Z9$
1440  PRINT D$;"WRITE";Z9$;",R0,B100": PRINT "*": PRINT D$;"WRITE";Z9$;",R0,B102": PRINT R: PRINT D$;"WRITE";Z9$;",R0,B107": PRINT L9
1450  PRINT D$;"CLOSE";Z9$: PRINT D$;"LOCK";Z9$
1460  PRINT "ENTER DISK FOR CALCULATED DATA AND HIT ANY KEY AND (RTN) TO STORE CALCULATIONS": INPUT II$
1470 Z9$ = Z9$ + "C":J% = 4:Q2 = R:X = R
1480  GOSUB 3460
1490  RETURN
1500  VTAB S%(L): HTAB 5: PRINT NMB1$(L): VTAB S%(L): HTAB 14: PRINT LBL1$(L): VTAB S%(L): HTAB 27: PRINT DIL1$(L): VTAB S%(L): HTAB 37: PRINT REP1$(L): RETURN
1510 GK = SH%(L):PK = 2: INVERSE
1520  FOR IO = 1 TO RE1%(L)
1530  VTAB (GK): HTAB (PK): PRINT PMAX$(L,IO):PK = PK + 5: IF PK )  = 35 THEN PK = 2:GK = GK + 1
1540  NEXT IO
1550  HTAB (PK): VTAB (GK): PRINT  LEFT$ (P4$(L),6): RETURN
1560 GK = SS%(L):PK = 2
1570  FOR IO = 1 TO Y1Y%(L)
1580  VTAB (GK): HTAB (PK): PRINT AEA$(L,IO):PK = PK + 7: IF PK )  = 33 THEN PK = 2:GK = GK + 1
1590  NEXT IO
1600  HTAB (PK): VTAB (GK): PRINT  LEFT$ (A4$(L),8): RETURN
1610  VTAB (20): HTAB (1): PRINT "ENTER RECORD # YOU WISH TO MODIFY (1 AT A TIME) OR HIT (RETURN) FOR NO CHANGES   "
1620  INPUT "";L$: IF L$ = "" GOTO 2270
1630 L =  VAL (L$): IF L ( 1 OR L ) X GOTO 1610
1640  IF L ( NM OR L ) (NM + 4) GOTO 1610
1650 Q1$ = LBL1$(L):Q2$ = NMB1$(L):Q3$ = DIL1$(L):Q4$ = REP1$(L)
1660  VTAB S%(L): HTAB (5): PRINT NMB1$(L): VTAB S%(L): HTAB 4: INPUT "";Q2$
1670  IF  LEN (Q2$) ) 9 GOTO 1660
1680  IF  LEN (Q2$) ) 0 THEN NMB1$(L) = Q2$
1690  GOSUB 1500
1700  VTAB S%(L): HTAB (14): PRINT LBL1$(L): VTAB S%(L): HTAB 13: INPUT "";Q1$
1710  IF  LEN (Q1$) ) 4 GOTO 940
1720  IF  LEN (Q1$) ) 0 THEN LBL1$(L) = Q1$
1730  GOSUB 1500
1740  VTAB S%(L): HTAB (27): PRINT DIL1$(L): VTAB S%(L): HTAB 26: INPUT "";Q3$
1750  IF  LEN (Q3$) ) 6 GOTO 1740
1760  IF  LEN (Q3$) = 0 GOTO 1810
1770  IF  VAL (Q3$) (  = 0 GOTO 1740
1780  FOR II = 1 TO  LEN (Q3$)
1790  IF  ASC ( MID$ (Q3$,II,1)) ( 46 OR  ASC ( MID$ (Q3$,II,1)) ) 57 GOTO 1740
1800  NEXT II:DIL1$(L) = Q3$
1810  GOSUB 1500
1820  VTAB S%(L): HTAB 37: PRINT REP1$(L): VTAB S%(L): HTAB 36: INPUT "";Q4$
1830  IF  LEN (Q4$) ) 2 GOTO 1820
```

```
1840  IF  LEN (Q4$) = 0 GOTO 1890
1850  IF  VAL (Q4$) (  = 0 GOTO 1820
1860  FOR II = 1 TO  LEN (Q4$)
1870  IF  ASC ( MID$ (Q4$,II,1)) ( 48 OR  ASC ( MID$ (Q4$,II,1)) ) 57 GOTO 1820
1880  NEXT II:REP1$(L) = Q4$
1890  GOSUB 1500
1900  IF Q2 = 0 GOTO 2270
1905  IF Q8% = 3 OR Q8% = 4 GOTO 2270
1910  IF J% ( 4 GOTO 2270
1920  REM F Y1Y%(L) = 0 GOTO 1209
1930 PE = 2:C2 = 0:A2 = 0:YY = 0: INVERSE :I2 = 0.0:A3 = 0.0:OO = 0:I1 = 0
1940  FOR II = 1 TO RE1%(L)
1950  REM  IFRIGHT$ (PMAX$(L,II),1) = "*" GOTO 1980
1960  HTAB (PE): VTAB (SH%(L)) + C2: PRINT PMAX$(L,II): HTAB (PE - 1): VTAB (SH%(L)): INPUT "";QT$
1970  REM  GOTO1990
1980  REM HTAB(PE): VTAB (SH%(L)) + C2: PRINT PMAX$(L,II): HTAB (PE + ( LEN (PMAX$(L,II)) - 1)): VTAB (SH%(L)): INPUT "";CK$: IF CK$ = "/" THEN HX = ( LEN (PMAX$(L,II)) - 1):PMAX$(L,II) =  LEFT$ (PMAX$(L,II),HX)
1981  IF  LEN (QT$) ) 5 GOTO 1960
1985  IF  RIGHT$ (QT$,1) = "*" THEN PMAX$(L,II) = QT$: GOTO 2000
1986  IF  LEN (QT$) = 0 GOTO 1999
1991  FOR JF = 1 TO  LEN (QT$)
1992  IF  ASC ( MID$ (QT$,JF,1)) ( 46 OR  ASC ( MID$ (QT$,JF,1)) ) 57 GOTO 1960
1994  NEXT JF:PMAX$(L,II) = QT$
1999 A3 = A3 +  VAL (PMAX$(L,II)):OO = OO + 1
2000  GOSUB 1510
2010 PE = PE + 5: IF PE )  = 35 THEN PE = 2:C2 = C2 + 1
2020  NEXT II:C2 = 0:PE = 2: IF OO ) 0 THEN P4$(L) =  STR$ (A3 / OO): GOTO 2040
2030 P4$(L) = "0*"
2040  FOR II = 1 TO Y1Y%(L)
2050  IF  RIGHT$ (AEA$(L,II),1) = "*" GOTO 2080
2060  HTAB (PE): VTAB (SS%(L)) + C2: PRINT AEA$(L,II): HTAB (PE +  LEN (AEA$(L,II))): VTAB (SS%(L)) + C2: INPUT "";CK$: IF CK$ = "*" THEN AEA$(L,II) = AEA$(L,II) + "*"
2070  GOTO 2090
2080  HTAB (PE): VTAB (SS%(L)) + C2: PRINT AEA$(L,II): HTAB (PE +  LEN (AEA$(L,II)) - 1): VTAB (SS%(L) + C2): INPUT "";CK$: IF CK$ = "/" THEN HX = ( LEN (AEA$(L,II)) - 1):AEA$(L,II) =  LEFT$ (AEA$(L,II),HX)
2090  GOSUB 1560
2100  IF  RIGHT$ (AEA$(L,II),1) (  ) "*" THEN A2 = A2 +  VAL (AEA$(L,II)):YY = YY + 1
2110 PE = PE + 7: IF PE )  = 30 THEN C2 = C2 + 1:PE = 2
2120  NEXT II: NORMAL : IF YY ) 0 THEN A4$(L) =  STR$ ((A2 * 1.000001) / YY): GOTO 2140
2130 A4$(L) = "0*"
2140  IF YY = 1 OR YY = 0 THEN S2D(L) = 0.0: GOTO 2200
2150 I2 = 0.0
2160  FOR I = 1 TO Y1Y%(L)
2170  IF  RIGHT$ (AEA$(L,I),1) = "*" GOTO 2190
2180 I2 = I2 + ( ABS ( VAL (AEA$(L,I)) -  VAL (A4$(L)))) ^ 2
2190  NEXT I:S2D(L) = (( SQR (I2 / (YY - 1))) /  VAL (A4$(L))) * 100.0
2200  IF OO = 1 OR OO = 0 THEN S1D(L) = 0.0: GOTO 2260
2210 I1 = 0.0
2220  FOR I = 1 TO RE1%(L)
2230  IF  RIGHT$ (PMAX$(L,I),1) = "*" GOTO 2250
2240 I1 = I1 + ( ABS ( VAL (PMAX$(L,I)) -  VAL (P4$(L)))) ^ 2
2250  NEXT I:S1D(L) = (( SQR (I1 / (OO - 1))) /  VAL (P4$(L))) * 100.0
2270  RETURN
2280 D$ =  CHR$ (4):I = 1:X = 0:K = 1:K% = 3: TEXT : HOME : IF  RIGHT$ (Z9$,1) (  ) "C" THEN  PRINT D$;"CLOSE";Z9$: PRINT "NAME FORMAT INCORRECT": GOTO 500
2290  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE";Z9$:FG = 1: GOTO 2350
2300  PRINT D$;"READ";Z9$;",R0,B100": INPUT FLAG$
2310  IF FLAG$ = "*" THEN  PRINT D$;"CLOSE";Z9$: PRINT "THIS IS RAW DATA FILE -ENTER CORRECT NAME": GOTO 500
2320  PRINT D$;"READ";Z9$;",R0,B0": INPUT Q1: PRINT D$;"READ";Z9$;",R0,B4": INPUT Q2: PRINT D$;"READ";Z9$;",R0,B8": INPUT G: PRINT D$;"READ";Z9$;",R0,B15": INPUT AJW$: PRINT D$;"CLOSE";Z9$
2330  IF Q1 ) 0 GOTO 2450
2340  IF Q8% = 2 OR Q8% = 5 THEN  PRINT "NO LABEL INFORMATION CURRENTLY ON DISK- (2ND PASS THROUGH DATA AND SAMPLE WT./LABEL INPUT CANNOT BE DONE WITHOUT LABEL INFORMATION": GOTO 500
2350 AJW$ = "*"
2360  PRINT D$;"UNLOCK";Z9$
2370  PRINT D$;"OPEN";Z9$;"L350": PRINT D$;"WRITE";Z9$;",R0,B0": PRINT "0": PRINT D$;"WRITE";Z9$;",R0,B15": PRINT AJW$: PRINT D$;"WRITE";Z9$;",R0,B18": PRINT "*": PRINT D$;"CLOSE";Z9$
```

```
2380  IF Q2 ) 0 THEN FA = 1: GOTO 2450
2390  PRINT "ENTER DISK WITH RAW DATA IN DRIVE#";R2%;" AND HIT ANY KEY AND (RTN)": INPUT HJ$
2400 Z1$ =  LEFT$ (Z9$,( LEN (Z9$) - 1)): PRINT D$;"OPEN";Z1$;",L350"
2410  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE";Z1$: PRINT "THIS DISK HAS NO RAW DATA FILE": GOTO 3810
2420  PRINT D$;"READ";Z1$;",R0": INPUT G: INPUT SY$: INPUT N: INPUT RI: INPUT RP
2430  PRINT D$;"CLOSE";Z1$
2440  PRINT "REINSERT DISK WITH FILE ";Z9$;" AND HIT (RTN)": INPUT BZ$
2450  DIM SS%(G),S%(G),RE1%(G),PMAX$(G,9),AEA$(G,9),A4$(G),LBL1$(G),NMB1$(G),REP1$(G),DIL1$(G),AJW1(G),S2D(G),S1D(G),Y1Y%(G),P4$(G),SH%(G)
2460  IF Q8% = 5 THEN FX = 1: GOTO 2530
2470  IF FA = 1 OR FG = 1 GOTO 2840
2480  PRINT "FILE ALREADY EXISTS- DO YOU WISH TO ADD TO FILE(1), MODIFY FILE(2) , CREATE NEW FILE(3)"
2490  IF Q2 ) 0 THEN  PRINT "OR EDIT DATA RECORDS(4)":K% = 4
2500  INPUT J%
2510  IF J% ) K% OR J% ( 1 GOTO 2470
2520  IF J% = 3 GOTO 3810
2530  PRINT D$;"OPEN";Z9$;",L350";",D";R2%"
2540  FOR N = 1 TO Q1
2550  PRINT D$;"READ";Z9$;",R";N;",B2"
2560  INPUT NMB1$(N): INPUT LBL1$(N)
2570  INPUT DIL1$(N): INPUT REP1$(N)
2580  PRINT D$;"READ";Z9$;",R";N;",B52"
2590  INPUT AJW1(N)
2600  IF FX = 1 GOTO 2780
2610  IF Q2 = 0 GOTO 2780
2620  IF J% ( 4 GOTO 2780
2630  PRINT D$;"READ";Z9$;",R";N;",B77"
2640  INPUT RE1%(N)
2650  PRINT D$;"READ";Z9$;",R";N;",B80": INPUT P4$(N)
2660  PRINT D$;"READ";Z9$;",R";N;",B88"
2670  FOR IK = 1 TO RE1%(N)
2680  INPUT PMAX$(N,IK)
2690  NEXT IK
2700  PRINT D$;"READ";Z9$;",R";N;",B140": INPUT S1D(N)
2710  PRINT D$;"READ";Z9$;",R";N;",B177": INPUT Y1Y%(N)
2720  PRINT D$;"READ";Z9$;",R";N;",B180": INPUT A4$(N)
2730  PRINT D$;"READ";Z9$;",R";N;",B190"
2740  FOR IK = 1 TO Y1Y%(N)
2750  INPUT AEA$(N,IK)
2760  NEXT IK
2770  PRINT D$;"READ";Z9$;",R";N;",B254": INPUT S2D(N)
2780  NEXT N
2790  PRINT D$;"CLOSE";Z9$
2800  IF FX = 1 THEN  GOSUB 10
2805  IF FX = 1 AND Y$ = "N" GOTO 3810
2810  IF FX = 1 THEN  PRINT D$;"MON,C,I,O": SPEED= 20: GOTO 3450
2820  IF J% = 2 OR J% = 4 THEN X = Q1: GOTO 3100
2830  IF J% = 1 THEN I = Q1 + 1:X = Q1
2840 Z$ = "DIL FTR":YY$ = "REP#":X$ = "SAMPLE #":W$ = "LABEL":V$ = "DATA": HOME
2850  HTAB 1: VTAB 6: PRINT "ENTER ";X$;"(";I;")  9 CHARACTERS ALLOWED OR HIT (/) KEY TO TERMINATE ENTRY"
2860  INPUT "";KEY$: IF KEY$ = "/" AND X = 0 GOTO 3810
2870  IF KEY$ = "/" GOTO 3030
2880  IF  LEN (KEY$) ) 9 GOTO 2850
2890  IF  LEN (KEY$) ) 0 THEN NMB1$(I) = KEY$
2900  HTAB 1: VTAB 9: PRINT "ENTER ";W$;"(";I;") 4 CHARACTERS ALLOWED": IF AJW$ = "#" THEN AJW1(I) = 1.0000
2910  INPUT "";Q2$: IF  LEN (Q2$) ) 4 GOTO 2900
2920  IF  LEN (Q2$) ) 0 THEN LBL1$(I) = Q2$
2930  HTAB 1: VTAB 12: PRINT "ENTER ";Z$;"(";I;") 6 CHARACTERS ALLOWED"
2940  INPUT "";Q3$: IF  LEN (Q3$) ) 6 GOTO 2930
2950  IF  LEN (Q3$) = 0 GOTO 3000
2960  IF  VAL (Q3$) (  = 0 GOTO 2930
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2970  FOR II = 1 TO  LEN (Q3$)
2980  IF  ASC ( MID$ (Q3$,II,1)) ( 46 OR  ASC ( MID$ (Q3$,II,1)) ) 57 GOTO 2930
2990  NEXT II:DIL1$(I) = Q3$
3000  HTAB 1: VTAB 15: PRINT "ENTER ";YY$;"(";I;") 2 CHARACTERS ALLOWED"
3010  INPUT "";Q4$: 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$,II,1)) ( 48 OR  ASC ( MID$ (Q4$,II,1)) ) 57 GOTO 3000
3060  NEXT II:REP1$(I) = Q4$
3070 X = I:I = I + 1
3075  IF Q2 = 0 GOTO 3080
3077  IF I ) Q2 THEN  PRINT "# DATA ENTRIES=";Q2;" CANNOT ENTER MORE LABELS": FOR HQ = 1 TO 1000: NEXT HQ: GOTO 3090
3080  GOTO 2840
3090  REM
3100  HOME : VTAB (1): HTAB (2): PRINT W$: VTAB (1): HTAB (14): PRINT X$
3110  VTAB (1): HTAB (26): PRINT YY$: VTAB (1): HTAB (34): PRINT Z$
3120  FOR NM = 1 TO X STEP 5:S = 4: HOME
3130  FOR NN = NM TO NM + 4
3140  IF NN ) X GOTO 3380
3150 S%(NN) =  INT (S)
3160  VTAB (S): HTAB (1): PRINT NN;")": VTAB (S): HTAB (5): PRINT NMB1$(NN)
3170  VTAB (S): HTAB (14): PRINT LBL1$(NN)
3180  VTAB (S): HTAB (27): PRINT DIL1$(NN)
3190  VTAB (S): HTAB (37): PRINT REP1$(NN)
3200  IF Q2 = 0 GOTO 3370
3210  IF J% ( 4 GOTO 3370
3220  INVERSE :S = S + 1
3230 PE = 2:SH%(NN) =  INT (S)
3240  FOR IK = 1 TO RE1%(NN)
3250  HTAB (PE): VTAB (S): PRINT PNAX$(NN,IK)
3260 PE = PE + 5: IF PE )  = 35 THEN S = S + 1:PE = 2
3270  NEXT IK
3280  HTAB (PE): VTAB (S)
3290  PRINT  LEFT$ (P4$(NN),6):S = S + 1:PE = 2
3300 SS%(NN) =  INT (S)
3310  FOR IK = 1 TO Y1Y%(NN)
3320  HTAB (PE): VTAB (S): PRINT AEA$(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$ (A4$(NN),8)
3370 S = S + 1: NORMAL
3380  NEXT NN
3390  HTAB 1: VTAB 20: PRINT "PRESS(1) TO CONTINUE OR (2) TO MODIFY
3400  INPUT Q3%
3410  IF Q3% ( 1 OR Q3% ) 2 GOTO 3400
3420  IF Q3% = 2 THEN  GOSUB 1610
3430  NEXT NM
3440  HOME : PRINT "DO YOU WISH TO GET A LISTING OF RECORDS, FIVE ITEMS AT A TIME?   ": INPUT D$: IF  RIGHT$ (D$,1) = "Y" GOTO 3100
3450  PRINT D$;"UNLOCK";Z9$
3460  PRINT D$;"OPEN";Z9$;",L350";",D";R2%
3470  IF  PEEK ( - 18962) ( 2 THEN FD = 2
3480  PRINT D$;"MON C,I,O"
3490  FOR N = 1 TO X
3500  IF W ) 0 GOTO 3560
3505  IF FX = 1 GOTO 3732
3510  PRINT D$;"WRITE";Z9$;",R";N;",B2"
3520  PRINT NMB1$(N): PRINT LBL1$(N)
3530  PRINT DIL1$(N): PRINT REP1$(N)
```

```
3540  PRINT D$;"WRITE";Z9$;",R";N;",B52"
3550  PRINT AJW1(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$;",R";N;",B88"
3610  FOR II = 1 TO RE1%(N)
3620  PRINT PMAX$(N,II)
3630  NEXT II
3640  PRINT D$;"WRITE";Z9$;",R";N;",B140": PRINT  LEFT$ (( STR$ (S1D(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$;",R";N;",B190"
3680  FOR II = 1 TO Y1Y%(N)
3690  PRINT AEA$(N,II)
3700  NEXT II
3710  PRINT D$;"WRITE";Z9$;",R";N;",B254": PRINT  LEFT$ (( STR$ (S2D(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$ (T1C$(N),10): PRINT  LEFT$ (T2C$(N),10)
3735  PRINT D$;"WRITE";Z9$;",R";N;",B52": PRINT  LEFT$ ( STR$ (AJW1(N)),8)
3740  NEXT N
3750  IF W ) 0 OR J% = 4 THEN  PRINT D$;"WRITE";Z9$;",R0,B4": PRINT Q2: PRINT D$;"WRITE";Z9$;",R0,B8": PRINT 6
3760  IF Q8% = 3 OR Q8% = 4 THEN  PRINT D$;"WRITE";Z9$;",R0,B0": PRINT X
3770  PRINT D$;"WRITE";Z9$;",R0,B100": PRINT 1
3780  IF FD = 2 THEN  PRINT D$;"WRITE";Z9$;",R0,B0": PRINT 0: PRINT D$;"WRITE";Z9$;",R0,B15": PRINT "*"
3785  IF Q8% = 5 THEN  PRINT D$;"WRITE";Z9$;",R0,B15": PRINT "1"
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) 2ND PASS THROUGH DATA-EDIT DATA/LABELS"
3850  PRINT "(3) MAKE 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 "CATALOG TO LOCATE FILE? (Y/N)": INPUT Y$
3930  IF ( LEFT$ (Y$,1)) = "Y" THEN  PRINT "DRIVE #?": INPUT R2%: IF R2% = 1 OR R2% = 2 THEN  PRINT D$;"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 FORMAT IS RAW DATA FILE NAME APPENDED WITH A 'C' ": INPUT Z9$,R2%
3950  IF R2% ( 1 OR R2% ) 2 GOTO 3940
3960  IF  ASC ( LEFT$ (Z9$,1)) ( 65 OR  ASC ( LEFT$ (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 D$ =  CHR$ (4)
20  GOTO 2680
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 APARTICULAR BLOCK
40 SUM = SUM + CRFT(I)
45  IF I = Q2 THEN J = J + 1:NRFT(J) = SUM / K:K = 0:SUM = 0.0: PRINT "NRFT";J;"=";NRFT(J): GOTO 60: REM ECUTED ONLY IF AT LAST POINT IN ARRAY
50  IF LBL1$(I + 1) (  ) "STD" THEN J = J + 1:NRFT(J) = SUM / K:K = 0:SUM = 0.0: PRINT "NRFT";J;"=";NRFT(J): REM AKING AN AVERAGE NOW IF NEXT POINT IS NOT A STD
55  REM F P = 0 AND LBL1$(I + 1) (  ) "STD" THEN RMSD =  SQR (RMSD / CTR)
60  RETURN
65  FOR IL = 1 TO 2
66 CTR = 0
67  IF QA% = 2 AND IL = 2 GOTO 81
69  IF QA% = 3 AND IL = 1 GOTO 81
71  FOR I = 1 TO Q1
73  IF I = Q1 THEN  PRINT "NO CONSECUTIVE STDS IN FILE": GOTO 83
74  IF LBL1$(I) (  ) "STD" THEN CTR = 0: GOTO 79
75  IF IL = 1 AND P4$(I) = "0*" GOTO 79
76  IF IL = 2 AND A4$(I) = "0*" GOTO 79
77 CTR = CTR + 1:CS%(CTR) = I
78  IF CTR ) 1 AND LBL1$(I + 1) (  ) "STD" THEN  GOTO 80
79  NEXT I
80 A(1) = CTR: GOSUB 84
81  PRINT "MMM": PRINT IL
83  NEXT IL: RETURN
84 D = 2: IF IL ) 2 THEN  RETURN
85  FOR UU = 1 TO CTR
86  PRINT "UU=";UU;" NUM=";CS%(UU)
87 I = CS%(UU)
88 YX =  VAL (DIL1$(I)):C(UU) = YX: PRINT "C=";C(UU)
90 X =  VAL (P4$(I))
95  IF IL = 2 THEN X =  VAL (A4$(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(D + 2) = T(D + 2) + Y ^ 2
145  NEXT UU
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)
```

```
215 R(J,I) = R(K,I)
220 R(K,I) = S
225  NEXT I
230 Z = 1 / R(J,J)
235  FOR I = 1 TO D + 2
240 R(J,I) = Z * R(J,I)
245  NEXT I
250  FOR K = 1 TO D + 1
255  IF K = J THEN 280
260 Z =  - R(K,J)
265  FOR I = 1 TO D + 2
270 R(K,I) = R(K,I) + Z * R(J,I)
275  NEXT I
280  NEXT K
285  NEXT J
290  PRINT
295  PRINT "    CONSTANT=";
300 P0 = R(1,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:XX = 0:SUM = 0.0:K = 0:J = 0
335  FOR I = 1 TO Q2
338  IF IL = 1 AND P4$(I) = "0*" GOTO 380
340  IF IL = 2 AND A4$(I) = "0*" GOTO 380
345 RC(I) =  VAL (P4$(I))
350  IF IL = 2 THEN RC(I) =  VAL (A4$(I)): PRINT "RC=";RC(I)
355 NCNC(I) = RC(I) / (P0 + P1 * RC(I) + P2 * (RC(I) ^ 2))
356  FOR JK = 1 TO CTR
357 KK = CS%(JK)
358  IF NMB1$(I) = NMB1$(KK) GOTO 360
359  GOTO 367
360 CRFT(I) = NCNC(I) / C(KK): PRINT "CRFT=";CRFT(I):DX(I) = CRFT(I): GOSUB 30
361  IF I ) CS%(CTR) GOTO 367
363 MRSD = MRSD + (SD(IL,I) / RC(I)) ^ 2
364 RMSD = RMSD + ((1 - CRFT(I)) ^ 2)
365  REM   IF SENSITIVITY HAS DROPPED THEN CRFT 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 CRF
)
367  NEXT JK
380  NEXT I
385 MRSD =  SQR (MRSD / CTR): PRINT "MRSD=";MRSD
388 RMSD =  SQR (RMSD / CTR): PRINT "RMSD=";RMSD
390  IF MRSD ( .01 THEN MRSD = .01
392 MRSD = MRSD * 100.0
395 P = 0: REM  RMSD=0?
400  FOR I = 1 TO Q2: REM  THIS LOOP 1ST SENSIT. RATIO FOR ALL STDS W/R/T CONCEN RETURNED FROM CALIB FOR 1ST GROUP OF STDS
405  IF IL = 1 AND P4$(I) = "0*" GOTO 460
410  IF IL = 2 AND A4$(I) = "0*" GOTO 460
450  IF SD(IL,I) ( MRSD THEN SD(IL,I) = MRSD
455 SCER(I) =  SQR (((SD(IL,I) ^ 2) / (P0 + P1 * RC(I) + P2 * RC(I) ^ 2)) + ((RMSD * NCNC(I)) ^ 2))
457  PRINT "SCER=";SCER(I)
460  NEXT I
465 KM = 1
470  FOR I = 2 TO J: REM  THIS LOOP TO GET AVERAGES FOR BLOCKS OF STDS SURROUNDING A GROUP OF SAMPLES
475  IF KM = 1 AND LBL1$(1) (  ) "STD" THEN NNCRFT(KM) = NRFT(1):KM = KM + 1
480 NNCRFT(KM) = (NRFT(I - 1) + NRFT(I)) / 2.0: PRINT "NNCRFT(";I - 1;")=";NNCRFT(I - 1)
485  REM  NNCRFT IS THE AVERAGE OF NCRFTS SURROUNDING A BLOCK OF DATA
490 KM = KM + 1
```

```
495  NEXT I
500  IF LBL1$(Q2) (  ) "STD" THEN NNCRFT(KM) = NRFT(J)
505 J = 0
510  IF LBL1$(I) (  ) "STD" THEN J = 1
515  FOR I = 1 TO Q2: REM   THIS LOOP DETERMINES IF SAMPLE IS A STD OFR NOT -IF IT IS A REGULAR SAMPLE THEN THE PROPER VALUE OF J IS ASSIGNED, VALUE GOES TO A SUB AND A NEW NCNC IS ASSIGNED BY DIVIDING BY THE PROPER NNCRFT
520  IF I = Q2 GOTO 535
522  IF IL = 1 AND P4$(I) = "0*" GOTO 540
525  IF IL = 2 AND A4$(I) = "0*" GOTO 540
530  IF LBL1$(I) = "STD" AND LBL$(I + 1) (  ) "STD" THEN J = J + 1
535  IF LBL1$(I) (  ) "STD" THEN NCNC(I) = ((NCNC(I) / NNCRFT(J)) *  VAL (DIL1$(I))):DX(I) = NCNC(I) * AJW1(I): PRINT "NCNC=";NCNC(I)
540  NEXT I
550 J = 1
552  PRINT "HIT ANY KEY TO CONTINUE BEFORE STORAGE": INPUT Y$
553  PRINT D$;"MON,C,I,O"
554  PRINT D$;"UNLOCK";Z9$
555  PRINT D$;"OPEN";Z9$;",L350"
560  FOR I = 1 TO Q1
565  PRINT D$;"WRITE";Z9$;",R";I;",B";L2%(IL): PRINT NCNC(I)
570  PRINT D$;"WRITE";Z9$;",R";I;",B";L0%(IL): PRINT  LEFT$ ( STR$ (SD(IL,I)),4)
572  SPEED= 255
575  PRINT D$;"WRITE";Z9$;",R";I;",B";L4%(IL): PRINT SCER(I)
580  PRINT D$;"WRITE";Z9$;",R";I;",B";L6%(IL): PRINT DX(I)
585  NEXT I
590  PRINT D$;"WRITE";Z9$;",R0,B";L8%(IL): PRINT P0: PRINT P1: PRINT P2
592 MK% = L8%(IL) + 40: PRINT D$;"WRITE";Z9$;",R0,B";MK%: PRINT RMSD:MK% = MK% + 16: PRINT D$;"WRITE";Z9$;",R0,B";MK%: PRINT CTR
593 MK% = L9%(IL)
594  FOR II = 1 TO CTR
595  PRINT D$;"WRITE";Z9$;",R0,B";MK%: PRINT CS%(II)
597 MK% = MK% + 4: NEXT II
598  PRINT D$;"WRITE";Z9$;",R0,B18": PRINT "1"
600  PRINT D$;"CLOSE";Z9$
602  PRINT D$;"LOCK";Z9$
610  PR# 0
620  GOTO 700
650  FOR IL = 1 TO 2
652  PRINT D$;"MON,C,I,O"
653  SPEED= 50
655  PRINT D$;"UNLOCK";Z9$;",D";R2%
660  PRINT D$;"OPEN";Z9$;",L350"
662  PRINT D$;"READ";Z9$;",R0,B18": INPUT RS$: IF RS$ = "1" GOTO 665
663  PRINT D$;"CLOSE";Z9$: PRINT "REGRESSION NOT PREVIOUSLY DONE": FOR NB = 1 TO 1000: NEXT NB: GOTO 2660
665  PRINT D$;"READ";Z9$;",R0,B";L8%(IL)
670  INPUT P0: INPUT P1: INPUT P2
675  PRINT D$;"CLOSE";Z9$
680  PRINT D$;"LOCK";Z9$
700  POKE  - 16304,0: POKE  - 16297,0: POKE  - 16299,0: POKE  - 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 279,137: HPLOT 279,137 TO 279,0: HPLOT 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,I
872  IF R = 2 THEN  GOTO 920
880  IF I ( 10 THEN  GOTO 920
888  DRAW 15 AT 6,I
896  IF P ) 26 THEN P = 17
904  DRAW P AT 11,I
```

```
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 I,Y: GOTO 1064
976  IF R = 2 THEN  GOTO 1064
984  ROT= 0
992  IF K ) 26 THEN  GOTO 1016
1000  DRAW K AT I,150
1008  GOTO 1056
1016  DRAW 18 AT I,150
1024  IF K = 27 THEN  DRAW 17 AT I + 5,150
1032  IF K = 28 THEN  DRAW 18 AT I + 5,150
1040  IF K = 29 THEN  DRAW 19 AT I + 5,150
1048  ROT= 16
1056 K = K + 1
1064  NEXT I
1072  NEXT R
1080 X = 0
1088  ROT= 0
1096 A$ = "A"
1104 B$ = "CONC"
1112  FOR I = 1 TO  LEN (A$)
1120  DRAW ( ASC ( MID$ (A$,I,1)) - 31) AT X,70
1128 X = X + 7
1136  NEXT I
1144 X = 133
1152  FOR I = 1 TO  LEN (B$)
1160  DRAW ( ASC ( MID$ (B$,I,1)) - 31) AT X,159
1168 X = X + 7
1176  NEXT I
1255  SCALE= 1:X2 = 150
1257  IF IL = 2 GOTO 1265
1260 V = .200:U = 258.9 / (700.0 / (P0 + P1 * 700.0 + P2 * (700.0 ^ 2)))
1261 CH$ =  STR$ ((350.0 / (P0 + P1 * 350.0 + P2 * (350.0 ^ 2)))):CH$ =  LEFT$ (CH$,5)
1263 CF$ =  STR$ ((700.0 / (P0 + P1 * 700.0 + P2 * (700.0 ^ 2)))):CF$ =  LEFT$ (CF$,5)
1264 IV = 650:IW = 10: GOTO 1275
1265 V = .002456:U = 258.9 / (57000 / (P0 + P1 * 57000 + P2 * (57000 ^ 2)))
1268 CH$ =  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$,5)
1273 IV = 53000:IW = 815
1275  FOR I = 1 TO IV STEP IW
1280  HPLOT  INT ((I / (P0 + P1 * I + P2 * (I ^ 2))) * U) + 20, INT (136 - I * V)
1285  NEXT I
1290  FOR I = 1 TO  LEN (Z9$)
1295  DRAW ( ASC ( MID$ (Z9$,I,1)) - 31) AT X2,10
1300 X2 = X2 + 7
1305  NEXT I
1310 X2 = 130
1315  FOR I = 1 TO  LEN (CH$)
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
```

```
1355  NEXT I
1360 PO$ =  STR$ (PO):P1$ =  STR$ (P1):P2$ =  STR$ (P2):XE = 10
1365  FOR I = 1 TO  LEN ( STR$ (PO))
1370  DRAW ( ASC ( MID$ (PO$,I,1)) - 31) AT XE,165
1385 XE = XE + 6
1390  NEXT I
1392 XE = 10
1395  FOR I = 1 TO  LEN ( STR$ (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$,I,1)) - 31) AT XE,185
1430 XE = XE + 6
1435  NEXT I
1490  FOR PX = 1 TO 5000: NEXT PX
1500  TEXT : HOME
1505 A = 1:B = 0:C = 0:D = 1
1510  HTAB 1: VTAB 22: PRINT "(1)-PRINT CURRENT PLOT"
1520  HTAB 1: VTAB 23: PRINT "(2) CHG PRINT FORMAT/VIEW INSTRUCTIONS"
1530  HTAB 1: VTAB 24: PRINT "(3) CONTINUE WITH ROUTINE"
1550  VTAB 24: HTAB 1: INPUT BJ%
1560  IF BJ% ( 1 OR BJ% ) 3 GOTO 1500
1570  IF BJ% = 3 GOTO 2580
1580  IF BJ% = 1 GOTO 1910
1600  HOME
1610  HTAB 1: VTAB 1: PRINT "TO PRINT A HIRES SCREEN YOU MUST USE THE 'USR' FUNCTION"
1620  HTAB 1: VTAB 3: PRINT "'PRINT USR(ABCD)' MUST BE ENTERED WHERE A,B,C,D SUBFUNCTIONS ARE DESCRIBED BELOW"
1630  HTAB 1: VTAB 5: PRINT "A-HIRES PAGE (0=PAGE 1;1=PAGE 2)"
1640  HTAB 1: VTAB 6: PRINT "B=SIZE (0=SMALL;1=LARGE)"
1650  HTAB 1: VTAB 7: PRINT "C=PICTURE TYPE (0=REG.;1=INV.)"
1660  HTAB 1: VTAB 8: PRINT "D=PRINTER SLOT (1 TO 7)"
1670  HTAB 1: VTAB 9: PRINT "TYPING 'PRINT USR(1011)' MEANS DUMPING"
1680  HTAB 1: VTAB 10: PRINT "PAGE 1 OF GRAPHICS WITH A SMALL INVERSE"
1690  HTAB 1: VTAB 11: PRINT "PICTURE TO A PRINTER LOCATED IN SLOT 1"
1700  PRINT "CURRENT PARAMETERS ARE USR(";A;B;C;"1)"
1710  HTAB 1: VTAB 14: PRINT "HIT (CR) TO ACCEPT CURRENT PARAMETERS OR ENTER VALUE FOR A"
1720  INPUT "";AG$
1730  IF AG$ = "" GOTO 1910
1731 A =  VAL (AG$)
1732  IF A ( 0 OR A ) 1 GOTO 1710
1735  IF A (  ) 1 THEN  HTAB 1: VTAB 14: PRINT "PICTURE ON PAGE 2 OF GRAPHICS-DO YOU WISH TO CONTINUE ": INPUT UY$: 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  POKE 10,76: POKE 11,00: POKE 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 (0101)
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 (1011)
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  POKE 10,76: POKE 11,00: POKE 12,96: PRINT  USR (1001)
2580  FOR I = 1 TO 13
2590 A(I) = 0.0: NEXT I
```

```
2600  FOR I = 1 TO 7
2610  FOR J = 1 TO 8
2620 R(I,J) = 0.0:T(J) = 0.0
2630  NEXT J
2640  NEXT I
2650 J = 0:K = 0:SUM = 0.0:CTR = 0:S = 0.0:KK = 0:MRSD = 0.0:RMSD = 0.0:KM = 0:MK% = 0:XX = 0:X2 = 0:XE = 0
2652  IF QA% (  ) 4 GOTO 2660
2654  NEXT IL
2660  TEXT : RETURN
2670  RETURN
2680  PRINT "ENTER DISK WITH SHAPE TABLE/EPSON.HIRES.OBJ IN DRIVE 1 AND HIT ANY KEY AND (RTN) TO CONTINUE"
2690  INPUT YY$
2700  REM RINT D$;"BLOAD PIC22,A16384";",D1"
2710  PRINT D$;"BLOAD FFFF,A36847";",D1": POKE 233, INT (36847 / 256): POKE 232,((36847 / 256) -  INT (36847 / 256)) * 256: HIMEM: 36846
2720  REM OKE 10,76: POKE 11,00: POKE 12,96:
2730  PRINT D$;"BLOAD EPSON.HIRES.OBJ,A$6000": LOMEM: 25400: REM  LOADED AT 24576 FOR LENGTH OF APP. 3 SECTORS
2740  CLEAR : HOME : HTAB 1: VTAB 2: PRINT "MENU OPTIONS"
2750  HTAB 1: VTAB 3: PRINT "(1) HT/AREA CALIBRATION & REGRESSION"
2760  HTAB 1: VTAB 4: PRINT "(2) HT CALIBRATION & REGRESSION"
2770  HTAB 1: VTAB 5: PRINT "(3) AREA CALIBRATION & REGRESSION"
2780  HTAB 1: VTAB 6: PRINT "(4) CALIBRATION PLOT/HARDCOPY"
2790  HTAB 1: VTAB 7: PRINT "(5) QUIT"
2800  INPUT QA%
2810  IF QA% ( 1 OR QA% ) 5 THEN  GOTO 2740
2820  IF QA% = 5 GOTO 3225
2830  PRINT "CATALOG TO LOCATE FILENAME NEEDED?": INPUT Y$
2840  IF  LEFT$ (Y$,1) = "Y" THEN  PRINT "DRIVE# ?": INPUT R2%: IF R2% ( 1 OR R2% ) 2 THEN  GOTO 2830
2850 D$ =  CHR$ (4)
2860  IF  LEFT$ (Y$,1) = "N" GOTO 2880
2870  PRINT D$;"CATALOG,D";R2%
2880  PRINT "ENTER NAME OF FILE AND DRIVE # (FILENAME  MUST BE RAW DATA FILENAME APPENDED WITH A 'C' FOR THIS CALCULATED DATA FILE)": INPUT Z9$,R2%
2890  IF R2% ( 1 OR R2% ) 2 GOTO 2830
2900  IF  ASC ( LEFT$ (Z9$,1)) ( 65 OR  ASC ( LEFT$ (Z9$,1)) ) 90 GOTO 2830
2910  IF  RIGHT$ (Z9$,1) (  ) "C" GOTO 2830
2920  PRINT D$;"UNLOCK";Z9$
2930  PRINT D$;"OPEN";Z9$;",L350,D";R2%
2940  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE";Z9$: PRINT "THIS FILE NAME HAS NO LABEL/DATA RECORDS": GOTO 25
2950  PRINT D$;"READ";Z9$;",R0,B0": INPUT Q1: PRINT D$;"READ";Z9$;",R0,B4": INPUT Q2: PRINT D$;"READ";Z9$;",R0,B8": INPUT G
2960  IF Q2 ( 1 THEN  PRINT D$;"CLOSE";Z9$: PRINT "THIS FILE HAS NO DATA RECORDS YET": GOTO 25
2970  IF Q1 ( 1 THEN  PRINT D$;"CLOSE";Z9$: PRINT "NOT ENOUGH LABELS IN RECORD TO CONTINUE WITH ROUTINE": GOTO 25
2980  IF Q1 (  ) Q2 THEN  PRINT D$;"CLOSE";Z9$: PRINT "# DATA RECORDS NOT = # OF LABELS IN FILE": GOTO 25
2990  REM F ( PEEK (106) * 256 +  PEEK (105)) = 16390 THEN  PRINT D$;"CLOSE";Z9$:LM = 16390: GOTO 2210: REM   LOMEM AT 16390 IF CHAIN HAS BEEN USED FROM EARLIER SUB
3000  DIM LBL1$(Q1),NMB1$(Q1),DIL1$(Q1),A4$(Q1),AJW1(Q1),AEA$(Q1,9),PMAX$(Q1,9),SD(2,Q1),P4$(Q1),S1D(Q1),S2D(Q1),REP1$(Q1),Y1Y%(Q1),RE1%(Q1)
3010  FOR II = 1 TO Q1
3020  PRINT D$;"READ";Z9$;",R";II;",B2"
3030  INPUT NMB1$(II): INPUT LBL1$(II)
3040  INPUT DIL1$(II): INPUT REP1$(II)
3050  PRINT D$;"READ";Z9$;",R";II;",B52": INPUT AJW1(II)
3060  PRINT D$;"READ";Z9$;",R";II;",B77": INPUT RE1%(II)
3070  PRINT D$;"READ";Z9$;",R";II;",B80": INPUT P4$(II)
3080  PRINT D$;"READ";Z9$;",R";II;",B88"
3090  FOR IK = 1 TO RE1%(II)
3100  INPUT PMAX$(II,IK): NEXT IK
3110  PRINT D$;"READ";Z9$;",R";II;",B140": INPUT SD(1,II)
3120  PRINT D$;"READ";Z9$;",R";II;",B177": INPUT Y1Y%(II): PRINT D$;"READ";Z9$;",R";II;",B180": INPUT A4$(II)
3130  PRINT D$;"READ";Z9$;",R";II;",B190"
3140  FOR IK = 1 TO Y1Y%(II)
3150  INPUT AEA$(II,IK): NEXT IK
3160  PRINT D$;"READ";Z9$;",R";II;",B254": INPUT SD(2,II)
3170  NEXT II: PRINT D$;"CLOSE";Z9$: PRINT D$;"LOCK";Z9$
```

```
3180  DIM NCNC(Q2),C(30),CRFT(30),NRFT(15),NNCRFT(15),A(13),R(7,8),T(8),RC(Q1),SCER(Q1),DX(Q1)
3190 LO%(1) = 140:LO%(2) = 254:L2%(1) = 145:L2%(2) = 260:L4%(1) = 276:L4%(2) = 292:L6%(1) = 308:L6%(2) = 324:L8%(1) = 20:L8%(2) = 200:L9%(1) = 102:L9%(2) = 280
3200  IF QA% = 4 THEN  GOSUB 650
3210  IF QA% = 1 OR QA% = 2 OR QA% = 3 THEN  GOSUB 65
3220  GOTO 2740
3225 D$ =  CHR$ (4)
3230  REM PRINTD$;"CLOSE";Z9$
3235  REM PRINTD$;"LOCK";Z9$
3240  END
```

Report Program

```
1  TEXT :D$ =  CHR$ (4): GOTO 3820
200  REM
210  FOR IB = 1 TO 6
211  FOR IU = 1 TO ANX
213  IF IB = (ISIDE%(IU) + 1) THEN  PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)": INPUT TE$
215  NEXT IU
217  PRINT D$;"OPEN";Z9$;",L";RI
220  PRINT D$;"WRITE";Z9$;",R";IB;",B";1654
230  PRINT "0"
240  PRINT D$;"CLOSE";Z9$
300  NEXT IB
500  RETURN
720  PRINT D$;"OPEN";Z9$;",L350";",D";R2%
725  IF  RIGHT$ (Z9$,1) (  ) "C" THEN  PRINT D$;"CLOSE";Z9$: PRINT "INCORRECT NAME FORMAT FOR READING CALCULATED DATA FILE": GOTO 3000
730  IF  PEEK ( - 18962) ( 2 THEN  PRINT D$;"CLOSE";Z9$: PRINT "FILE HAS NO INFORMATION": GOTO 3000
740  PRINT D$;"READ";Z9$;",R0,B100": INPUT FLAG$
750  IF FLAG$ = "*" THEN  PRINT D$;"CLOSE";Z9$: PRINT "THIS IS RAW DATA FILE - ENTER CORRECT NAME ": GOTO 3000
760  PRINT D$;"READ";Z9$;",R0,B0": INPUT Q1: PRINT D$;"READ";Z9$;",R0,B4": INPUT Q2: PRINT D$;"READ";Z9$;",R0,B8": INPUT G: PRINT D$;"READ";Z9$;",R0,B15": INPUT AJW$: PRINT D$;"READ";Z9$;",R0,B18": INPUT RS$: PRINT D$;"CLOSE";Z9$
770  IF Q2 = 0 THEN  PRINT "NOT ENOUGH DATA OR LABELS ON DISC TO CONTINUE WITH PRINTOUT": GOTO 3000
771  IF Q1 = 0 AND Q8% = 5 THEN  PRINT "NOT ENOUGH DATA OR LABELS ON DISC TO CONTINUE WITH PRINTOUT": GOTO 3000
775  IF Q1 = 0 AND Q8% = 4 THEN  PRINT "NOT ENOUGH DATA OR LABELS ON DISC TO CONTINUE WITH PRINTOUT": GOTO 3000
778  IF Q8% = 5 AND RS$ (  ) "1" THEN  GOTO 3000
800  PRINT D$;"UNLOCK";Z9$
810  DIM SS%(6),S%(6),RE1%(6),PMAX$(6,9),AEA$(6,9),A4$(6),LBL1$(6),NMB1$(6),REP1$(6),DIL1$(6),AJW1(6),S2D(6),S1D(6),Y1Y%(6),P4$(6),SH%(6),SCER(6),NCNC(6),DX(6),D2X(6),N2CNC(6),C2SER(6)
830  PRINT D$;"OPEN";Z9$;",L350,D";R2%
831  IF Q8% (  ) 5 GOTO 848
832  PRINT D$;"READ";Z9$;",R0,B20": INPUT P0: INPUT P1: INPUT P2
833  PRINT D$;"READ";Z9$;",R0,B200": INPUT P3: INPUT P4: INPUT P5
834  PRINT D$;"READ";Z9$;",R0,B60": INPUT T0: PRINT D$;"READ";Z9$;",R0,B240": INPUT T3
836  PRINT D$;"READ";Z9$;",R0,B76": INPUT U0
837  PRINT D$;"READ";Z9$;",R0,B256": INPUT U3:MK% = 102
838  FOR IY = 1 TO U0
839  PRINT D$;"READ";Z9$;",R0,B";MK%
840  INPUT F0(IY):MK% = MK% + 4
841  NEXT IY:MK% = 280
842  FOR IY = 1 TO U3
843  PRINT D$;"READ";Z9$;",R0,B";MK%
844  INPUT F3(IY):MK% = MK% + 4
845  NEXT IY
848  FOR N = 1 TO Q2
849  IF Q8% (  ) 4 AND Q8% (  ) 5 THEN  GOTO 870
850  PRINT D$;"READ";Z9$;",R";N;",B2"
860  INPUT NMB1$(N): INPUT LBL1$(N): INPUT DIL1$(N): INPUT REP1$(N)
870  PRINT D$;"READ";Z9$;",R";N;",B52"
880  INPUT AJW1(N)
890  PRINT D$;"READ";Z9$;",R";N;",B77"
900  INPUT RE1%(N)
910  PRINT D$;"READ";Z9$;",R";N;",B80": INPUT P4$(N)
920  PRINT D$;"READ";Z9$;",R";N;",B88"
930  FOR IK = 1 TO RE1%(N)
940  INPUT PMAX$(N,IK)
950  NEXT IK
960  PRINT D$;"READ";Z9$;",R";N;",B140": INPUT S1D(N)
965  IF Q8% (  ) 5 GOTO 970
967  PRINT D$;"READ";Z9$;",R";N;",B145": INPUT NCNC(N): PRINT D$;"READ";Z9$;",R";N;",B276": INPUT SCER(N): PRINT D$;"READ";Z9$;",R";N;",B308": INPUT DX(N)
968  PRINT D$;"READ";Z9$;",R";N;",B260": INPUT N2CNC(N): PRINT D$;"READ";Z9$;",R";N;",B292": INPUT C2SER(N): PRINT D$;"READ";Z9$;",R";N;",B324": INPUT D2X(N)
970  PRINT D$;"READ";Z9$;",R";N;",B177": INPUT Y1Y%(N)
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980  PRINT D$;"READ";Z9$;",R";N;",B180": INPUT A4$(N)
990  PRINT D$;"READ";Z9$;",R";N;",B190"
1010  FOR IK = 1 TO Y1Y%(N)
1020  INPUT AEA$(N,IK)
1030  NEXT IK
1040  PRINT D$;"READ";Z9$;",R";N;",B254": INPUT S2D(N)
1050  NEXT N
1051  PRINT D$;"CLOSE";Z9$
1055  POKE 33,33
1060  PR# 1
1062  PRINT  CHR$ (15)
1065  PRINT  CHR$ (27)"D" CHR$ (1) CHR$ (11) CHR$ (21) CHR$ (36) CHR$ (46) CHR$ (56) CHR$ (68) CHR$ (86) CHR$ (101)
1067 H$ =  CHR$ (9): PRINT Z9$: PRINT ZZ$: PRINT Z%: PRINT "  "
1068  PRINT H$;"SAMPLE";H$;"LABEL";H$;"DILUTION";H$;"REP.";H$;"ADJ.";H$;"AVG.HT";H$;"REL";H$;"AVG.AREA";H$;"REL"
1074  PRINT H$;"NUM.";H$;H$;"FTR.";H$;"NO.";H$;"S.WT";H$;H$;"S.D. HT";H$;H$;"S.D. AREA"
1075  IF Q8% (  ) 5 GOTO 1078
1076  PRINT H$;H$;H$;H$;H$;H$;H$;"(CONCENTRATION)";H$;H$;"(CONCENTRATION)": PRINT H$;H$;H$;H$;H$;H$;H$;"(SOLN CONC ERR)";H$;H$;"(SOLN CONC ERR)": PRINT H$;H$;H$;H$;H$;H$;H$;"(CORRECTION FTR)";H$;H$;"(CORRECTION FTR)"
1078  PRINT "   ": PRINT "    "
1080  FOR N = 1 TO Q2
1081  PRINT "  ": PRINT "  "
1082  IF Q8% (  ) 4 GOTO 1084
1083  PRINT H$;NMB1$(N);H$;LBL1$(N);H$;DIL1$(N);H$;REP1$(N);H$;AJW1(N);H$;P4$(N);H$;S1D(N);H$;A4$(N);H$;S2D(N): GOTO 1088
1084  IF Q8% (  ) 5 GOTO 1087
1085  PRINT H$;NMB1$(N);H$;LBL1$(N);H$;DIL1$(N);H$;REP1$(N);H$;AJW1(N);H$;P4$(N);H$;S1D(N);H$;A4$(N);H$;S2D(N): PRINT "  "
1086  PRINT H$;H$;H$;H$;H$;H$;H$;"(";NCNC(N);")";H$;H$;"(";N2CNC(N);")": PRINT H$;H$;H$;H$;H$;H$;H$;"(";SCER(N);")";H$;H$;"(";C2SER(N);")": PRINT H$;H$;H$;H$;H$;H$;H$;"(";DX(N);")";H$;H$;"(";D2X(N);")": GOTO 1088
1087  PRINT H$;H$;H$;H$;H$;AJW1(N);H$;P4$(N);H$;S1D(N);H$;A4$(N);H$;S2D(N)
1088  PRINT "  "
1090  FOR IIK = 1 TO 10
1091  IF RE1%(N) ( IIK GOTO 1097
1092  PRINT H$;H$;H$;H$;H$;H$;PMAX$(N,IIK);H$;
1094  IF Y1Y%(N) ( IIK THEN  PRINT H$;H$: GOTO 1099
1095  PRINT H$;AEA$(N,IIK);H$: GOTO 1099
1097  IF Y1Y%(N) ( IIK GOTO 1099
1098  PRINT H$;H$;H$;H$;H$;H$;H$;H$;AEA$(N,IIK);H$
1099  NEXT IIK
2000  NEXT N
2010  IF Q8% (  ) 5 GOTO 2100
2020  PRINT "  "
2030  PRINT "REGRESSION PARAMETERS - HT.: ";P0;" , ";P1;" , ";P2
2040  PRINT "# OF STANDARDS REGRESSION BASED ON: ";U0
2050  PRINT "RECORD NUMBERS OF STANDARDS THAT REGRESSION BASED ON:"
2052  FOR IY = 1 TO U0
2054  PRINT F0(IY)
2056  NEXT IY
2058  PRINT "RMSD OF STANDARDS: ";T0
2060  PRINT "  ": PRINT "REGRESSION PARAMETERS - AREA: ";P3;" , ";P4;" , ";P5
2065  PRINT "# OF STANDARDS REGRESSION BASED ON: ";U3
2070  PRINT "RECORD NUMBERS OF STANDARDS THAT REGRESSION BASED ON:"
2075  FOR IY = 1 TO U3
2080  PRINT F3(IY)
2085  NEXT IY
2090  PRINT "RMSD OF STANDARDS: ";T3
2100  PR# 0
2110  RETURN
2150  IF  RIGHT$ (Z9$,1) = "C" THEN  PRINT "WRONG NAME FORMAT": GOTO 3000
2160  REM  IFPEEK ( - 18962) ( 2 THEN  PRINT "THIS FILE HAS NO RAW DATA": GOTO 3000
2200  PRINT D$;"OPEN";Z9$;",L350";",D";R2%
2210  PRINT D$;"READ";Z9$;",R0,B100": INPUT FLAG$
2211  IF FLAG$ (  ) "*" THEN  PRINT D$;"CLOSE";Z9$: PRINT "THIS IS NOT RAW DATA FILE": GOTO 3000
2214  PRINT D$;"READ";Z9$;",R0,B0": INPUT G: INPUT SY$: INPUT N: INPUT RI: INPUT RP: PRINT D$;"CLOSE";Z9$
```

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2216  DIM ACCRT%(N),PMAX%(6),RE1%(6),Y1Y%(6),LOC(6),P(6),IREC%(6)
2218  PRINT "HOW MANY SIDES OF DISK ARE USED FOR DATA?": INPUT AN%
2219  IF AN% < 1 OR AN% > 6 GOTO 2218
2220  FOR IU = 1 TO AN%
2221  PRINT "ENTER LAST TRANSIENT # ON SIDE";IU
2222  INPUT ISIDE%(IU): IF ISIDE%(IU) < 1 OR ISIDE%(IU) > 6 THEN  GOTO 2221
2223  NEXT IU: IF Q8% = 2 THEN  GOTO 2225
2224  GOSUB 200: GOTO 3000
2225  PRINT "DO YOU WISH TO GET A REPORT OF THESE VALUES?": INPUT YYR$
2226  IF  RIGHT$ (YYR$,1) < > "Y" THEN  GOTO 2600
2227  PRINT "HOW MANY RECORDS NEED TO BE RECALLED?": INPUT NUM%
2228  IF NUM% < 0 OR NUM% > 6 THEN  GOTO 2227
2229  FOR IIK = 1 TO NUM%
2231  PRINT "RECORD #";IIK: INPUT IREC%(IIK)
2233  IF IREC%(IIK) < 1 OR IREC%(IIK) > 6 THEN  GOTO 2231
2235  NEXT IIK
2236  FOR KIK = 1 TO 6
2237  PRINT D$;"MON,C,I,O"
2239  FOR IU = 1 TO AN%
2240  IF KIK = (ISIDE%(IU) + 1) THEN  PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)": INPUT TT$: GOTO 2244
2242  NEXT IU
2244  FOR IIK = 1 TO NUM%
2245  IF KIK < > IREC%(IIK) THEN  GOTO 2256
2248  PRINT D$;"OPEN";Z9$;",L";RI
2250  PRINT D$;"READ";Z9$;",R";IREC%(IIK);",B1": INPUT P(IREC%(IIK)): INPUT PMAX%(IREC%(IIK)): INPUT LOC(IREC%(IIK))
2255  PRINT D$;"CLOSE";Z9$
2256  NEXT IIK
2260  NEXT KIK
2500  REM
2550  POKE 33,33: PR# 1: PRINT  CHR$ (15)
2555  PRINT  TAB( 2);"TRAY ID"; TAB( 20);"PEAK MAX."; TAB( 35);"PEAK LOCATION"
2560  FOR IIK = 1 TO NUM%
2570  PRINT  TAB( 2);P(IREC%(IIK)); TAB( 20);PMAX%(IREC%(IIK)); TAB( 35);LOC(IREC%(IIK))
2580  NEXT IIK
2590  PR# 0
2600  PRINT "WOULD YOU LIKE TO OVERWRITE ANY OF THE VALUES?": INPUT RT$
2603  IF  RIGHT$ (RT$,1) < > "Y" THEN  GOTO 3000
2605  PRINT "ENTER TYPE OF CHANGE DESIRED"
2606  PRINT "(1) TRAY POSITION"
2607  PRINT "(2) DISCLUDE RECORD"
2608  PRINT "(3) BOTH": INPUT RT%
2610  IF RT% < 1 OR RT% > 3 THEN  GOTO 2605
2614  FOR IC = 1 TO 2
2615  IF RT% = 1 AND IC = 2 GOTO 2763
2616  IF RT% = 2 AND IC = 1 GOTO 2763
2620  PRINT "ENTER # OF RECORDS YOU WOULD LIKE TO OVERWRITE FOR OPTION";IC: INPUT KNUM%
2630  IF KNUM% < 1 OR KNUM% > 6 THEN  GOTO 2620
2640  FOR IJ = 1 TO KNUM%
2650  PRINT "ENTER RECORD #";IJ: INPUT IREC%(IJ)
2660  IF IREC%(IJ) < 1 OR IREC%(IJ) > 6 THEN  GOTO 2650
2662  IF IC = 1 THEN  PRINT "ENTER NEW VALUE FOR TRAY POSITION": INPUT P(IREC%(IJ))
2670  NEXT IJ
2680  FOR KI = 1 TO 6
2710  FOR II = 1 TO AN%
2720  IF KI = (ISIDE%(II) + 1) THEN  PRINT "TURN OVER DISK AND HIT ANY KEY AND (RTN)": INPUT YT$: GOTO 2740
2730  NEXT II
2740  FOR IJ = 1 TO KNUM%
2741  IF KI < > IREC%(IJ) GOTO 2760
2743  PRINT D$;"OPEN";Z9$;",L";RI
2745  IF IC = 2 THEN  PRINT D$;"WRITE";Z9$;",R";IREC%(IJ);",B1654": PRINT "*"
```

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2748  IF IC = 1 THEN  PRINT D$;"READ";Z9$;",R";IREC%(IJ);",B1": INPUT PX%: INPUT PMAX%(IREC%(IJ)): INPUT LOC(IREC%(IJ))
2750  IF IC = 1 THEN  PRINT D$;"WRITE";Z9$;",R";IREC%(IJ);",B1": PRINT P(IREC%(IJ)): PRINT PMAX%(IREC%(IJ)): PRINT LOC(IREC%(IJ))
2755  PRINT D$;"CLOSE";Z9$
2760  NEXT IJ
2761  NEXT KI
2763  NEXT IC
2765 NUM% = KNUM%
2770  REM GOTO2500
3000  FOR IU = 1 TO 3000: NEXT IU: RETURN
3820  TEXT : HOME : PRINT "MENU OPTIONS": CLEAR :D$ =  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$,1)) = "Y" THEN  PRINT "DRIVE# ?": INPUT R2%: IF R2% = 1 OR R2% = 2 THEN  PRINT D$;"CATALOG,D";R2%
3940  PRINT "ENTER FILENAME AND DRIVE # (SEPARATE RESPONCES 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$,1)) ) 90 GOTO 3940
3965  PRINT "ENTER VARC RUN #": INPUT ZZ$
3970  PRINT "ENTER DISC BACKUP NUMBER": INPUT Z%
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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