Elemental Analysis of Sediment Cores from Mahoning Valley Lakes by

Inductively Coupled Plasma - Atomic Emission Spectroscopy

by

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Dean of Graduate Studies   Date

Abstract

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The Center for Environmental Studies at Youngstown State University has been investigating several of the lakes in the Mahoning Valley. The lakes are being tested to see if there has been any affect to the lakes physiological activities due to the presence of heavy metals. The lakes analyzed in this study were Pine, Evan's, and Girard. One sediment core was taken from each lake and freeze-dried for later analysis.

The samples were digested using the EPA Method 3051 Microwave Assisted Acid Dissolution. The acid used to extract the metal ions was doubly-distilled 6M Nitric acid. The digestion produced a solution which could be analyzed by Inductively-Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). ICP-AES is a technique which utilizes the characteristic wavelength of metals to determine the metal ion content in solutions.

Sixteen heavy metals were determined for each sample. They were Al, Ba, Be, Cd, Ca, Cu, Fe, Pb, Mg, Mn, K, Na, Ti, V, Zn. The instrument used for analysis was an ARL Model 3410 ICP spectrometer. Several other metals were considered for testing but due to the lack of sensitivity in the ICP, the metals were left to be determined in another study by a different method.

Acknowledgments

I wish to thank Dr. Daryl W. Mincey for his encouragement and guidance throughout this project and my graduate program.

I would also like to thank Dr. James H. Mike, and Dr. Tim Wagner, the faculty and staff of the Department of Chemistry, family, and friends for all the help and encouragement during the completion of this work.

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List of Symbols

Symbol	Definition
AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
Attn.	Attenuation
^{o}C	Degree Celsius
cm	Centimeter
EPA	Environmental Protection Agency
g	Gram
ICP	Inductively-Coupled Plasma
Int.	Integration
K	Kelvin
L.Q.D.	Limited Quantitative Detection
mg/L	Milligram per liter
MHz	Megahertz
mL	Milliliter
nm	Nanometer
PAH	Polycyclic Aromatic Hydrocarbon
PMT	Photomultiplier tube
RF	Radio frequency
®	Registered Trademark

Chapter I

Introduction

The analysis of lake sediments for heavy metals can be accomplished by many techniques. Of the available techniques, those used in this study included Microwave Assisted Acid Dissolution and Inductively-Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The task of sample preparation was performed by the relatively new technique of microwave digestion. ICP-AES is a technique that gives high sensitivity and low detection limits for the analysis of heavy metals. The metals of interest were those that are essential or detrimental to the survival of living organisms. They include the following: Aluminum (Al), Barium (Ba), Beryllium (Be), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Potassium (K), Sodium (Na), Titanium (Ti), Vanadium (V), Zinc (Zn).

History of Valley

The extent to which a community uses its resources depends on the needs of the people, the raw materials that are available, and the methods available for the transportation of materials[1]. The Mahoning Valley provided its residents with an enormous amount of raw materials that helped to shape the industry that we know today. The most abundant of these natural resources were iron ore, coal, and limestone, all of which are very valuable to the steel-making industry. The use of blast furnaces to melt

the iron ore became commonplace throughout the valley. In the late 1960's and early 1970's, steel production capacity in the Mahoning River Valley was one of the largest in the world. The great success of the steel mills brought businesses and people to the area. Economic and social growth was increasing at a remarkable rate. The major downside to all this activity was the onset of environmental pollution. The largest contributors to this growing problem were large industrial and municipal waste dischargers. During this time of industrial productivity, the Mahoning River became one of the most polluted rivers in the world. It was polluted mainly with heavy metals and organics. In more recent times, the steel-making industry has curtailed its operation and many of the giant blast furnaces that once covered the horizon have since been shut down. Life, that was for a time non-existent in the Mahoning River is slowly returning and on-going clean-up efforts of these industrial sites gives great promise for the future. These efforts will not only clean up the river, they will also give new life to the lakes throughout the valley.

Heavy Metals

Heavy metals is a term that refers to metals and metalloids that are associated with pollution and toxicity[2]. Heavy metals can be found everywhere in the environment. Most metals occur naturally in the environment, usually in a setting where their presence is necessary to sustain life. Metals such as iron, zinc, copper, and manganese are used as micronutrients for aquatic life but in large amounts can be toxic[3]. Other metals that have a toxic effect in any concentration include mercury, silver, and lead. Although metallic

elements are ubiquitous, over-abundant concentrations of even the most natural of elements can be lethal to living organisms[3]. Sediments take in heavy metals from extraneous sources. The major sources of concern are:

1) Combustion of fossil fuels.

2) Disposal of urban and industrial waste products.

3) Atmospheric pollution from motor vehicles.

4) Agricultural fertilizers and pesticides.

Upon entering a water system, heavy metals can be adsorbed to the surface of the sediment by several mechanisms. These mechanisms can be cation exchange, specific adsorption, organic complexation, and co-precipitation. Regardless of the method of adsorption, the sediment becomes the principle source of transportation for the metal attached to it. In rivers, sediments are continually being carried down-stream by the currents. The effects of heavy metals can be felt far down-stream of the point where they entered the waterway. The Mahoning River system has several lakes built in to it (see figure 1.1). Currents entering a lake are gradually slowed down and the sediments carrying heavy metals settle out.

The Elements

The elements can have a variety of sources. Most of these sources are naturally occuring, although industry has taken advantage of the physical properties exhibited by individual elements. The use of raw materials has lead to an increase in waste products
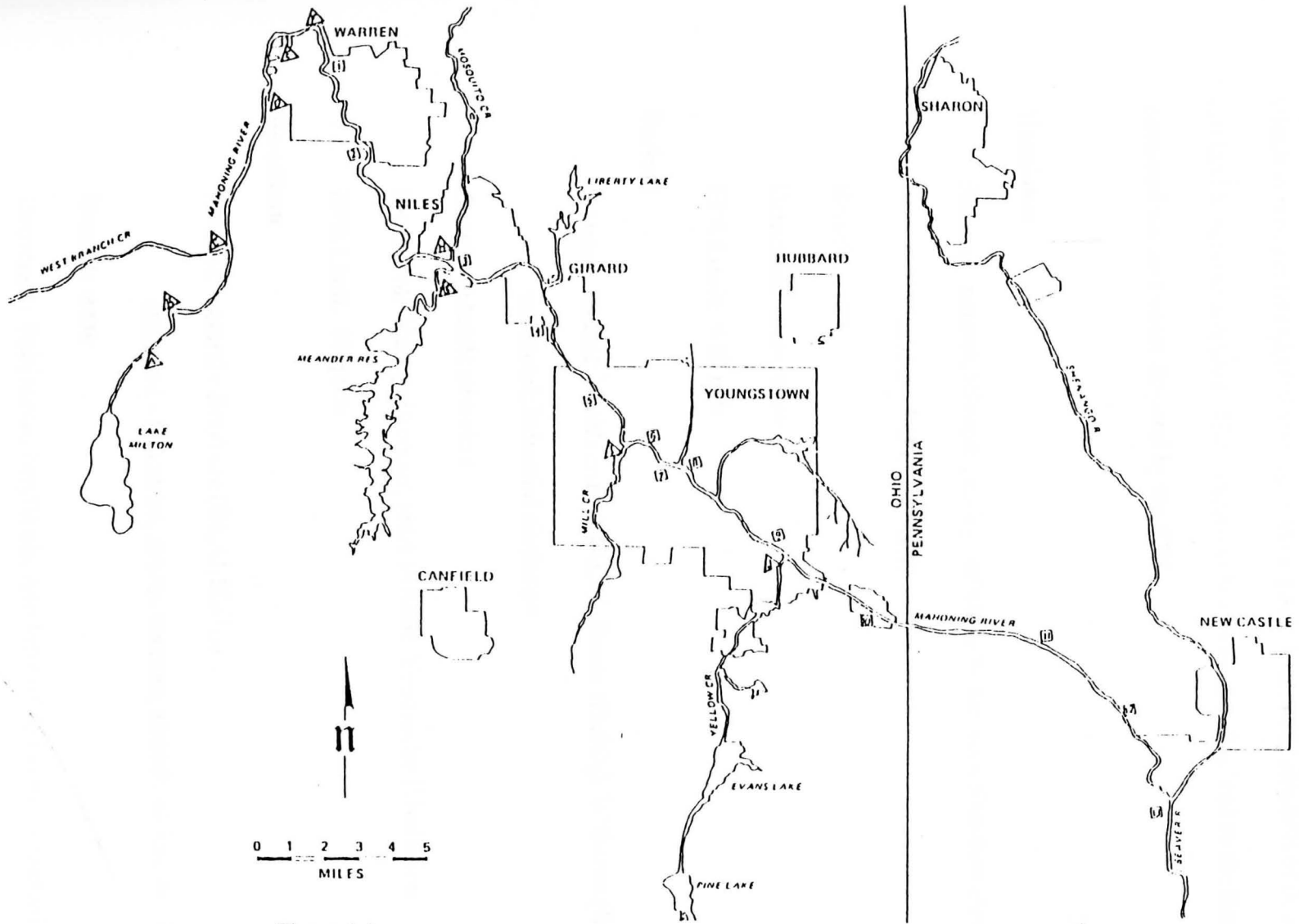
Figure 1.1

Mahoning Valley Watershed

which in turn get transported into the environment. Increasing amounts of heavy metals can lead to serious illnesses. The increase in health hazards has lead to the limitation of elemental use and waste disposal by the EPA.

Aluminum

Sources: natural; Minerals, rocks, and clays (Third most abundant element)

unnatural; Industrial waste

Benefit: none

Detriment: aluminosis

EPA Limit: < 50 ppb

Barium

Sources: nautral; Earth's crust 0.4-0.5%, Barite ($BaSO_4$), Witherite ($BaCO_3$)

unnatural; Industrial discharge

Benefit: Muscle stimulant

Detriment: Very poisionous, toxic to heart, Ventricular Fibrillation

EPA Limit: 100ppm

Beryllium

Sources: natural - Beryl ore ($Be_3Al_2Si_6O_{18}$)

unnatural - Industries, atomic reactors, aircraft, rocket, and missile fuels.

Benefit: none

Detriment: Poisionous, berylliosis, also form of dermatitis, conjunctivitis, acute

pneumontis and chromic pulmonary berylliosis

EPA Limit: 0.01-0.7 ppb

Cadmium

Sources: natural - Very few, soil

unnatural - Zinc & Lead production by-product, Insecticides,

Galvanized or Plastic pipes, Solder, Industrial contamination

Benefit: Antiviral Agent, Antiseborrheic Shampoo

Detriment: High Tumor Incidence, Shortened life span, Hepatic Cirrhosis,

Neurologic Disorders, Kidney Damage, High blood pressure,

Emphysema

EPA Limit: 0.01 ppm

Calcium

Sources: natural - Dolomite Limestone

unnatural - Industrial waste

Benefit: Bone, protects against effect of Cadmium, Heart tone

Detriment: Abnormal Calcification of tissue

EPA Limit: none

Chromium

Sources: natural - Very Few - Chromite ($FeCr_2O_4$)

unnatural - Electroplating, Steel, Pipes

Benefit: Glucose Factor, helps prevent Artery disease, Cataracts

Detriment: Hexavalent Ion may cause cancer

EPA Limit: 0.05 ppm

Copper

    Sources: natural - Very few, Ores Metal

                    unnatural - Plumbing, Industrial waste, Algicide

    Benefit: Proteins, Enzymes

    Detriment: Gastrointestinal Tract Irritation, Mental disorders, Liver damage,

                 Taste

    EPA Limit: 1.0 ppm

Iron

    Sources: natural - Soil, Ancient buried forests & swamps

                    unnatural - Industrial waste, mining

    Benefit: RBC, Most scavenged mineral in the body, prevents Iron-Deficiency-

                 Anemia

    Detriment: Stains, Gastrointestinal Tract Irritation, Hemosiderosis - Iron in

                 tissues

    EPA Limit: 0.3 ppm

Lead

    Sources: natural - Soil, Galena (PbS), Cerussite ($PbCO_3$), Anglesite ($PbSO_4$)

                    unnatural - Industrial wastes, gasoline, piping

    Benefit: none

    Detriment: Lead poisoning - CNS (Hallucinations), Gastrointestinal, Renal,

                 Hematologic

    EPA Limit: 0.05 ppm

Magnesium

Sources: natural - Dolomite Limestone, Brinewells

unnatural - Industrial Waste

Benefit: Assoc. with Enzymes & Muscle (Heart) Tone, Lowers blood pressureof

Hypertensives

Detriment: Respiratory Depression Cardiac Arrest

EPA Limit: none

Manganese

Sources: natural - Soil, with Iron ore deposits, Pyrolusite (MnO_2)

unnatural - Industrial Wastes, Steel & Batteries

Benefit: Involved with enzymes

Detriment: Gastrointestinal Disorders, Parkinson's Like disorders, CNS

difficulties

EPA Limit: 0.05 ppm

Potassium

Sources: natural - Sea water, Soil, Mineral deposits

unnatural - Industrial waste

Benefit: Major cation in cells

Detriment: Myocardial Irritability

EPA Limit: none

Sodium

    Sources: natural - Sea/Fresh water, mineral deposits

                unnatural - Water softeners, Street deicing

    Benefit: Major cation in blood

    Detriment: Hypertension, Edema, Added ground burden

    EPA Limit: none

Titanium

    Sources: natural - Ores, Rutile (TiO_2), Ilmenite ($FeTiO_3$)

                unnatural - Industrial waste

    Benefit: none

    Detriment: pneumatic disorders

    EPA Limit: N/A

Vanadium

    Sources: natural - Mineral deposits, Carnolite

                unnatural - Mining & oil refining by-product

    Benefit: Protects against Atherosclerosis, decreases Cholesterol

    Detriment: Gastrointestinal Disturbances

    EPA Limit: none

Zinc

Sources: natural - Soil, mineral deposits - Sphalerite (ZnS)

unnatural - Urbal & Industrial Runoff

Benefit: Physical Health, Mental Well Being, Reduces night blindness, cures

Acrodermatitis Enterophathica (AE), treats Acne, protects against

Lead & Cadmium, heals stomach ulcers, reduces swollen prostrate

glands

Detriment: Growth retardation, bone mineralization at very large doses

EPA Limit: 5.0 ppm

Chapter Two

Project Information

The Mahoning Valley watershed encompasses the greater Youngstown, Ohio area and its suburbs. The Mahoning River is 108 miles long and has a total drainage area of 1,131 square miles[4]. As a result of the large industrial and municipal discharges throughout the years, the Mahoning Valley seemed to lend itself to scientific investigation. The work completed in this study was done in conjunction with the Center for Environmental Studies at Youngstown State University. The elemental analysis performed here was a small part of a much larger project that was on-going in the Environmental Studies department. The larger project was focused on the entire watershed in the Mahoning Valley.

The Mahoning Valley lakes under investigation are Evan's, Girard, and Pine. One sediment core was taken from each lake. The cores were between 30-45 cm in length and were divided into 0.69 cm sections. The sections were then freeze-dried and stored for later analysis. The cores were also sampled in duplicate to ensure that there would be enough sediment to perform all the prescribed tests. The samples were tested for % dry matter, carbon, nitrogen, sulfur content, polycyclic aromatic hydrocarbons (PAH) and elemental concentrations. PAH's are pollutants of air, soil, water, and sediments, which are emitted into the atmosphere during combustion and other processes that heat organic matter.

The results of these tests will be very helpful in answering some questions about the sediment content. Some proposed questions may be:

1. What was the source and how far from the source did the extraneous contents of the sediments travel?

2. How long have the contents been there?

3. Do the characteristics of the lake (chemical/physical/biological) have any effect on what is present in the sediments?

The focus of the elemental investigation was to determine what elements were present and their concentrations. The core samples were solids. The problem with solid samples was that they had to be digested to give a solution that could be analyzed by ICP-AES. The digestion of solid material brought about the need for a quality assurance mechanism. A way of determining if the sample had been digested consistently. Quality assurance was done by digesting control samples and spiked samples to obtain recovery rates. Percentages could then be determined to see if the difference in the spike and the control gave the amount added to the spike. The use of nitric acid to digest a sample was technically a leaching procedure and not a total digestion. A total digestion would have included an array of acids.

Chapter Three

Materials and Methods

Materials

The sample preparation was done with a Microwave Digestion Systems 81D microwave oven (CEM Corp., Mathews). CEM is also responsible for the Advanced Composite Vessel used in the digestion of samples. The sample matrix for the digestion's in this study was doubly-distilled 6M nitric acid (GFS Chemicals, Columbus). Controls and spikes were made using certified soil samples (Environmental Resource Associates, Arvada). Ashless filter paper #42 was used to separate any materials that may have been undigested (Whatman, England)

An Applied Research Labortories Model 3410 Inductively Coupled Plasma-Atomic Emission Spectrometer was used to perform the analysis (Fisions Instruments, Valencia). Certified standards were used to calibrate the ICP for the elements analyzed (Environmental Resource Associates, Arvada).

Methods

There is a wide variety of instrumentation available to determine elemental concentrations. The techniques can be divided into two categories: single-element methods and simultaneous multi-element methods. Atomic absorption spectroscopy falls into the category of single element, while the techniques of Inductively-Coupled Plasma-Atomic Emission Spectrometry and X-ray Fluorescence Spectrometry fit into the multi-element slot. Another difference to consider is the type of sample that can be analyzed. AAS and ICP-AES methods are carried out in solution, whereas X-ray Fluorescence can directly analyze solids. Whatever method is chosen, the factors of sensitivity, precision, accuracy, and reproducibility have to be taken into account. A set of ideal requirements has been derived for ICP-AES Methods.

Table 3-1. <u>Ideal requirements for Elemental Analysis by ICP-AES</u>[2]
1. Applicable to all elements
2. Simultaneous or rapid sequential multi-element determination capability at the major, minor, trace, and ultra trace concentration levels without change of operating conditions.
3. No interelement interference effects.
4. Applicable to the analysis of microliter or microgram samples.
5. Applicable to the analysis of solids, liquids, and gases with minimal preliminary sample preparation or manipulation.
6. Capable of providing rapid analysis; amendable to process control.
7. Acceptable precision and accuracy.

ICP-AES is a very effective excitation source as compared to the absorption methods mentioned earlier. Uncertainties begin to show up when dealing with volatile

elements. The error occurs when an element or substance goes from the atomization phase into the plasma. The temperature of the plasma is so high, elements such as arsenic, mercury, and selenium evaporate off before their ions become excited.

Emission Spectroscopy

Emission Spectroscopy, specifically the use of ICP, came about in the mid 1960's[5] and became commercially available in 1974[2]. In emission spectroscopy, a sample is introduced into an excitation source where it is atomized. The excitation source in this case is an argon plasma. Once in the plasma, atoms or ions become energetically excited by a process called collisional excitation. The atoms or ions in the plasma collide with the already excited argon ions, causing a transfer of energy that results in an excited atom or ion. When an atom or ion enters the excited state it is said to be unstable, meaning that they would prefer to reside in the ground state at all times. Upon returning to the ground state, light is given off. The light emitted by each element is characteristic to that element. Knowing that each element typically has its own distinct wavelength, the light quanta can be sorted in the spectrometer (monochromator). The resulting wavelengths are then measured by a photoelectric component (photomultiplier tube).

The Excitation Source

One of the most appealing aspects of ICP, is its capability to reach extremely high temperatures and still have the plasma remain constant and homogeneous. The

temperature can reach the vicinity of 6000-10,000 K. This temperature is approximately two times higher than the other available flame methods, namely AAS.. The plasma is basically a cloud of electrons and ions that are kept at a high temperature[6]. A radiofrequency is applied to the gas (usually argon) flowing through a quartz tube (see figure 3.1). The upper part of the tube is surrounded by an induction coil made of copper wire tubing. The coil has to be water cooled to avoid being damaged by the heat of the plasma. An RF field is generated through the coil and operates between 5 and 75 MHz. The RF power induces a magnetic field axially through the torch[6]. The atoms and ions in the torch are forced by the magnetic field to follow circular paths at extremely high velocities (see figure 3.2). The direction that these atoms and ions take, changes twice during each cycle. The changing of direction in the torch, causes resistance to the motion of atoms and ions. The resistance causes an increase in temperature. Argon atoms, that are continually being introduced into the plasma, eventually collide with charged particles, raising their temperature until they to become ionized. The result of this process is the continuity of the plasma.

The temperature obtained by the ICP plays an extremely significant role in the factors of sensitivity and detection limits. The number of excited atoms or ions in an ICP is enormous. The Boltzmann Equation, which explains the relationship between N_u/N_o and temperature, can be written as follows:

$$N_u/N_o = G_u/G_o \exp^{-(E_u-E_o)/KT} \qquad 1$$
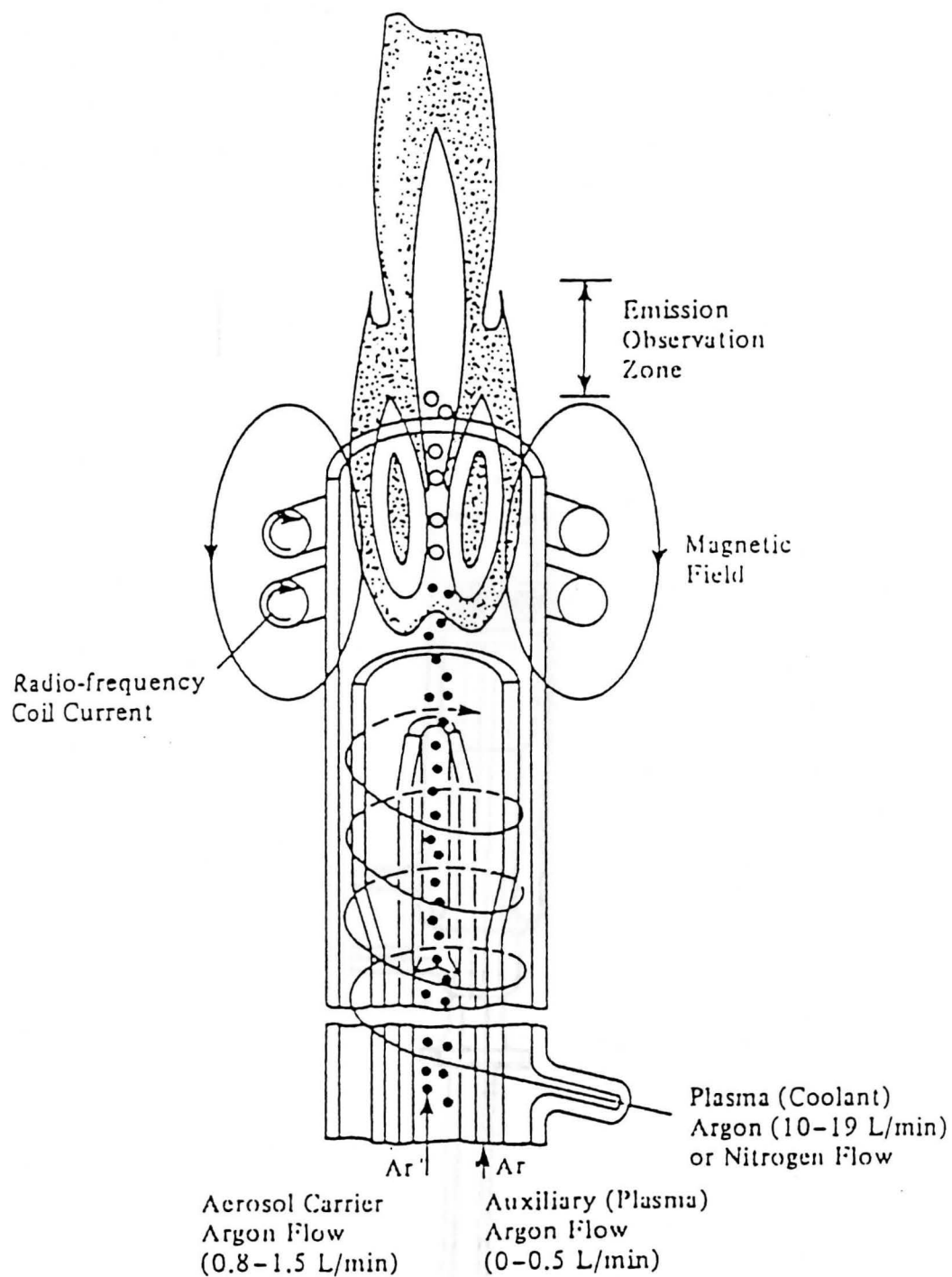
Figure 3.1   *Schematic representation of an inductively coupled plasma discharge. From R. M. Barnes*, Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss., 28(4), 383 (1979), *by permission of the publisher.*
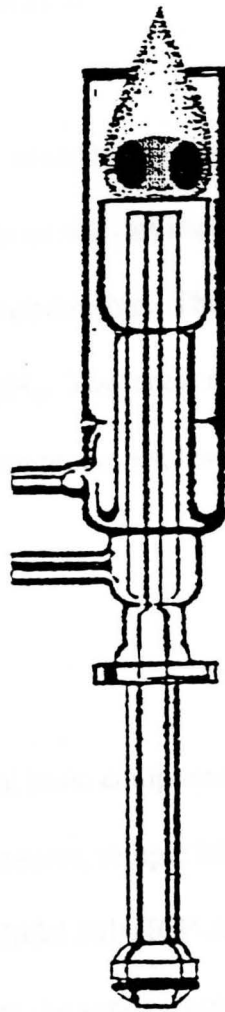
Figure 3.2   *Magnetic and Electric Fields Generated by the Induction Coil*

where N_u = the number of atoms in an excited state

N_o = the number of atoms in the ground state

G_u & G_o = statistical weight of the excited state and ground state

E_u & E_o = energy of the excited state and ground state

K = Boltzmann constant

T = temperature K

In the Boltzmann equation, all the variables are fixed, except the ratio between N_u/N_o which is dependent on the varying temperature. effects on emission spectroscopy can be predicted by this relationship. The higher the temperature of the excitation source, the larger the ratio of N_u/N_o. The larger ratio results in better efficiency in the atomization and excitation processes, leading to higher sensitivity and lower detection limits.

ICP Components

There are several basic components of an ICP emissions spectrometer. They consist of an emission source, sample introduction, optical system, and electronics and readout. In the ARL Model 3410 ICP-AES, the sample is converted from solution into an aerosol and sprayed into the spray chamber by a concentric nebulizer (see figure 3.3). Once the sample is turned into a mist, the droplets are fed into the plasma by the continuous stream of argon atoms being introduced to the system. The plasma, operating
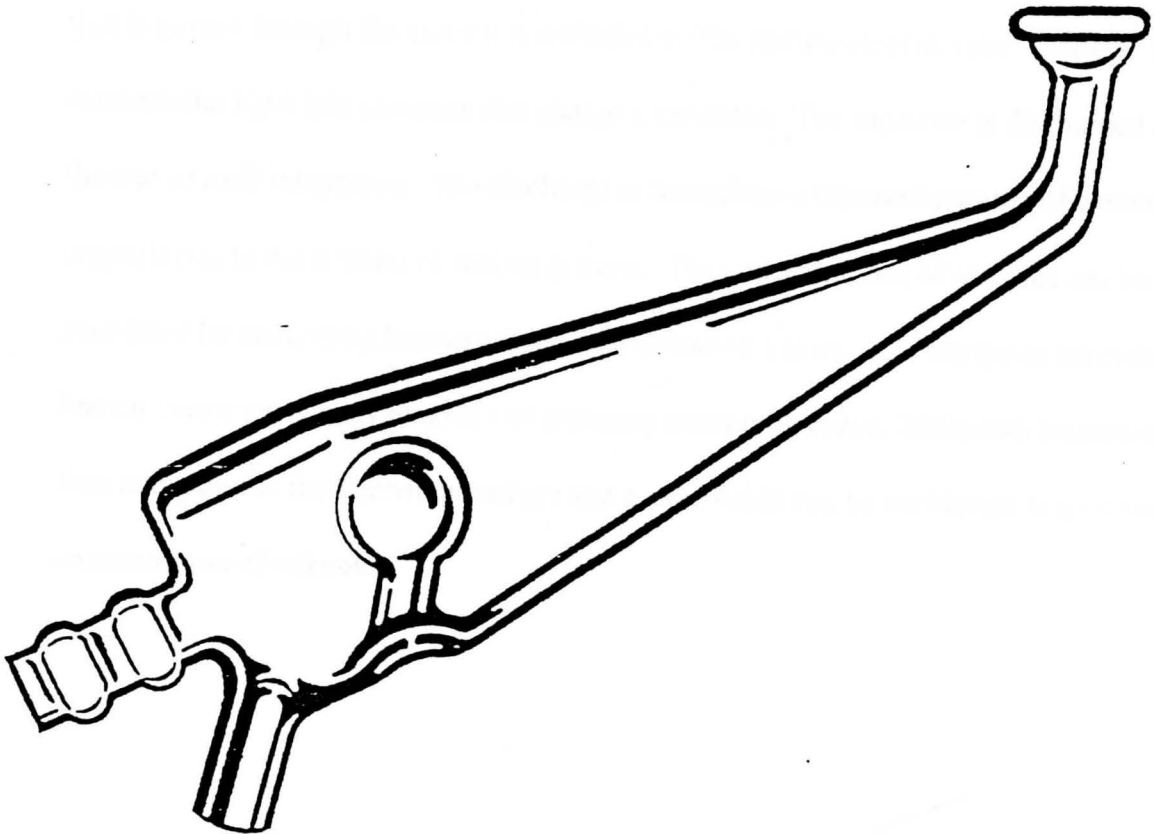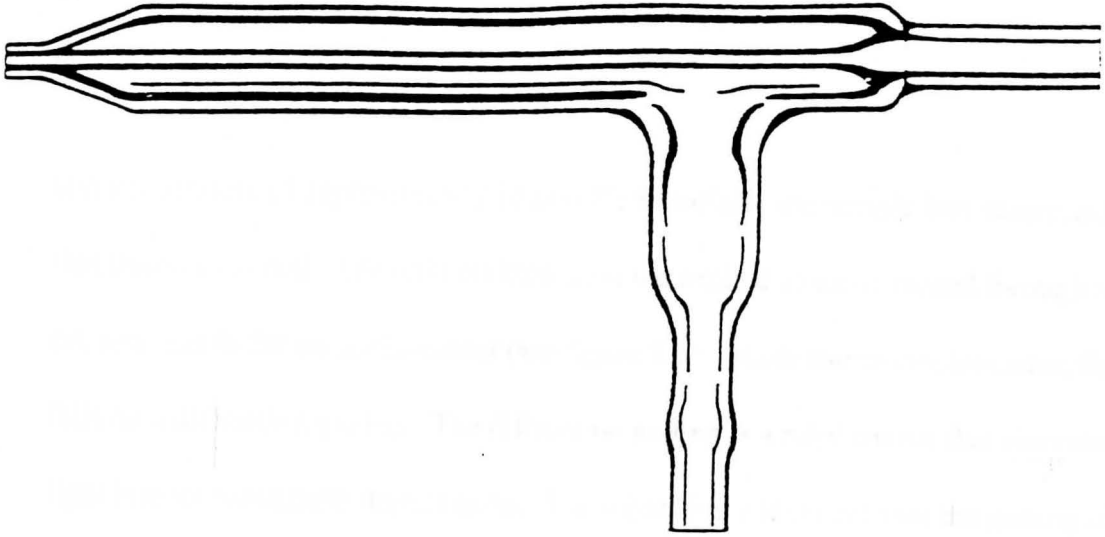
Figure 3.3 *The Spray Chamber*

at a temperature of approximately 10,000 K, dissociates the sample into atoms and ions that become excited. The light emitted from the excited atoms is passed through an entrance slit in the monochromator (see figure 3.4). Inside the monochromator, the light falls on a diffraction grating. The diffraction grating is a ruled mirror that separates the light into its constituent wavelengths. The separation occurs because the grating sits on a stepper motor (see figure 3.5). The stepper motor positions the grating so that light near the expected peak passes through the exit slit. Only a small portion of the light in the monochromator can pass through the exit slit at any one time. The stepper motor allows the diffraction grating to pause for the specified integration time at each step. The light that is passed through the exit slit is collected by the photomultiplier tube. The PMT converts the light into electrons that charge a capacitor. The capacitor is discharged at the end of each integration. The discharge is then given a digitized number of counts proportional to the amount of analyte present. The concentrations of analytes can be calculated by comparing known values with unknown values. The computer takes the known values previously entered and creates a calibration curve. Unknown intensities are then compared to the known intensities and a calculation can be performed to give the concentration of unknown.

CAMERA
MIRROR

COLLIMATOR
MIRROR

PLANE
DIFFRACTION
GRATING

PRIMARY SLIT
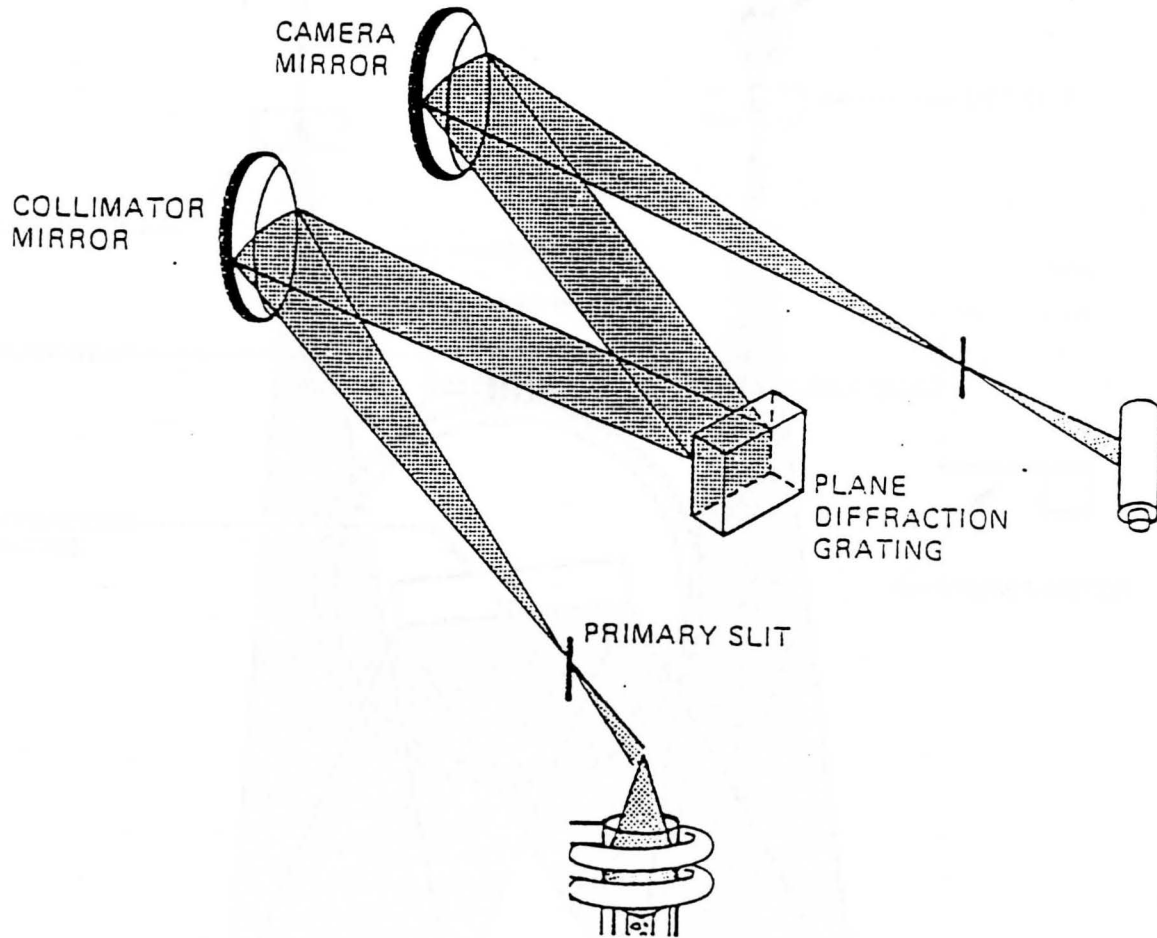
Figure 3.4 *Light Path in the Monochromator*
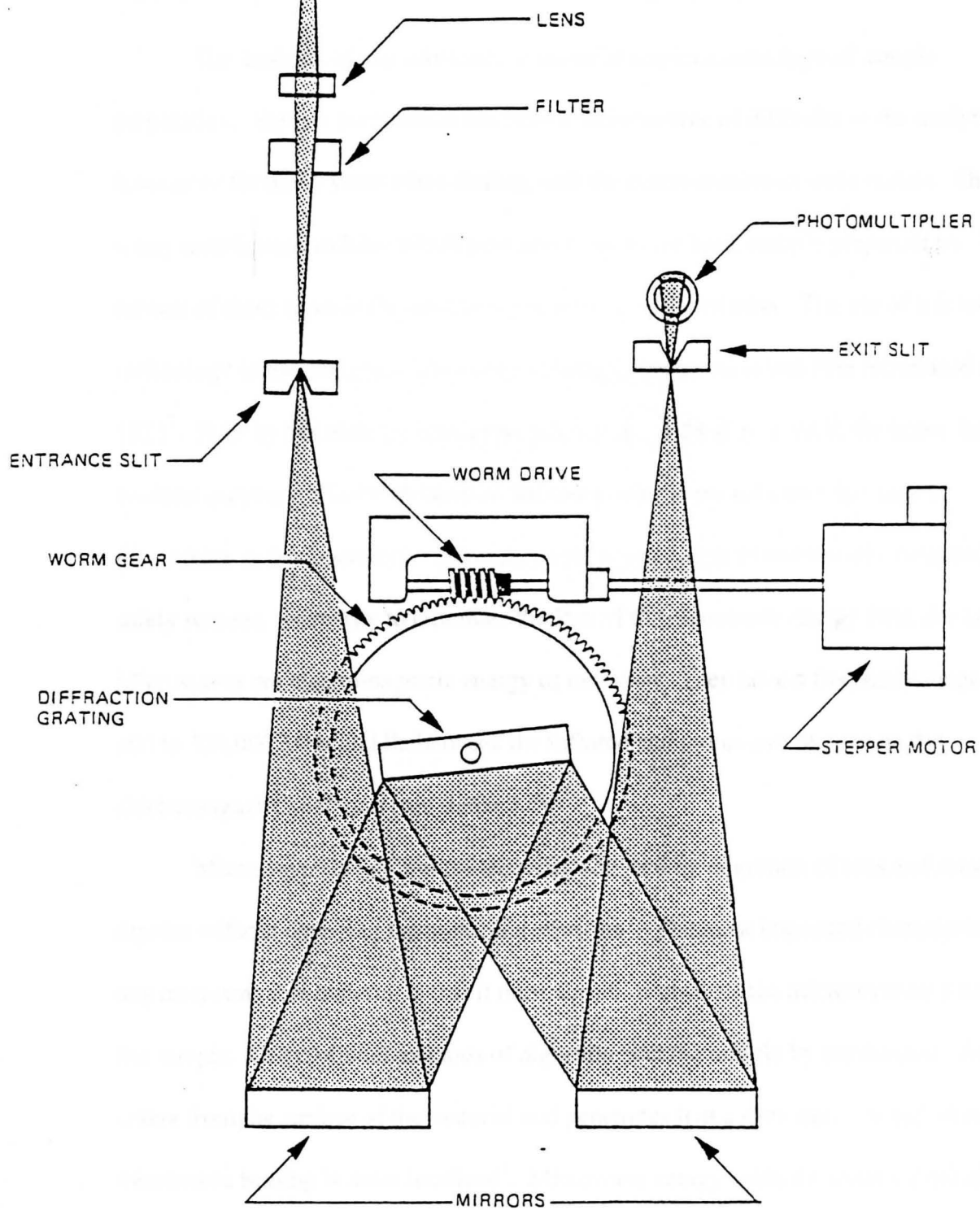
Figure 3.5   *Schematic Representation of Model 3410 ICP Spectrometer System*

Microwave Assisted Dissolution as a sample preparation technique.

The analysis of any substance or material requires some type of sample preparation. Sample preparation has been a major source of difficulty in the analytical laboratory for many years when dealing with the determination of trace metals. There are many techniques available which give good results for basic sample preparations. The newest of these types is the microwave assisted acid dissolution. The use of microwave technology in the analytical laboratory for sample preparation was first introduced in 1975[7]. Prior to this time the microwave oven was, and still is, used in the home for cooking purposes. Home versions of the microwave oven were initially used by researchers in the laboratory. These domestic ovens had to be extensively modified for safety reasons, primarily to eliminate the loss of the microwave energy from the cavity. Microwaves are electromagnetic energy or radiation. They have a frequency range from 300 to 300,000 MHz and lie between the infrared and radiowave regions on the electromagnetic spectrum (see figure 3.6).

Microwave energy induces molecular motion by migration of ions and rotation of dipoles without changing the molecular structure[7]. The most important characteristic for any microwavable material is that it must absorb or obstruct the microwave as it enters the sample. Conventional methods of digestion heat the sample by conduction. Heat enters from the surface of the material and penetrates it at a slow rate. On the other hand, microwave heating is more localized[7]. Microwave energy heats the sample from all sides and penetrates the sample from the beginning of the digestion (see figures 3.7-3.8). The effect produced by the microwave irradiation varies depending on the type of sample that is being digested. Materials either absorb, reflect, or transmit microwave energy. As

| X-Rays | Ultraviolet | Visible | Infrared | Microwaves | Radiowaves |

Laser Radiation

Wave Length (meters)

Frequency (MHz)

Inner-shell electrons

Outer-shell (valence) electrons

Molecular vibrations

Molecular rotations
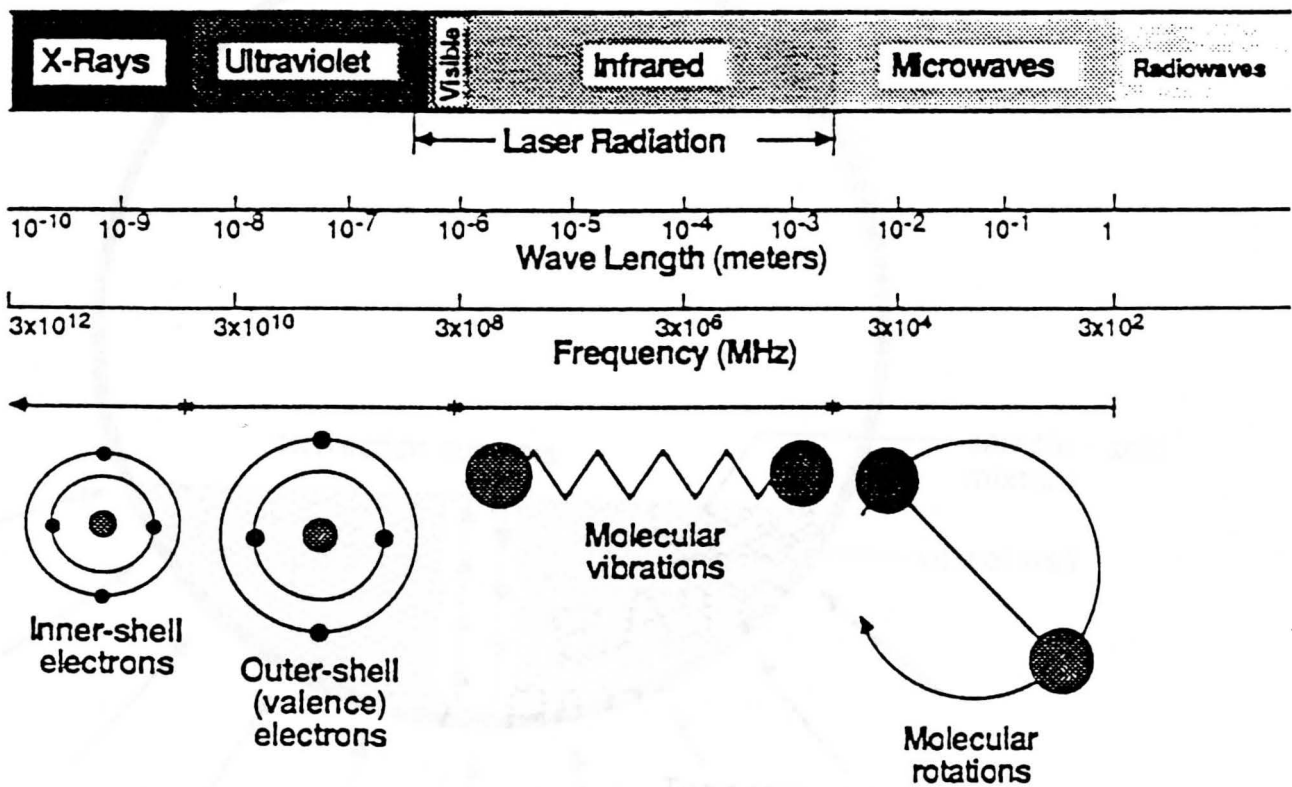
Figure 3.6   *Electromagnetic spectrum.*
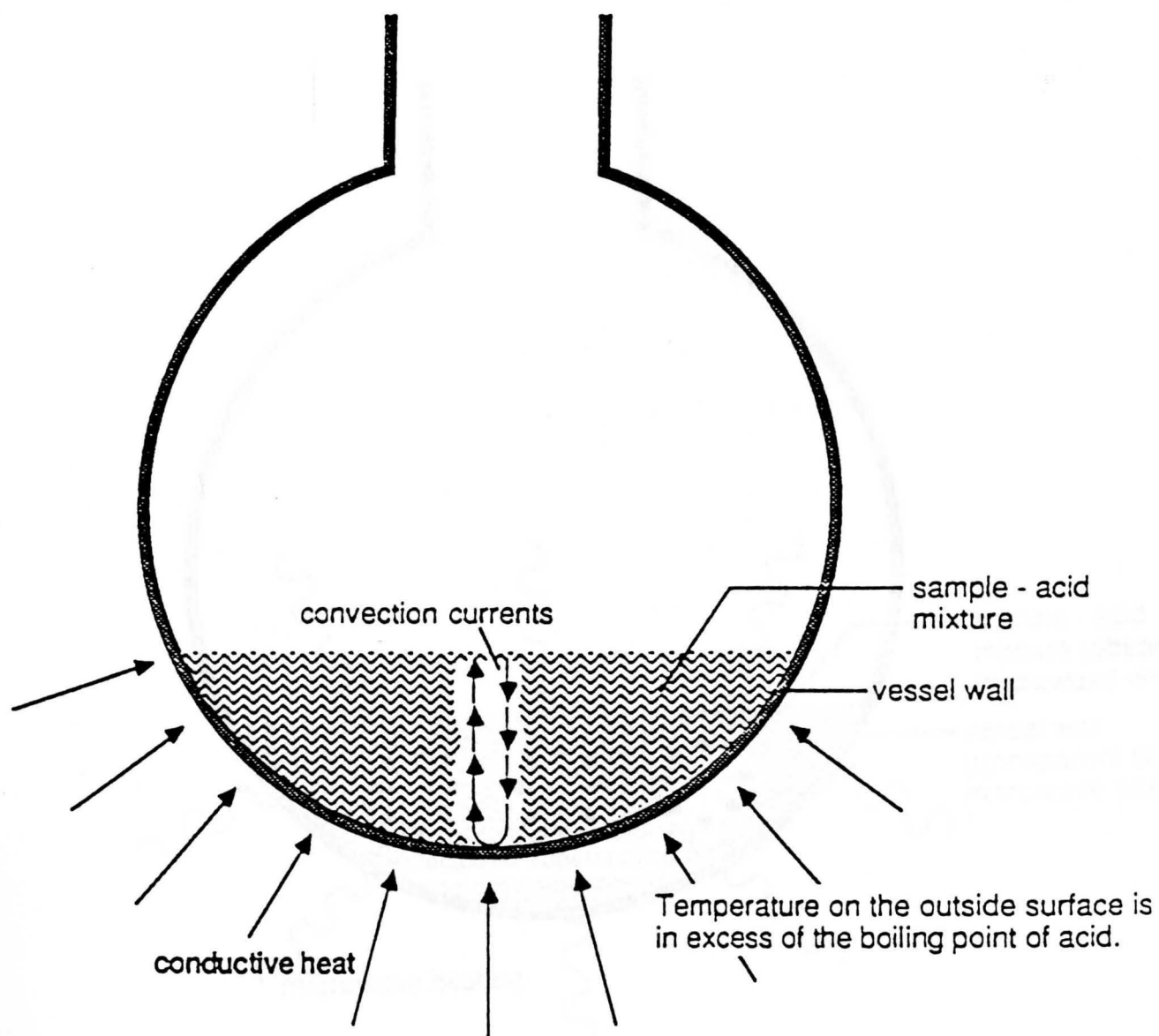
Figure 3.7   *Schematic of sample heating by conduction.*
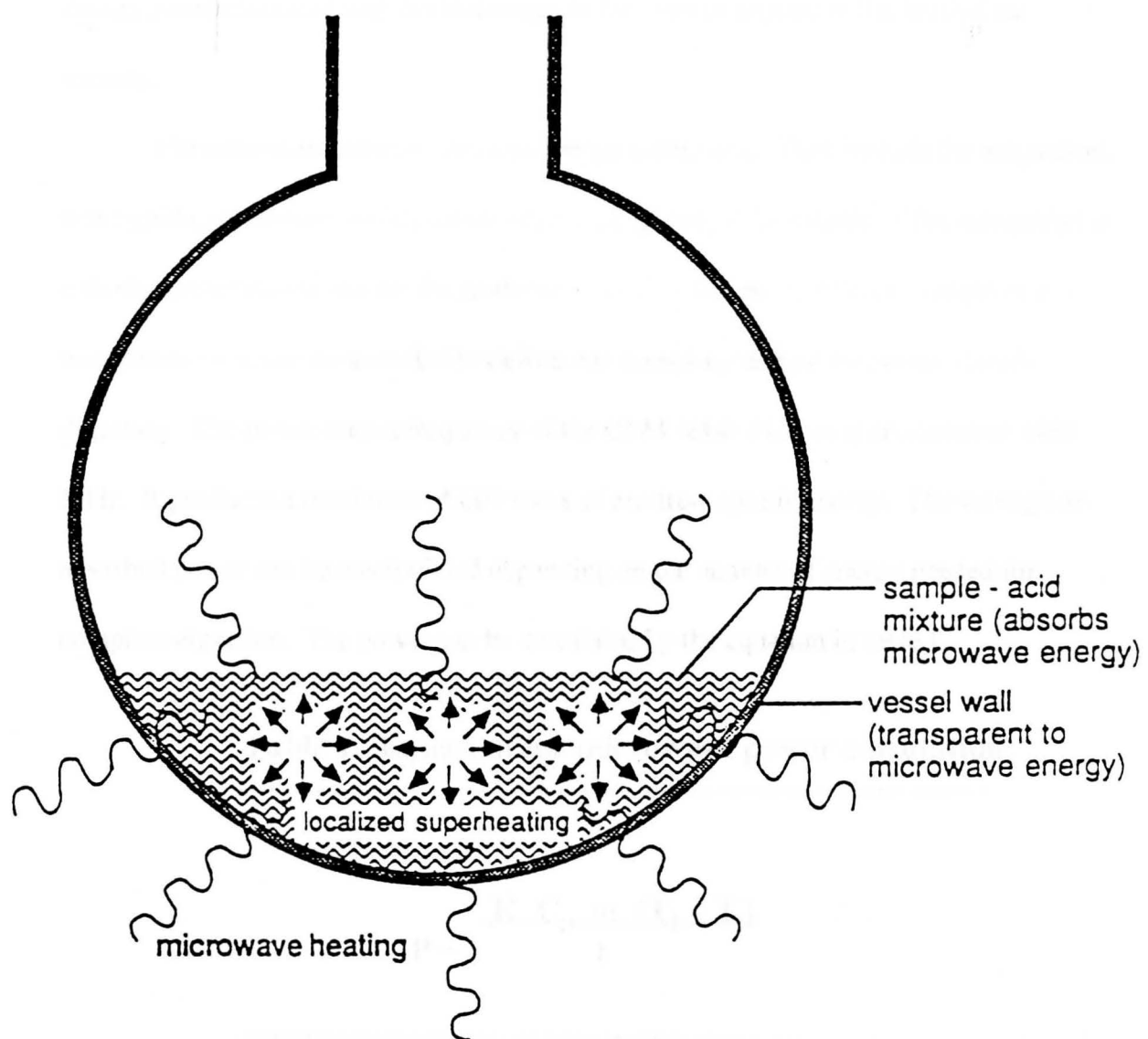
Figure 3.8   *Schematic of sample heating by microwave energy.*

stated earlier, absorption is needed for sample heating. Materials completely transparent to microwaves do not become heated. Since no heating occurs, this type of material works well for digestion vessels. A sample that reflects microwaves does not allow for energy penetration and may cause damage to the oven or anyone in the immediate vicinity.

The microwave oven is composed of six main parts. They include the magnetron, wave guide, microwave cavity, mode stirrer, circulator, and turntable[6]. The magnetron is a diode that is responsible for the production of microwaves. The power output of a microwave oven can be modified to deliver the necessary energy for proper sample digestion. The power output frequency of the CEM MDS-81D is approximately 2450 MHz. It produces a maximum of 600 watts of electromagnetic energy. The wattage or absorbed power can be manipulated depending on the amount of energy needed for complete digestion. The power can be calculated by the equation in table 1.

Table 1. Equation for microwave power calculation.

$$P = \frac{K\ C_p\ m\ (T_f - T_i)}{t}$$

----

where P = absorbed power
       K = conversion factor
       C_p = heat capacity
       m = mass of sample
       $(T_f - T_i)$ = change in temperature
       t = time.

Wave guides do just what the name implies. They guide the generated microwaves to the microwave cavity. The mode stirrer breaks up the energy before it enters the cavity. The circulator then distributes the energy throughout the cavity where the samples become irradiated. The turntable is responsible for the rotating the vessels to allow for uniform heating. The vessels used in microwave digestions differ greatly from materials used in conventional methods of sample digestion.

Microwave digestion vessels are made of Teflon ® [poly(tetrafluoroethylene)][7]. The vessels are completely sealed from the outside environment and are totally transparent to microwave energy. They are comprised of several component parts (see Figures 3.9-3.10). The smallest and probably most important is the rupture membrane. The rupture membrane separates the inner cavity of the vessel form the outside. Its major purpose is to release the pressure inside the vessel, should the pressure become to great for the vessel's material to withstand. The vessel itself is just a Teflon® liner that has a cover. The cover fits down over the sleeve and the sleeve sets into a threaded ring. The cap is placed over the cover and is screwed onto the threaded ring to completely seal the vessel. A vent fitting is put on the stem of the cover to house the rupture membrane. A ferrule nut attaches to the vent fitting to allow for a vent tube to be connected to the vessel. The vent tube is present to contain any overflow that may occur if the rupture membrane gives way. Once the vessel is together, it is placed into the carousel that sits on the microwave oven turntable (see figure 3.11). The temperature and pressure of the vessel system is monitored through a single vessel. The cover is modified to permit insertion of a temperature and a pressure probe (see figure 3.12). Open-vessel digestions
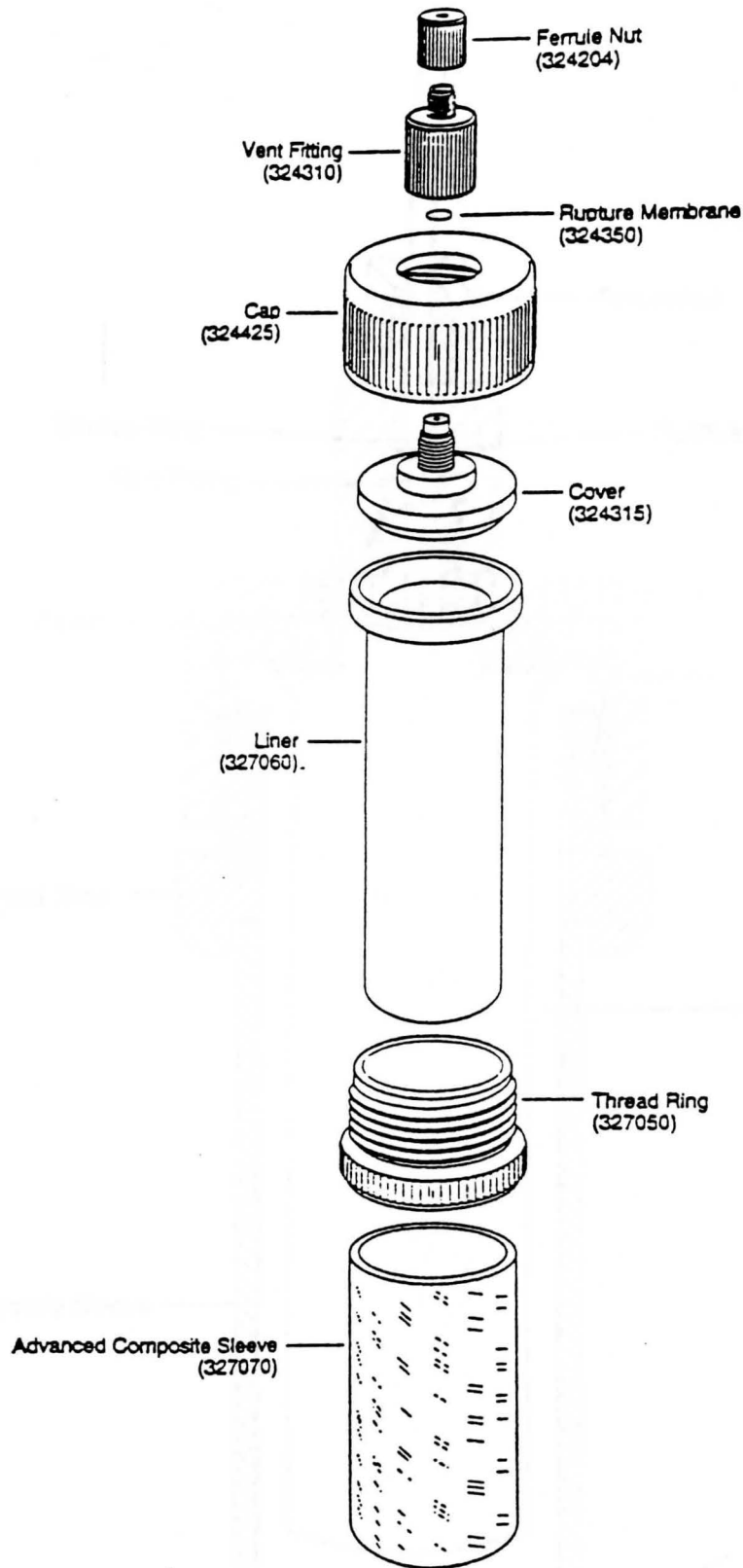
Figure 3.9   **Standard Advanced Composite Vessel Components**

Vent Tube

Ferrule Nut

Backup Ring

Rupture Membrane

Vent Fitting

Cover

Cap

Thread Ring

Liner

Advanced Composite Sleeve
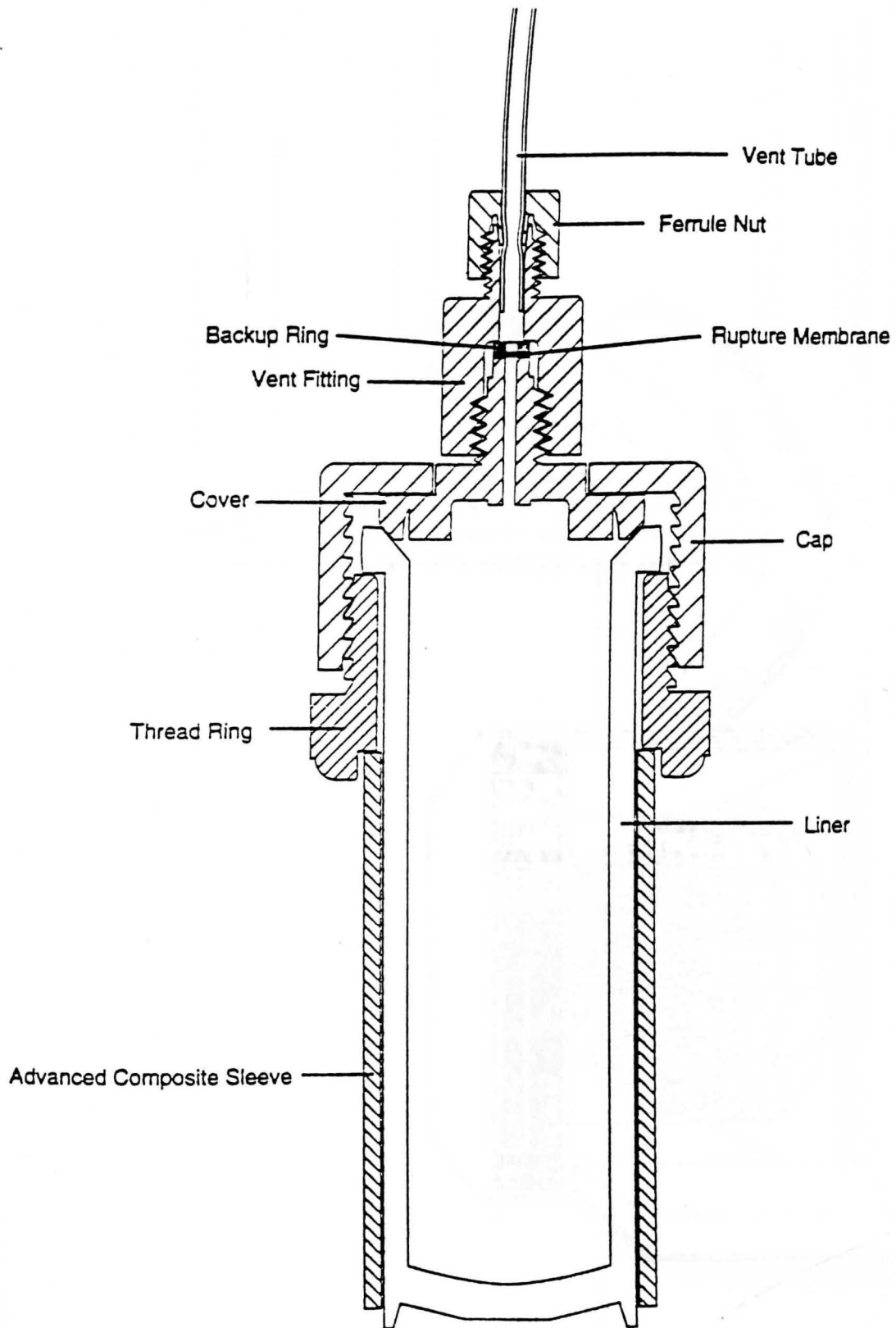
Figure 3.10 **Standard Advanced Composite Vessel (Cross Section)**

30

Exhaust
tubing
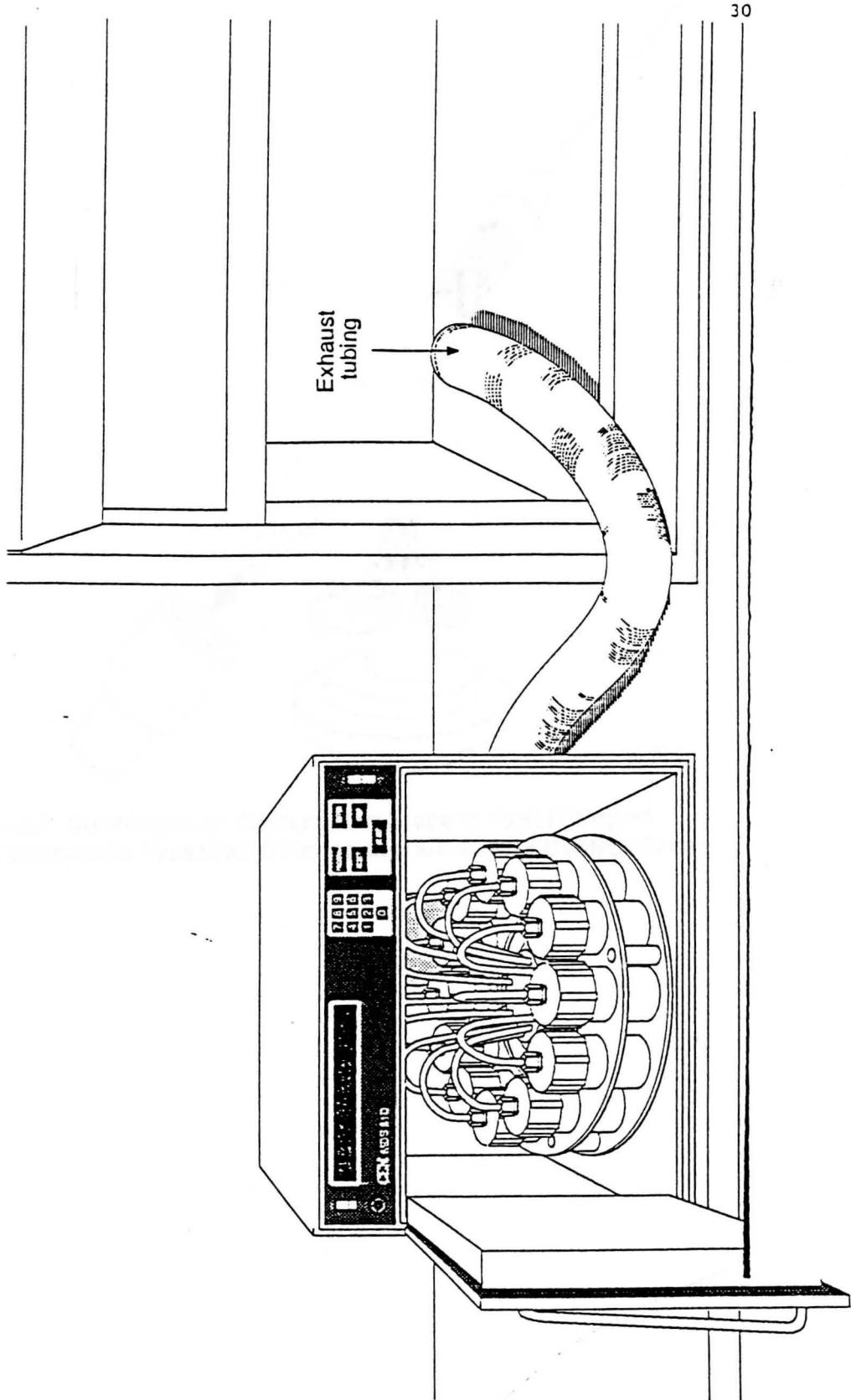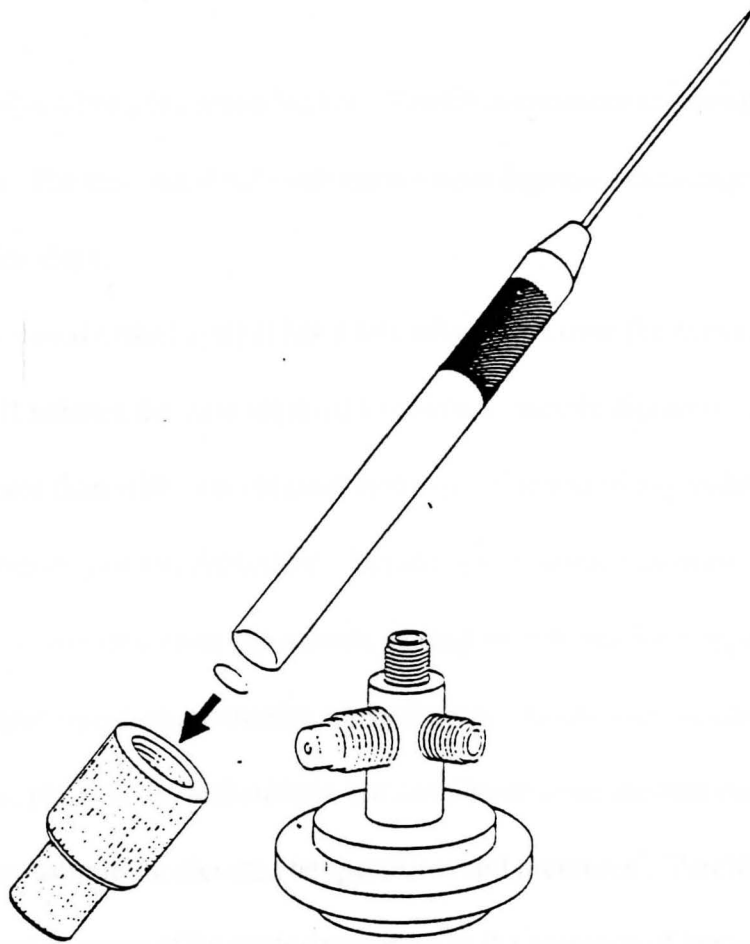
Figure 3.11

Figure 3.12   **Installation of Rupture Membrane in Vent Fitting of Advanced Composite Vessel with Temperature/Pressure Control Cover**

usually involve a hot plate and a beaker. Volatile substances are inevitably lost to evaporation. The time involved in an open-vessel digestion can range from a couple of hours to a few days.

The closed-vessel system has a few advantages over the conventional open-vessel technique. It reduces the time required to obtain a sample digestion. Also, digestions are more complete than with conventional methods. The loss of any volatile analytes through fumes or gases is eliminated. Sample size is greatly reduced. The reduction of sample size in turn decreases the amount of reagents needed for a digestion. The reagents used in sample digestion are usually mineral acids. Acids such as nitric, hydrochloric, hydrofluoric, phosphoric, and sulfuric are considered to be the best reagents when digesting any samples at elevated temperatures and pressures[7]. Perchloric acid is not generally used because of its explosive nature in the presence of heavy metals.

Nitric acid is the preferred acid for the digestion of soils and sediments. This is due to its oxidizing attack on metals. Hydrochloric acid is used to digest the salts of weak acids (i.e. CO_3^{--} & PO_4^{---}). Hydrofluoroic acid is a very dangerous material when it comes in contact with the skin; it is used primairly for the digestion of silicates. Sulfuric acid has the highest boiling point of all the mineral acids. Its major purpose is two-fold. First, it is used as a dehydration mechanism for soils and metals. Secondly, in the presence of peroxides, H_2SO_4 is added to char the extraneous material that forms. The mineral acids have their own inherent characteristics which makes their selection much easier. It has now been determined that acid mixtures can be used to obtain complete digestions. For example, hydrochloric and nitric are particularly efficient at extracting

precious metals. A nitric and sulfuric acid mixture is used for the digestion of high

molecular weight organics. A combination of hydrochloric-nitric-hydrofluoric acids is

used for the breakdown of alloys, silicates, and flyash.

Chapter Four

Procedures and Results

A. Calibration of Microwave Oven

According to EPA Method 3051 (see Appendix A), a microwave oven must be calibrated before its initial use as a digestion tool. There are two different ways to calibrate the oven. They are a three-point calibration and a multipoint calibration. In this study, a multi-point calibration was performed. Several power settings were chosen: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40%. The steps involved in calibrating the microwave oven used in this study are listed below:

1. The first step was to equilibrate a large volume of water to room temperature. This was done by filling a large carboy with water and leaving it sit overnight.

2. One kilogram of water was accurately measured into a one liter Teflon ® bottle (Teflon ® does absorb microwave energy). The initial temperature of the water was recorded and found to be 23 +/- 2° C by using an alcohol thermometer.

3. The liter bottle was covered and placed in the microwave unit and circulated through the cavity for two (2) minutes at the prescribed partial power setting with the exhaust fan at 100%.

4. Once irradiation was complete, the liter bottle was removed and placed on a magnetic stirrer. A stir bar was added and the water was stirred vigorously for one minute. The maximum temperature was recorded within the first thirty seconds.

5. A new sample of water was used for each trial. The absorbed power was determined by using Equation 2 and resulting in the calibration curve in Table 4.1.

B. Sample Preparation for ICP Analysis

1. The digestion vessels were weighed to the nearest 0.001g prior to use.

2. A 0.5g unknown solid sample was weighed in the digestion liner to the nearest 0.001g.

3. Once the samples were weighed, 10 mL of concentrated nitric acid was added to each vessel (see Table 4.2).

4. The vessel was then closed and placed into the microwave (max. of six vessels) and irradiated at 99% power for 10 minutes.

5. At the end of the program, the vessels were allowed to cool in the microwave for a minimum of 10 minutes. After being taken out of the microwave, the vessels were allowed to cool to room temperature before being reweighed to see if the final weight was the same as the initial weight.

6. The vessels were checked to determine if there was any significant loss of mass during the digestion. A large loss meant that the vessel integrity was broken, thus rendering the sample in that vessel invalid.

7. The final part of the preparation was to remove any particulate matter that might be present. This was done by using a gravity funnel and Whatman #42 filter paper. The samples were filtered into a 100 mL volumetric flask and diluted to the mark with deionized water.

Table 4.1 Calibration Data for Microwave Oven

Power (%)	Absorbed Power (watts)
40	177.74
50	240.47
60	320.62
70	372.9
80	435.63
90	491.39
95	522.75
97	529.72
98	543.66
99	554.12
100	616.85
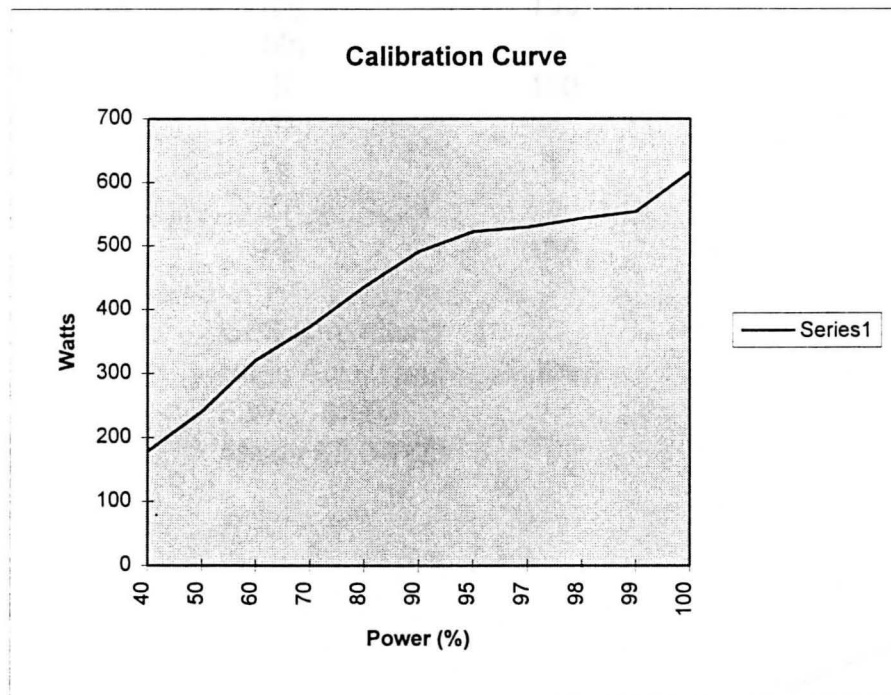
Calibration Curve

Table 4.2 Liquid Reagents

Environmental Resource Association
ICP Calibration Standards

Element	Concentration (mg/L)
Al	1
Ba	1
Be	1
Cd	1
Ca	100
Cr	1
Cu	1
Fe	1
Pb	1
Mg	100
Mn	1
K	100
Ti	1
V	1
Zn	1
Na	100

GFS Chemicals
Nitric Acid, Double Distilled
F.W. : 63.01
Assay 68.0-70%

and end of each day of digestion. The purpose of these constituents was to insure the integrity of the digestion. See table 4.4 for the breakdown of spike material.

ICP Program

The first step in performing an ICP analysis was to set up and edit a task file. The task file contained all the information necessary to run the instrument. The variables such as elements to be analyzed, emission wavelengths, PMT settings,and integration times had to be preset in this file. The second step in creating a task file was to enter all the information correctly. After all the parameters had been set, a solutions file was created. This file contains the number and content of solutions that would be used in the calibration of the ICP (see Table 4.2). The determination of emission wavelength was based on several factors (see Table 4.3). The first and most important was the presence of spectral interference's. Interference's were due to the overlap of emission lines. Sensitivity also played an important role.

The initial step in instrument operation was to light the torch and allow it to stabilize for a minimum of five (5) minutes. Once stable, the monochromator was calibrated using the argon triplet at 355.47. This wis known as a zero calibration. After the zero calibration, the wavelengths were refined to determine the number of steps needed to reach an emission line. The number of steps were then stored in memory. A solution containing a known amount of elements was then aspirated into the torch and a two-point calibration curve is determined. The initial set-up was then complete and the analysis of unknowns could be performed.

Table 4.3 Variables Used in the ICP Analysis

Element Symbol	Line Lib. Wavelength	L.Q.D.	PMT Attn.	Int. Time	Line Lib. Interferences
Ba	455.403	0.002	8	1	CR NI TI
Mn	257.61	0.005	8	1	AL CR FE V
Be	234.861	0.001	8	1	FE TI
Cd	214.438	0.01	8	1	AL FE PT
Cr	205.552	0.01	8	1	AL CU FE NI
Cu	327.396	0	8	1	FE IN MO NB
Pb	220.353	0.1	8	1	AL CR PD SN
Ti	336.121	0.01	8	1	
V	309.311	0	8	1	AL CR FE MG
Zn	213.856	0.005	8	1	CU NI TI V
Al	396.152	0.075	8	1	CA TI V
Fe	259.94	0.01	5	0.7	MN TI
Ca	393.366	0.0003	4	0.1	V
Mg	279.553	0.0005	4	0.5	FE MN
K	766.491	0.5	6	0.5	CU TI
Na	588.995	0	4	0.5	

Table 4.4 Concentration of Spikes

Element	Concentration (mg)
Al	0.25
Be	0.05
Cr	0.05
Cu	0.05
Fe	0.05
Pb	0.05
Mn	0.05
Zn	0.05
Ti	0.05
Ba	0.05
Na	0.05
Ca	0.05
Mg	0.05
K	0.05
Cd	0.0125
V	0.125

Results

The results of this study have been tabulated and plotted in unknown time increments. The known factor is that number one is the newest material. The first set of data numbers are from the quality control samples run with the digestions. The blanks were averaged and subtracted from each individual vessel. The controls and spikes were numbered from one to ten. The data was collected in mg/L and then converted to mg/kg. For each of the control and spiked samples, % recoveries were calculated and tabulated. The samples were named by taking the name of the lake and adding a couple of numbers. Example, Pine Lake samples are labeled P2-1. The letter is followed by two digit number separated by a hyphen. The first number refers to the core from which the sample came from. The cores were taken in duplicate to give enough material for analysis. The second number is the section number within the core. The same goes for Evan's and Girard lakes as well. Each core sample has two columns of data. The First column is the results in mg/L and the second column is in mg/kg. Following the data is a plot of each of the individual lake and its element.

Quality Control Data

Element	Blank Avg.	Control 1 mg/L	Control 2 mg/L	Spike 1 mg/L	Spike 2 mg/L	Con 1 mg/kg	Con 2 mg/kg	Spk 1 mg/kg	Spk 2 mg/kg	Avg. Con. mg/kg	Avg. Spk. mg/kg	Difference
Ba	0.002	0.541	0.918	1.628	1.458	106.4959	177.5596	308.913	282.5604	142.0277	295.7367	153.709
Mn	0.19	1.176	1.609	2.397	2.116	231.4956	311.2128	454.8308	410.0808	271.3542	432.4558	161.1016
Be	0.001	0.571	0.729	1.313	1.167	112.4014	141.0032	249.1418	226.1646	126.7023	237.6532	110.9509
Cd	0.011	0.417	0.52	0.662	0.582	82.08645	100.5784	125.6145	112.7916	91.33243	119.2031	27.87063
Cr	0.024	0.356	0.441	0.924	0.885	70.0786	85.29822	175.329	171.513	77.68841	173.421	95.73259
Cu	0.004	0.719	1.056	1.749	1.523	141.5352	204.2515	331.8728	295.1574	172.8933	313.5151	140.6217
Pb	0.1	0.21	0.322	0.853	0.767	41.3385	62.28124	161.8568	148.6446	51.80987	155.2507	103.4408
Ti	0.018	0.716	1.209	1.917	1.658	140.9446	233.8448	363.7508	321.3204	187.3947	342.5356	155.1409
V	0.001	0.453	0.643	2.023	1.696	89.17305	124.3691	383.8643	328.6848	106.7711	356.2745	249.5035
Zn	0.05	0.68	0.643	1.188	1.148	133.858	124.3691	225.423	222.4824	129.1135	223.9527	94.83917
Al	0.075	21.87	37.792	46.51	41.937	4305.11	7309.729	8825.273	8127.391	5807.419	8476.332	2668.912
Fe	15.169	43.743	0	80.362	0	8610.81	0	15248.69	0	4305.405	7624.345	3318.94
Ca	1	19.832	19.922	21.395	21.236	3903.929	3853.313	4059.701	4115.537	3878.621	4087.619	208.9978
Mg	0.184	13.762	14.084	14.139	14.38	2709.05	2724.127	2682.875	2786.844	2716.588	2734.86	18.27114
K	0.5	0	0	0	0	0	0	0	0	0	0	0
Na	0.279	1.105	1.015	1.55	1.42	217.5193	196.3213	294.1125	275.196	206.9203	284.6543	77.73398

* 0 indicates sample was not completely digested

Quality Control Data

Element	Blank Avg.	Control 3 mg/L	Control 4 mg/L	Spike 3 mg/L	Spike 4 mg/L	Con 3 mg/kg	Con 4 mg/kg	Spk 3 mg/kg	Spk 4 mg/kg	Avg. Con. mg/kg	Avg. Spk. mg/kg	Difference
Ba	0.002	0.827	1.057	0.895	1.478	159.9583	200.9463	161.2611	284.781	180.4523	223.0211	42.56877
Mn	0.024	1.6	2.029	1.757	2.372	309.472	385.7332	316.5763	457.037	347.6026	386.8066	39.20402
Be	0.001	0.635	0.821	0.9	1.21	122.8217	156.0803	162.162	233.1428	139.451	197.6524	58.2014
Cd	0.014	0.461	0.633	0.527	0.659	89.16662	120.3396	94.95486	126.9761	104.7531	110.9655	6.212365
Cr	0.029	0.386	0.513	0.756	0.959	74.66012	97.52643	136.2161	184.7801	86.09328	160.4981	74.40483
Cu	0.018	0.925	1.164	1.132	1.596	178.9135	221.288	203.9638	307.5173	200.1008	255.7405	55.63975
Pb	0.1	0.277	0.406	0.591	0.821	53.57734	77.18466	106.4864	158.1903	65.381	132.3383	66.95733
Ti	0.016	0	1.419	0	2.016	0	269.7661	0	388.4429	134.883	194.2214	59.3384
V	0	0.576	0.736	1.321	1.874	111.4099	139.921	238.0178	361.0823	125.6654	299.5501	173.8846
Zn	0.018	0.663	0.781	0.94	1.212	128.2375	148.4759	169.3692	233.5282	138.3567	201.4487	63.092
Al	0.075	0	39.519	0	42.768	0	7512.957	0	8240.538	3756.479	4120.269	363.7906
Fe	0.082	72.171	72.916	73.996	74.838	13959.31	13862.06	13332.6	14419.79	13910.69	13876.19	-34.4952
Ca	0.168	21.231	0	24.219	0	4106.5	0	4363.779	0	2053.25	2181.89	128.6397
Mg	0.053	14.105	14.359	16.082	14.444	2728.189	2729.789	2897.655	2783.07	2728.989	2840.362	111.373
K	0.5	17.412	17.412	18.717	18.243	3367.829	3310.195	3372.429	3515.061	3339.012	3443.745	104.733
Na	0.539	0.801	0.942	1.516	1.315	154.9294	179.0836	273.1529	253.3742	167.0065	263.2635	96.25702

*0 indicates sample was not digested completely

Quality Control Data

Element	Blank Avg.	Control 5 mg/L	Control 6 mg/L	Spike 5 mg/L	Spike 6 mg/L	Con 5 mg/kg	Con 6 mg/kg	Spk 5 mg/kg	Spk 6 mg/kg	Avg. Con. mg/kg	Avg. Spk. mg/kg	Difference
Ba	0.002	0.815	0.867	1.492	1.334	140.0341	167.6986	287.4756	268.0833	153.8664	277.7794	123.9131
Mn	0.025	1.449	1.586	2.172	2.012	248.9686	306.7705	418.4966	404.3355	277.8695	411.4161	133.5465
Be	0.001	0.597	0.659	1.13	1.098	102.5771	127.4664	217.7261	220.6563	115.0218	219.1912	104.1694
Cd	0.01	0.428	0.486	0.617	0.598	73.53939	94.00406	118.8823	120.1753	83.77173	119.5288	35.75708
Cr	0.234	0.091	0.142	0.589	0.564	15.63571	27.46621	113.4873	113.3426	21.55096	113.415	91.864
Cu	0.023	0.903	0.912	1.531	1.375	155.1544	176.4027	294.99	276.3228	165.7785	285.6564	119.8779
Pb	0.1	0.259	0.265	0.772	0.682	44.50164	51.25736	148.7474	137.0561	47.8795	142.9018	95.02225
Ti	0.01	0.984	1.061	1.58	1.287	169.0719	205.2229	304.4312	258.6381	187.1474	281.5347	94.3873
V	0	0.52	0.585	1.697	1.669	89.34692	113.153	326.9746	335.4056	101.25	331.1901	229.9401
Zn	0.017	0.547	0.611	1.046	1.04	93.98609	118.1821	201.5412	209.0005	106.0841	205.2708	99.18676
Al	0.075	31.404	33.813	42.775	35.17	5395.867	6540.246	8241.801	7067.834	5968.056	7654.817	1686.761
Fe	1.333	63.687	0	75.034	0	10942.76	0	14457.4	0	5471.382	7228.701	1757.319
Ca	0.412	21.881	22.437	25.691	22.991	3759.615	4339.854	4950.09	4620.317	4049.735	4785.204	735.4691
Mg	0.075	12.944	0	14.932	0	2224.051	0	2877.068	0	1112.026	1438.534	326.5084
K	0.744	43.006	0	51.042	0	7389.334	0	9834.67	0	3694.667	4917.335	1222.668
Na	0.868	1.939	2.078	3.428	3.182	333.1609	401.9351	660.5002	639.4611	367.548	649.9806	282.4326

*0 indicates sample was not digested completely

Quality Control Data

Element	Blank Avg.	Control 7 mg/L	Control 8 mg/L	Spike 7 mg/L	Spike 8 mg/L	Con 7 mg/kg	Con 8 mg/kg	Spk 7 mg/kg	Spk 8 mg/kg	Avg. Con. mg/kg	Avg. Spk. mg/kg	Difference
Ba	0.002	0.902	0.927	1.408	1.32	169.8682	163.2039	271.2906	260.869	166.5361	266.0798	99.54371
Mn	0.009	1.73	1.711	2.174	1.989	325.8005	301.2318	418.882	393.0821	313.5162	405.982	92.46586
Be	0.001	0.718	0.719	1.197	1.082	135.2166	126.5843	230.6356	213.8335	130.9004	222.2345	91.33408
Cd	0.01	0.529	0.498	0.64	0.571	99.6234	87.67589	123.3139	112.8456	93.64964	118.0798	24.43011
Cr	0.016	0.416	0.419	0.937	0.813	78.34278	73.76746	180.5393	160.6716	76.05512	170.6054	94.5503
Cu	0.012	0.966	1.002	1.421	1.353	181.921	176.4081	273.7954	267.3907	179.1645	270.5931	91.42851
Pb	0.1	0.318	0.337	0.773	0.691	59.88703	59.33087	148.9401	136.5609	59.60895	142.7505	83.14157
Ti	0.036	0.989	1.14	1.651	1.615	186.2524	200.7038	318.1114	319.1692	193.4781	318.6403	125.1622
V	0.002	0.61	0.636	1.714	1.614	114.8776	111.9716	330.2501	318.9716	113.4246	324.6108	211.1862
Zn	0.026	0.667	0.649	1.135	1.034	125.6121	114.2603	218.6895	204.3474	119.9362	211.5184	91.58222
Al	0.075	31.852	35.435	37.495	35.7	5998.496	6238.544	7224.462	7055.32	6118.52	7139.891	1021.37
Fe	0.119	64.408	0	70.153	0	12129.57	0	13516.94	0	6064.786	6758.47	693.6838
Ca	0.481	21.432	0	21.678	0	4036.16	0	4176.874	0	2018.08	2088.437	70.35686
Mg	0.144	13.693	0	14.745	0	2578.721	0	2841.037	0	1289.36	1420.519	131.1583
K	0.5	15.048	0	16.874	0	2833.9	0	3251.249	0	1416.95	1625.624	208.6745
Na	0.567	0.857	1.082	1.366	1.152	161.3937	190.4926	263.1981	227.6675	175.9431	245.4328	69.48967

* 0 indicates sample was not digested completely

Quality Control Data

Element	Blank Avg.	Control 9 mg/L	Control 10 mg/L	Spike 9 mg/L	Spike 10 mg/L	Con 9 mg/kg	Con 10 mg/kg	Spk 9 mg/kg	Spk 10 mg/kg	Avg. Con. mg/kg	Avg. Spk. mg/kg	Difference
Ba	0.002	0.87	0.95	1.433	1.431	171.2595	175.6009	275.5774	279.4929	173.4302	277.5351	104.105
Mn	0.005	1.584	1.854	2.203	2.294	311.8104	342.6989	423.6545	448.048	327.2547	435.8513	108.5966
Be	0.001	0.645	0.757	1.16	1.195	126.9683	139.9262	223.0773	233.399	133.4472	228.2382	94.79096
Cd	0.017	0.517	0.59	0.672	0.668	101.7715	109.0574	129.231	130.4691	105.4144	129.85	24.43562
Cr	0.01	0.371	0.449	0.912	0.982	73.03135	82.99451	175.3849	191.7974	78.01293	183.5911	105.5782
Cu	0.007	0.959	1.043	1.484	1.52	188.7792	192.7912	285.3851	296.8758	190.7852	291.1304	100.3452
Pb	0.1	0.319	0.334	0.79	0.797	62.79515	61.73756	151.9233	155.6645	62.26636	153.7939	91.52753
Ti	0.01	1.136	1.224	1.527	1.67	223.6216	226.2478	293.6543	326.1727	224.9347	309.9135	84.9788
V	0	0.57	0.653	1.672	1.825	112.2045	120.7025	321.539	356.4462	116.4535	338.9926	222.5391
Zn	0.016	0.602	0.724	1.125	1.21	118.5037	133.8263	216.3465	236.3287	126.165	226.3376	100.1726
Al	0.075	33.28	36.122	36.958	38.599	6551.168	6676.899	7107.319	7538.886	6614.033	7323.103	709.0694
Fe	0.131	0	0	0	0	0	0	0	0	0	0	0
Ca	0.22	20.527	0	22.522	0	4040.74	0	4331.161	0	2020.37	2165.58	145.2104
Mg	0.092	13.992	14.501	14.618	15.294	2754.325	2680.408	2811.158	2987.117	2717.367	2899.138	181.7709
K	0.5	0	16.477	0	16.696	0	3045.658	0	3260.946	1522.829	1630.473	107.6439
Na	0.284	1.259	0	1.831	0	247.8342	0	352.1159	0	123.9171	176.058	52.1409

* 0 indicates sample was not digested completely

Percent Recoveries of Quality Control Data

Element	Control 1	Control 2	Avg. Con.	Spike 1	Spike 2	Spk 1	Spk 2	% recovery	% recovery	average %	Certified Controls
Ba	0.106496	0.177563	0.142029	0.07485	0.073287	0.08795	0.072513	175.90095	145.02559	160.4632703	161
Mn	0.231496	0.311219	0.271357	0.143005	0.14002	0.096695	0.07158	193.38939	143.15925	168.2743196	298
Be	0.112402	0.141006	0.126704	0.066773	0.065379	0.064527	0.051321	129.05431	102.64179	115.8480526	122
Cd	0.082087	0.10058	0.091333	0.048133	0.047128	0.018067	0.011072	144.53821	88.575549	116.556878	85.4
Cr	0.070079	0.0853	0.077689	0.040942	0.040088	0.051458	0.048412	102.91551	96.82467	99.87008788	71.6
Cu	0.141535	0.204255	0.172895	0.091116	0.089214	0.083784	0.063086	167.56827	126.17197	146.8701227	173
Pb	0.041339	0.062282	0.05181	0.027304	0.026734	0.057996	0.049966	115.99174	99.931574	107.9616583	70.4
Ti	0.140945	0.233849	0.187397	0.098758	0.096697	0.092942	0.069103	185.88356	138.20629	162.044923	326
V	0.089173	0.124371	0.106772	0.056269	0.055095	0.146031	0.114505	116.8248	91.604394	104.2145961	105
Zn	0.133858	0.124371	0.129115	0.068044	0.066623	0.050756	0.048177	101.51298	96.353505	98.93324221	110
Al	4.305118	7.309865	5.807491	3.060548	2.996666	1.590452	1.197034	636.18082	478.81378	557.497303	6070
Fe	8.610827	0	4.305413	2.268953	2.221593	5.767247	-2.22159	11534.494	-4443.187	3545.653839	12500
Ca	3.903937	3.853385	3.878661	2.044054	2.001389	0.095446	0.122211	190.89135	244.42189	217.6566183	3710
Mg	2.709055	2.724178	2.716617	1.431657	1.401774	-0.01776	0.036226	-35.51383	72.451737	18.46895513	2490
K	0	0	0	0	0	0	0	0	0	0	3250
Na	0.21752	0.196325	0.206922	0.109048	0.106772	0.045952	0.035228	91.903876	70.456167	81.18002197	167

Certified control values are in mg/kg

Percent Recoveries of Quality Control Data

Element	Control 3	Control 4	Avg. Con	Spike 3	Spike 4	Spike 3	Spike 4	average %	average %	average %	Certified Controls
Ba	0.159961	0.200951	0.180456	0.100153	0.093657	-0.01065	0.054143	-21.3061	108.28673	43.49031742	161
Mn	0.309478	0.385741	0.34761	0.192923	0.180409	-0.01722	0.056791	-34.44666	113.58123	39.56728898	298
Be	0.122824	0.156084	0.139454	0.077397	0.072377	0.012603	0.048623	25.206263	97.246938	61.22660016	122
Cd	0.089168	0.120342	0.104755	0.058139	0.054368	-0.00544	0.011532	-43.51327	92.256236	24.37148068	85.4
Cr	0.074662	0.097529	0.086095	0.047783	0.044683	0.027817	0.051217	55.634536	102.43338	79.03395614	71.6
Cu	0.178917	0.221293	0.200105	0.111058	0.103854	0.002142	0.055746	4.28367	111.49122	57.88744291	173
Pb	0.053578	0.077186	0.065382	0.036287	0.033933	0.022813	0.048167	45.62562	96.333148	70.97938384	70.4
Ti	0	0.269772	0.134886	0.074862	0.070006	-0.07486	0.131594	-149.7234	263.1884	56.73250951	326
V	0.111412	0.139924	0.125668	0.069746	0.065222	0.062354	0.122178	49.88342	97.742657	73.81303866	105
Zn	0.12824	0.148479	0.138359	0.07679	0.071809	0.01721	0.049391	34.420992	98.782874	66.60193313	110
Al	0	7.513118	3.756559	2.08489	1.949654	-2.08489	2.327146	-833.9561	930.85837	48.45114068	6070
Fe	13.95957	13.86236	13.91097	0	7.219791	0	0.264009	0	528.01735	264.0086765	12500
Ca	4.106576	0	2.053288	1.139575	1.065657	1.282325	-1.06566	2564.6501	-2131.313	216.668472	3710
Mg	2.72824	2.729848	2.729044	1.514619	1.416374	0.093581	0.028026	187.1613	56.052456	121.6068761	2490
K	3.367892	3.310266	3.339079	1.853189	1.732982	0.018511	0.091318	37.022397	182.63608	109.8292386	3250
Na	0.154932	0.179087	0.16701	0.09269	0.086678	0.05891	0.044822	117.81904	89.643748	103.731392	167

Certified control values are in mg/kg

Percent Recoveries of Quality Control Data

Element	Control 5	Control 6	Avg Con.	Spike 5	Spike 6	Spike 5	Spike 6	average %	average %	average %	Certified Controls
Ba	0.140034	0.167698	0.153866	0.079857	0.08001	0.069343	0.05339	138.68677	106.77904	122.7329021	161
Mn	0.248969	0.30677	0.277869	0.144214	0.144492	0.072986	0.056708	145.97151	113.41577	129.6936424	298
Be	0.102577	0.127466	0.115022	0.059696	0.059811	0.053304	0.049989	106.60744	99.977395	103.2924171	122
Cd	0.07354	0.094004	0.083772	0.043478	0.043561	0.018222	0.016239	145.77993	129.90975	137.844841	85.4
Cr	0.015636	0.027466	0.021551	0.011185	0.011206	0.047715	0.045194	95.430119	90.387017	92.9085683	71.6
Cu	0.155155	0.176402	0.165778	0.086039	0.086205	0.067061	0.051295	134.12194	102.59038	118.3561591	173
Pb	0.044502	0.051257	0.047879	0.024849	0.024897	0.052351	0.043303	104.70109	86.605335	95.65321425	70.4
Ti	0.169072	0.205222	0.187147	0.097129	0.097317	0.060871	0.031383	121.7411	62.766807	92.25395422	326
V	0.089347	0.113153	0.10125	0.052549	0.05265	0.117151	0.11425	93.721024	91.400024	92.56052417	105
Zn	0.093986	0.118182	0.106084	0.055058	0.055164	0.049542	0.048836	99.08477	97.672602	98.37868635	110
Al	5.395876	6.540232	5.968054	3.09742	3.103388	1.18008	0.413612	472.03195	165.44473	318.7383376	6070
Fe	10.94278	0	5.471392	2.839652	2.845124	4.663748	-2.84512	9327.4954	-5690.247	1818.623969	12500
Ca	3.759622	4.339845	4.049734	2.101812	2.105861	0.467288	0.193239	934.5765	386.47703	660.5267614	3710
Mg	2.224055	0	1.112027	0.577142	0.578254	0.916058	-0.57825	1832.1155	-1156.509	337.8034364	2490
K	7.389347	0	3.694674	1.917536	1.92123	3.186664	-1.92123	6373.3289	-3842.46	1265.434192	3250
Na	0.333162	0.401934	0.367548	0.190757	0.191125	0.152043	0.127075	304.08531	254.15021	279.1177589	167

Certified control values are in mg/kg

Percent Recoveries of Quality Control Data

Element	Control 7	Control 8	Avg. Con.	Spike 7	Spike 8	Spike 7	Spike 8	average %	average %	average %	Certified Controls
Ba	0.169868	0.163204	0.166536	0.086432	0.084267	0.054368	0.047733	108.73543	95.465366	102.1003957	161
Mn	0.3258	0.301232	0.313516	0.162715	0.158639	0.054685	0.040261	109.36999	80.521418	94.94570486	298
Be	0.135217	0.126585	0.130901	0.067937	0.066236	0.051763	0.041964	103.52524	83.928654	93.72694673	122
Cd	0.099623	0.087676	0.09365	0.048604	0.047387	0.015396	0.009713	123.16643	77.705997	100.4362126	85.4
Cr	0.078343	0.073768	0.076055	0.039473	0.038484	0.054227	0.042816	108.45473	85.63216	97.04344298	71.6
Cu	0.181921	0.176408	0.179165	0.092986	0.090657	0.049114	0.044643	98.227065	89.285347	93.75620574	173
Pb	0.059887	0.059331	0.059609	0.030937	0.030162	0.046363	0.038938	92.725862	77.875696	85.30077932	70.4
Ti	0.186252	0.200704	0.193478	0.100415	0.0979	0.064685	0.0636	129.36954	127.19997	128.2847531	326
V	0.114878	0.111972	0.113425	0.058867	0.057393	0.112533	0.104007	90.02606	83.205677	86.61586881	105
Zn	0.125612	0.114261	0.119936	0.062247	0.060688	0.051253	0.042712	102.50611	85.424456	93.96528424	110
Al	5.998493	6.238556	6.118525	3.175514	3.095974	0.573986	0.474026	229.59424	189.61057	209.602401	6070
Fe	12.12957	0	6.064783	3.147623	3.06878	3.867677	-3.06878	7735.3548	-6137.561	798.8969868	12500
Ca	4.036158	0	2.018079	1.047383	0	1.120417	0	2240.8339	0	1120.416949	3710
Mg	2.578719	0	1.28936	0.669178	0.652416	0.805322	-0.65242	1610.6446	-1304.832	152.9063089	2490
K	2.833898	0	1.416949	0.735397	0	0.952003	0	1904.0068	0	952.0033898	3250
Na	0.161394	0.190493	0.175943	0.091315	0.089027	0.045285	0.026173	90.570878	52.345403	71.4581407	167

Certified control values are in mg/kg

Percent Recoveries of Quality Control Data

Element	Con 9	Con 10	Avg. Con.	Spk 9	Spk 10	Spk 9	Spk 10	average %	average %	average %	Certified Controls
Ba	0.17126	0.175601	0.17343	0.090184	0.088796	0.053116	0.054304	106.2325	108.60738	107.4199397	161
Mn	0.311811	0.342699	0.327255	0.170173	0.167554	0.050127	0.061846	100.25494	123.69102	111.9729795	298
Be	0.126969	0.139926	0.133447	0.069393	0.068325	0.046607	0.051175	93.214825	102.34998	97.78240354	122
Cd	0.101772	0.109057	0.105414	0.054816	0.053972	0.012384	0.012828	99.075774	102.6223	100.8490372	85.4
Cr	0.073031	0.082994	0.078013	0.040567	0.039943	0.050633	0.058257	101.26651	116.51471	108.8906094	71.6
Cu	0.18878	0.192791	0.190785	0.099208	0.097682	0.049192	0.054318	98.383259	108.63582	103.509542	173
Pb	0.062795	0.061738	0.062266	0.032379	0.03188	0.046621	0.04782	93.242945	95.639207	94.44107587	70.4
Ti	0.223622	0.226248	0.224935	0.116966	0.115167	0.035734	0.051833	71.467737	103.66669	87.56721586	326
V	0.112205	0.120702	0.116454	0.060556	0.059624	0.106644	0.122876	85.315318	98.30062	91.80796891	105
Zn	0.118504	0.133826	0.126165	0.065606	0.064597	0.046894	0.056403	93.788304	112.80695	103.2976247	110
Al	6.551181	6.676895	6.614038	3.4393	3.386387	0.2565	0.473513	102.60012	189.40504	146.0025834	6070
Fe	0	0	0	0	0	0	0	0	0	0	12500
Ca	4.040748	0	2.020374	1.050594	1.034431	1.201606	-1.03443	2403.211	-2068.863	167.1740157	3710
Mg	2.754331	2.680407	2.717369	1.413032	1.391293	0.048768	0.138107	97.536571	276.21447	186.8755207	2490
K	0	3.045656	1.522828	0.791871	0.779688	-0.79187	0.889912	-1583.741	1779.824	98.04140481	3250
Na	0.247835	0	0.123917	0.064437	0.063446	0.118663	-0.06345	237.32598	-126.8913	55.21732283	167

Certified control values are in mg/kg

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	P2-1		P2-2		P2-3		P2-4		P2-5		P2-6	
Ba	1.157	223.3589	1.023	202.5745	1.089	217.4679	1.233	241.2919	1.187	224.8107	1.497	292.9554
Mn	5.532	1067.953	4.672	925.1494	5.143	1027.031	6.899	1350.1	6.278	1189.016	7.396	1447.36
Be	0.009	1.73745	0.008	1.58416	0.008	1.59756	0.02	3.9139	0.008	1.515152	0.018	3.52251
Cd	0.115	22.20075	0.103	20.39606	0.113	22.56554	0.138	27.00591	0.113	21.40152	0.154	30.13703
Cr	0.207	39.96135	0.189	37.42578	0.21	41.93595	0.259	50.68501	0.222	42.04547	0.28	54.7946
Cu	0.187	36.10035	0.162	32.07924	0.189	37.74236	0.215	42.07443	0.2	37.8788	0.258	50.48931
Pb	0.248	47.8764	0.203	40.19806	0.229	45.73016	0.274	53.62043	0.242	45.83335	0.365	71.42868
Ti	0.222	42.8571	0.222	43.96044	0.359	71.69051	0.354	69.27603	0.298	56.43941	0.313	61.25254
V	0.424	81.8532	0.389	77.02978	0.42	83.8719	0.534	104.5011	0.492	93.18185	0.574	112.3289
Zn	1.11	214.2855	0.972	192.4754	0.982	196.1005	1.178	230.5287	1.11	210.2273	1.408	275.5386
Al	135.754	26207.31	124.693	24691.71	135.425	27043.7	153.372	30014.13	150.747	28550.58	174.152	34080.68
Fe	177.125	34193.98	154.171	30528.94	155.779	31108.29	197.717	38692.23	191.306	36232.21	239.575	46883.63
Ca	24.884	4803.856	24.778	4906.54	22.322	4457.592	22.214	4347.169	23.878	4522.35	21.611	4229.165
Mg	16.931	3268.53	17.655	3496.043	16.429	3280.789	16.55	3238.752	18.136	3434.85	15.001	2935.621
K	8.483	1637.643	9.673	1915.447	10.539	2104.586	10.539	2062.43	9.998	1893.561	7.942	1554.21
Na	0.777	149.9999	0.759	150.2972	1.195	238.6355	0.795	155.5775	0.93	176.1364	0.66	129.1587

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	P2-7		P2-8		P2-9		P2-10		P2-11		P2-12	
Ba	1.537	295.5774	1.134	224.1102	1.147	220.154	1.003	199.8006	1.002	199.2046	1.075	212.0319
Mn	7.746	1489.618	4.481	885.5711	4.823	925.7218	3.878	772.5092	4.142	823.4586	4.457	879.0942
Be	0.014	2.692312	0.008	1.581024	0.008	1.535512	0.007	1.394421	0.007	1.391649	0.008	1.577912
Cd	0.18	34.61544	0.098	19.36754	0.118	22.6488	0.084	16.73305	0.087	17.29621	0.097	19.13218
Cr	0.341	65.57703	0.189	37.35169	0.207	39.73137	0.197	39.24299	0.183	36.38168	0.239	47.14012
Cu	0.28	53.84624	0.18	35.57304	0.179	34.35708	0.155	30.87647	0.161	32.00793	0.172	33.92511
Pb	0.435	83.65398	0.261	51.58091	0.255	48.94445	0.194	38.64538	0.211	41.94828	0.25	49.30975
Ti	0.278	53.46162	0.192	37.94458	0.244	46.83312	0.273	54.38242	0.21	41.74947	0.282	55.6214
V	0.625	120.1925	0.417	82.41088	0.443	85.02898	0.332	66.1354	0.314	62.4254	0.371	73.17567
Zn	1.657	318.6544	1.022	201.9758	1.015	194.8181	0.845	168.3265	0.889	176.7394	1.017	200.5921
Al	181.203	34846.79	132.711	26227.41	137.653	26420.98	128.887	25674.68	119.656	23788.45	138.196	27257.64
Fe	276.177	53111.05	165.593	32725.81	175.559	33696.62	136.729	27236.83	142.549	28339.74	153.036	30184.67
Ca	20.978	4034.237	23.12	4569.159	24.638	4728.993	24.813	4942.824	26.188	5206.358	24.046	4742.809
Mg	14.657	2818.658	17.263	3411.652	17.975	3450.104	17.96	3577.686	17.669	3512.721	18.003	3550.894
K	7.184	1381.541	8.374	1654.937	9.565	1835.897	10.431	2077.886	9.024	1794.034	10.323	2036.098
Na	0.696	133.8464	0.66	130.4345	0.849	162.9562	0.899	179.0835	0.629	125.0496	0.777	153.2547

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	P2-13		P2-14		P2-15		P2-16		P2-17		P2-18	
Ba	1.873	375.3511	1.09	214.5665	0.99	195.2666	1.002	198.416	1.99	371.2683	0.995	192.0848
Mn	8.163	1635.873	4.44	874.014	4.186	825.6425	3.888	769.9018	8.231	1535.633	3.926	757.9143
Be	0.016	3.206416	0.008	1.5748	0.007	1.380673	0.007	1.38614	0.018	3.358206	0.007	1.35135
Cd	0.196	39.2786	0.118	23.2283	0.105	20.7101	0.106	20.99012	0.217	40.48504	0.108	20.8494
Cr	0.38	76.15238	0.226	44.4881	0.216	42.60362	0.204	40.39608	0.474	88.43276	0.201	38.80305
Cu	0.341	68.33674	0.181	35.62985	0.173	34.12235	0.157	31.08914	0.336	62.68651	0.156	30.1158
Pb	0.493	98.79769	0.314	61.8109	0.252	49.70423	0.34	67.3268	0.554	103.3581	0.252	48.6486
Ti	0.538	107.8157	0.278	54.7243	0.261	51.47938	0.275	54.4555	0.573	106.9029	0.236	45.5598
V	0.655	131.2627	0.377	74.21245	0.348	68.63917	0.348	68.91096	0.731	136.3805	0.342	66.0231
Zn	1.87	374.7499	1.101	216.7319	0.995	196.2528	0.98	194.0596	2.112	394.0295	0.986	190.3473
Al	215.674	43221.29	126.874	24975.15	116.335	22945.8	117.965	23359.43	238.4	44477.57	117.154	22616.58
Fe	293.312	58780.02	173.109	34076.51	156.605	30888.61	158.091	31305.18	336.702	62817.48	166.288	32101.9
Ca	21.653	4339.283	24.63	4848.416	25.213	4972.987	26.211	5190.302	22.202	4142.161	25.669	4955.4
Mg	15.382	3082.568	17.452	3435.426	17.657	3482.649	17.542	3473.667	14.628	2729.102	17.091	3299.418
K	7.329	1468.739	8.397	1652.949	7.992	1576.334	8.397	1662.774	7.566	1411.566	8.16	1575.288
Na	0.277	55.51108	0.443	87.20455	0.413	81.45971	0.599	118.614	0.257	47.94772	0.473	91.31265

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	P2-19		P2-20		P2-21		P2-22		P2-23		P2-24	
Ba	1.753	337.7645	1.327	270.8168	1.941	388.9783	2.299	440.4217	0.941	183.0744	0.949	182.8514
Mn	6.872	1324.083	4.987	1017.757	7.505	1504.01	8.797	1685.25	3.222	626.8498	3.216	619.6524
Be	0.016	3.082848	0.01	2.04082	0.017	3.406817	0.021	4.022991	0.007	1.361871	0.007	1.348746
Cd	0.206	39.69167	0.162	33.06128	0.215	43.08622	0.254	48.65903	0.094	18.28798	0.1	19.2678
Cr	0.416	80.15405	0.301	61.42868	0.426	85.37083	0.529	101.3411	0.162	31.51759	0.173	33.33329
Cu	0.299	57.61072	0.217	44.28579	0.349	69.93995	0.403	77.20311	0.141	27.43197	0.142	27.36028
Pb	0.517	99.61453	0.396	80.81647	0.56	112.2246	0.659	126.2453	0.208	40.46702	0.214	41.23309
Ti	0.56	107.8997	0.413	84.28587	0.552	110.6214	0.622	119.1572	0.211	41.05068	0.254	48.94021
V	0.678	130.6357	0.496	101.2247	0.72	144.2887	0.852	163.2185	0.328	63.81338	0.347	66.85927
Zn	1.921	370.1344	1.371	279.7964	2.064	413.6277	2.525	483.7168	0.939	182.6853	0.941	181.31
Al	216.863	41784.73	161.573	32974.14	231.655	46423.89	274.282	52544.48	116.053	22578.46	122.123	23530.42
Fe	297.912	57401.09	213.458	43562.94	326.788	65488.64	382.069	73193.34	150.212	29224.2	154.608	29789.56
Ca	23.032	4437.76	24.124	4923.274	21.74	4356.718	22.394	4290.041	27.21	5293.787	27.185	5237.951
Mg	15.577	3001.345	16.046	3274.7	14.454	2896.596	15.046	2882.377	17.845	3471.798	18.312	3528.32
K	9.109	1755.104	8.99	1834.697	7.329	1468.739	6.973	1335.825	8.634	1679.771	9.346	1800.769
Na	0.277	53.37181	0.514	104.8981	0.176	35.27058	0.186	35.63221	0.529	102.9185	0.433	83.42957

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	P2-25		P2-26		E2-38		E2-39		E2-40		G1-25	
Ba	0.991	184.544	0.941	183.431	0.781	139.9638	0.75	136.3635	0.758	141.1548	1.018	200.0004
Mn	2.965	552.1423	2.748	535.6731	6.586	1180.284	5.525	1004.544	5.924	1103.167	9.715	1908.648
Be	0.006	1.11732	0.006	1.169592	0.009	1.612899	0.008	1.454544	0.009	1.67598	0.009	1.768176
Cd	0.09	16.7598	0.077	15.00976	0.12	21.50532	0.147	26.72725	0.141	26.25702	0.107	21.02165
Cr	0	0	0	0	0.227	40.6809	0.231	41.99996	0.22	40.9684	0.704	138.3107
Cu	0.15	27.933	0.125	24.3665	0.166	29.74903	0.161	29.2727	0.16	29.7952	0.342	67.19069
Pb	0.188	35.00936	0.201	39.18133	0.246	44.08591	0.282	51.27268	0.238	44.32036	0.856	168.1732
Ti	0.257	47.85854	0.266	51.85191	0.14	25.08954	0.154	27.99997	0.16	29.7952	0.225	44.2044
V	0.367	68.34274	0.351	68.42113	0.42	75.26862	0.418	75.99992	0.421	78.39862	0.355	69.74472
Zn	0.878	163.5012	0.857	167.0567	1.313	235.304	1.287	233.9998	1.302	242.4584	1.775	348.7236
Al	121.931	22705.99	116.579	22724.98	124.895	22382.56	122.9	22345.43	124.023	23095.56	93.451	18359.76
Fe	143.161	26659.44	135.756	26463.19	211.972	37987.71	192.981	35087.42	197.807	36835.62	174.776	34337.19
Ca	28.886	5379.151	26.539	5173.3	22.969	4116.297	20.983	3815.087	21.236	3954.568	161.411	31711.45
Mg	19.278	3589.949	17.371	3386.164	22.751	4077.229	23.027	4186.723	21.945	4086.598	40.264	7910.426
K	22.768	4239.857	25.149	4902.345	10.124	1814.332	9.796	1781.089	10.453	1946.558	15.048	2956.39
Na	1.5	279.33	1.5	292.398	0.963	172.5802	0.888	161.4544	0.879	163.6874	2.326	456.9753

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	E2-32		E2-33		E2-34		E2-35		E2-36		E2-37	
Ba	0.855	165.3775	0.866	160.3702	1.027	177.9894	0.834	163.851	0.805	152.174	0.835	157.547
Mn	9.397	1817.605	8.187	1516.11	7.24	1254.764	6.575	1291.751	6.171	1166.541	6.463	1219.432
Be	0.01	1.93424	0.01	1.85185	0.011	1.90641	0.008	1.571712	0.009	1.701324	0.009	1.698111
Cd	0.168	32.49523	0.159	29.44442	0.183	31.71573	0.155	30.45192	0.147	27.78829	0.149	28.11317
Cr	0.231	44.68094	0.227	42.037	0.274	47.48694	0.204	40.07866	0.2	37.8072	0.227	42.83013
Cu	0.179	34.6229	0.189	34.99997	0.248	42.98088	0.172	33.79181	0.165	31.19094	0.172	32.45279
Pb	0.282	54.54557	0.312	57.77772	0.319	55.28589	0.238	46.75843	0.26	49.14936	0.253	47.73579
Ti	0.187	36.17029	0.185	34.25923	0.275	47.66025	0.17	33.39888	0.146	27.59926	0.193	36.41505
V	0.413	79.88411	0.429	79.44437	0.496	85.96176	0.396	77.79974	0.379	71.64464	0.42	79.24518
Zn	1.462	282.7859	1.543	285.7405	1.653	286.4814	1.364	267.9769	1.36	257.089	1.394	263.0185
Al	119.571	23127.9	123.385	22849.05	149.877	25975.18	118.412	23263.7	112.237	21216.83	125.372	23655.06
Fe	215.211	41626.97	222.042	41118.85	251.137	43524.55	199.919	39276.89	198.622	37546.71	206.378	38939.19
Ca	28.591	5530.186	27.202	5037.402	24.082	4173.651	23.479	4612.778	22.832	4316.07	23.931	4515.277
Mg	24.003	4642.756	24.897	4610.551	25.638	4443.322	23.459	4608.849	23.135	4373.348	25.01	4718.862
K	9.139	1767.702	9.577	1773.517	11.986	2077.294	9.139	1795.484	8.153	1541.211	10.124	1910.186
Na	0.945	182.7857	0.982	181.8517	0.954	165.3377	0.982	192.9276	1.024	193.5729	1.02	192.4526

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	G1-1		G1-2		G1-3		G1-4		G1-5		G1-6	
Ba	0.904	175.8759	0.89	166.9791	0.926	168.9783	0.961	177.6341	0.908	172.6235	1.013	192.9522
Mn	7.514	1461.871	7.877	1477.859	8.247	1504.929	8.562	1582.626	8.57	1629.277	9.361	1783.046
Be	0.008	1.556424	0.008	1.500936	0.008	1.459856	0.008	1.478744	0.008	1.520912	0.008	1.523808
Cd	0.085	16.53701	0.08	15.00936	0.095	17.33579	0.093	17.1904	0.093	17.6806	0.061	11.61904
Cr	0.125	24.31913	0.068	12.75796	0.119	21.71536	0.105	19.40852	0.088	16.73003	0.125	23.8095
Cu	0.24	46.69272	0.244	45.77855	0.263	47.99277	0.268	49.53792	0.249	47.33839	0.268	51.04757
Pb	0.394	76.65388	0.4	75.0468	0.438	79.92712	0.432	79.85218	0.419	79.65777	0.426	81.14278
Ti	0.227	44.16353	0.162	30.39395	0.169	30.83946	0.19	35.12017	0.141	26.80607	0.156	29.71426
V	0.347	67.50989	0.317	59.47459	0.351	64.05118	0.351	64.87989	0.323	61.40682	0.356	67.80946
Zn	1.454	282.8801	1.406	263.7895	1.581	288.504	1.559	288.1702	1.545	293.7261	1.563	297.714
Al	94.99	18480.59	83.304	15629.25	88.344	16121.19	92.582	17113.13	82.71	15724.33	91.908	17506.27
Fe	155.804	30312.14	155.344	29145.18	164.775	30068.47	167.764	31010	161.308	30666.91	172.915	32936.16
Ca	77.652	15107.43	89.043	16705.98	87.477	15962.98	91.317	16879.31	85.847	16320.72	100.998	19237.7
Mg	21.254	4135.029	21.107	3960.032	22.162	4044.166	22.053	4076.343	20.357	3870.151	21.145	4027.615
K	32.887	6398.265	25.149	4718.38	26.637	4860.773	27.53	5088.728	22.768	4328.516	27.232	5187.042
Na	4.982	969.263	4.274	801.8751	3.717	678.2856	3.696	683.1797	3.3	627.3762	3.964	755.0469

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	G1-7		G1-8		G1-9		G1-10		G1-11		G1-12	
Ba	0.98	192.1564	0.915	177.6701	0.972	185.1427	0.999	189.9239	1.037	195.292	1.027	202.165
Mn	9.611	1884.506	8.969	1741.556	9.592	1827.046	9.484	1803.041	10.588	1993.975	10.573	2081.295
Be	0.009	1.764702	0.008	1.5534	0.009	1.714284	0.009	1.711026	0.011	2.071564	0.011	2.16535
Cd	0.069	13.52938	0.102	19.80585	0.103	19.61903	0.105	19.96197	0.123	23.16385	0.083	16.33855
Cr	0.108	21.17642	0.142	27.57285	0.171	32.5714	0.182	34.60075	0.512	96.42189	0.537	105.7085
Cu	0.259	50.7842	0.243	47.18453	0.281	53.52376	0.279	53.04181	0.287	54.04899	0.284	55.9054
Pb	0.471	92.35274	0.451	87.57293	0.483	91.99991	0.471	89.54369	0.514	96.79854	0.527	103.74
Ti	0.147	28.82347	0.167	32.42723	0.148	28.19045	0.164	31.1787	0.175	32.9567	0.211	41.53535
V	0.338	66.27436	0.335	65.04863	0.35	66.6666	0.372	70.72241	0.377	70.99815	0.394	77.5589
Zn	1.567	307.2542	1.521	295.3402	1.63	310.4759	1.644	312.5474	1.837	345.9512	1.839	362.0072
Al	85.837	16830.75	87.226	16937.11	89.49	17045.7	98.123	18654.56	94.225	17744.83	94.004	18504.69
Fe	169.699	33274.24	161.413	31342.37	165.905	31600.92	171.468	32598.47	190.804	35932.97	192.957	37983.59
Ca	84.9	16647.02	74.756	14515.75	92.071	17537.32	92.301	17547.71	88.346	16637.67	90.636	17841.7
Mg	20.08	3937.246	20.007	3884.859	21.113	4021.52	21.803	4145.056	24.245	4565.915	23.26	4578.731
K	22.768	4464.304	26.339	5114.375	22.768	4336.758	28.69	5454.371	10.218	1924.295	10.336	2034.642
Na	3.075	602.9399	2.817	546.991	2.7	514.2852	3.182	604.9427	1.152	216.9492	1.281	252.1649

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	G1-13		G1-14		G1-15		G1-16		G1-17		G1-18	
Ba	0.975	190.4302	1.122	222.1784	1.121	217.6702	1.105	206.9289	1.103	208.5067	0.996	194.5317
Mn	10.841	2117.388	10.785	2135.646	10.286	1997.284	10.304	1929.589	10.393	1964.651	9.644	1883.599
Be	0.011	2.148443	0.011	2.17822	0.011	2.135925	0.011	2.059926	0.011	2.079396	0.01	1.95313
Cd	0.096	18.75005	0.117	23.16834	0.036	6.9903	0.112	20.97379	0.118	22.30625	0.064	12.50003
Cr	0.618	120.7034	0.518	102.5744	0.509	98.83508	0.568	106.3671	0.534	100.9452	0.478	93.35961
Cu	0.262	51.17201	0.318	62.97036	0.323	62.71853	0.346	64.79404	0.35	66.1626	0.324	63.28141
Pb	0.558	108.9847	0.565	111.8813	0.622	120.7769	0.682	127.7154	0.615	116.2571	0.672	131.2503
Ti	0.263	51.36732	0.204	40.39608	0.209	40.58258	0.226	42.32212	0.239	45.1796	0.191	37.30478
V	0.416	81.25021	0.38	75.2476	0.38	73.7865	0.383	71.72288	0.382	72.21175	0.339	66.21111
Zn	1.926	376.1728	1.921	380.3964	1.953	379.2238	1.975	369.8504	1.983	374.8584	1.86	363.2822
Al	89.43	17466.84	95.048	18821.4	98.279	19083.32	100.856	18886.9	103.604	19584.89	87.574	17104.34
Fe	187.825	36684.66	187.112	37051.92	192.596	37397.33	199.347	37330.92	192.526	36394.34	170.382	33277.82
Ca	114.319	22327.99	132.361	26210.13	119.11	23128.18	97.343	18229.03	92.09	17408.33	86.057	16808.05
Mg	24.094	4705.871	23.112	4576.638	24.093	4678.258	25.09	4698.504	24.183	4571.458	22.505	4395.519
K	11.985	2340.826	10.336	2046.735	10.218	1984.08	10.69	2001.874	11.043	2087.525	8.805	1719.731
Na	1.206	235.5475	1.291	255.6438	1.241	240.9712	1.236	231.4608	1.057	199.8111	1.077	210.3521

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	G1-19		G1-20		G1-21		G1-22		G1-23		G1-24	
Ba	1.151	223.4954	1.185	223.5846	1.213	237.378	1.146	222.5246	1.842	346.2407	1.083	216.6
Mn	11.185	2171.847	11.06	2086.79	10.97	2146.774	8.911	1730.293	17.222	3237.219	10.044	2008.8
Be	0.011	2.135925	0.011	2.075469	0.011	2.152645	0.01	1.94175	0.018	3.38346	0.01	2
Cd	0.078	15.14565	0.083	15.66036	0.041	8.023495	0.034	6.60195	0.196	36.84212	0.11	22
Cr	0.605	117.4759	0.661	124.7168	0.652	127.5931	0.627	121.7477	1.366	256.767	0.742	148.4
Cu	0.396	76.8933	0.395	74.52821	0.4	78.278	0.398	77.28165	0.739	138.9098	0.401	80.2
Pb	0.672	130.4856	0.653	123.2074	0.685	134.0511	0.685	133.0099	1.311	246.4287	0.894	178.8
Ti	0.205	39.80588	0.256	48.30182	0.183	35.81219	0.189	36.69908	0.359	67.48123	0.218	43.6
V	0.382	74.17485	0.409	77.16971	0.356	69.66742	0.349	67.76708	0.597	112.2181	0.346	69.2
Zn	2.099	407.5733	2.044	385.6599	2.042	399.6092	1.782	346.0199	3.249	610.7145	1.83	366
Al	103.262	20050.9	109.43	20647.14	97.273	19035.84	91.248	17718.08	151.308	28441.36	91.311	18262.2
Fe	188.58	36617.52	189.134	35685.61	192.702	37710.82	184.837	35890.72	314.556	59127.09	180.461	36092.2
Ca	115.09	22347.6	184.173	34749.58	74.563	14591.61	153.851	29874.02	177.729	33407.72	180.474	36094.8
Mg	25.515	4954.375	46.563	8785.46	15.756	3083.37	38.072	7392.631	43.518	8180.078	41.547	8309.4
K	10.336	2006.993	24.117	4550.371	5.507	1077.692	15.165	2944.664	18.463	3470.49	14.459	2891.8
Na	1.027	199.4177	4.319	814.9046	1.157	226.4191	3.405	661.1659	3.694	694.3612	2.84	568

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	E2-20		E2-21		E2-22		E2-23		E2-24		E2-25	
Ba	0.731	141.3929	0.743	141.2547	0.774	148.8464	0.792	151.1453	0.725	143.8494	0.752	147.4507
Mn	14.977	2896.911	15.175	2884.98	14.571	2802.12	14.413	2750.577	12.725	2524.805	12.888	2527.053
Be	0.009	1.740816	0.009	1.711026	0.009	1.730772	0.009	1.71756	0.008	1.587304	0.009	1.764702
Cd	0.143	27.65963	0.138	26.23573	0.149	28.65389	0.147	28.05348	0.151	29.96036	0.145	28.43131
Cr	0.188	36.36371	0.2	38.0228	0.227	43.65392	0.22	41.9848	0.216	42.85721	0.204	39.99991
Cu	0.26	50.29024	0.268	50.95055	0.264	50.76931	0.251	47.90084	0.238	47.22229	0.244	47.84303
Pb	0.238	46.03491	0.238	45.24713	0.246	47.30777	0.238	45.41992	0.216	42.85721	0.253	49.60773
Ti	0.129	24.9517	0.142	26.99619	0.172	33.07698	0.232	44.27488	0.161	31.94449	0.161	31.56856
V	0.365	70.59976	0.368	69.96195	0.41	78.84628	0.424	80.91616	0.389	77.18266	0.408	79.99982
Zn	1.12	216.6349	1.153	219.2014	1.159	222.885	1.176	224.4278	1.144	226.9845	1.168	229.0191
Al	106.742	20646.46	113.355	21550.37	121.137	23295.61	125.652	23979.43	113.808	22580.99	117.378	23015.24
Fe	185.463	35873	191.167	36343.52	195.07	37513.52	202.837	38709.41	188.088	37319.1	196.257	38481.68
Ca	60.106	11625.94	56.063	10658.36	57.817	11118.67	55.609	10612.42	45.863	9099.815	40.234	7889.002
Mg	23.119	4471.769	25.003	4753.42	24.685	4747.123	25.949	4952.107	23.615	4685.523	22.084	4330.187
K	7.715	1492.266	8.81	1674.904	10.343	1989.042	11.22	2141.225	9.139	1813.296	7.934	1555.683
Na	1.292	249.9038	1.568	298.0988	1.289	247.885	1.245	237.5958	1.081	214.4845	0.996	195.2937

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	E2-26		E2-27		E2-28		E2-29		E2-30		E2-31	
Ba	0.918	164.8113	0.738	146.7196	0.853	159.1417	0.795	156.805	1.279	229.2109	1.252	232.7142
Mn	15.5	2782.762	11.272	2240.953	11.17	2083.953	10.552	2081.266	16.944	3036.551	17.276	3211.159
Be	0.011	1.974863	0.009	1.789263	0.009	1.679103	0.009	1.775151	0.015	2.688165	0.017	3.159858
Cd	0.187	33.57267	0.147	29.22463	0.168	31.34326	0.143	28.20518	0.229	41.03932	0.239	44.42389
Cr	0.258	46.31951	0.216	42.94231	0.231	43.09698	0.204	40.23676	0.317	56.80989	0.371	68.95925
Cu	0.279	50.08971	0.193	38.36975	0.197	36.7537	0.177	34.9113	0.284	50.89592	0.295	54.83283
Pb	0.297	53.3213	0.26	51.68982	0.268	49.99996	0.282	55.6214	0.429	76.88152	0.51	94.79574
Ti	0.2	35.9066	0.135	26.83895	0.168	31.34326	0.138	27.21898	0.284	50.89592	0.28	52.04472
V	0.494	88.6893	0.394	78.32996	0.443	82.64918	0.402	79.29008	0.668	119.7129	0.655	121.7475
Zn	1.463	262.6568	1.261	250.6956	1.348	251.4923	1.015	200.1976	1.844	330.4651	2.152	400.0008
Al	144.918	26017.56	114.794	22821.85	129.062	24078.71	117.976	23269.47	188.275	33740.95	177.757	33040.4
Fe	246.298	44218.62	206.157	40985.45	216.026	40303.32	205.593	40550.96	321.207	57563.83	322.163	59881.73
Ca	45.274	8128.177	34.356	6830.213	32.767	6113.241	29.037	5727.229	33.176	5945.504	31.228	5804.473
Mg	25.662	4607.176	23.047	4581.905	25.181	4697.944	23.631	4660.955	25.071	4492.999	23.252	4321.942
K	9.029	1621.003	8.81	1751.49	10.343	1929.662	9.139	1802.567	10.562	1892.827	9.029	1678.256
Na	1.184	212.5671	1.203	239.1648	1.043	194.5894	0.959	189.1522	1.071	191.935	1.278	237.547

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	E2-2		E2-3		E2-4		E2-5		E2-6		E2-7	
Ba	0.795	156.165	0.794	154.175	0.768	150.5879	0.791	147.0263	0.759	149.4092	0.794	152.1074
Mn	17.86	3508.311	16.724	3247.383	15.537	3046.464	16.294	3028.631	16.127	3174.6	16.122	3088.508
Be	0.009	1.767906	0.009	1.747575	0.009	1.764702	0.009	1.672866	0.008	1.5748	0.009	1.724139
Cd	0.074	14.53612	0.078	15.14565	0.069	13.52938	0.081	15.05579	0.071	13.97635	0.069	13.2184
Cr	0.208	40.85827	0.211	40.97093	0.189	37.05874	0.189	35.13019	0.186	36.6141	0.201	38.50577
Cu	0.359	70.51981	0.383	74.36903	0.318	62.3528	0.337	62.63954	0.29	57.0865	0.247	47.31804
Pb	0.229	44.98339	0.21	40.77675	0.204	39.99991	0.223	41.4499	0.204	40.1574	0.223	42.72033
Ti	0.2	39.2868	0.207	40.19423	0.196	38.43129	0.188	34.94431	0.189	37.20465	0.223	42.72033
V	0.389	76.41283	0.393	76.31078	0.367	71.96063	0.376	69.88862	0.364	71.6534	0.396	75.86212
Zn	1.077	211.5594	1.012	196.5051	0.974	190.98	0.987	183.4576	0.964	189.7634	0.98	187.7396
Al	110.998	21803.78	115.009	22331.87	106.851	20951.13	107.854	20047.25	106.83	21029.49	116.336	22286.6
Fe	202.5	39777.89	196.239	38104.71	185.189	36311.49	189.6	35241.71	182.385	35902.49	188.563	36123.2
Ca	41.077	8068.919	100.554	19525.07	73.334	14379.18	91.142	16940.93	88.411	17403.71	93.861	17981.05
Mg	19.249	3781.158	45.725	8878.652	32.668	6405.476	38.321	7122.878	33.273	6549.79	39.241	7517.438
K	5.507	1081.762	17.055	3311.655	11.514	2257.642	13.988	2600.006	13.752	2707.081	16.932	3243.68
Na	0.617	121.1998	2.645	513.5929	1.696	332.5483	2.031	377.5101	1.691	332.8734	2.371	454.2148

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	E2-8		E2-9		E2-10		E2-11		E2-12		E2-13	
Ba	0.745	143.2695	0.789	145.5721	1.252	245.9729	0.793	149.6224	0.711	137.2586	0.813	151.9627
Mn	15.815	3041.351	16.621	3066.608	30.537	5999.421	17.165	3238.675	14.731	2843.82	16.076	3004.862
Be	0.008	1.538464	0.009	1.660518	0.018	3.536352	0.009	1.698111	0.008	1.5444	0.009	1.682244
Cd	0.071	13.65387	0.117	21.58673	0.156	30.64838	0.12	22.64148	0.068	13.1274	0.123	22.99067
Cr	0.183	35.19236	0.229	42.25096	0.16	31.43424	0.208	39.24523	0.192	37.0656	0.217	40.56077
Cu	0.242	46.53854	0.26	47.97052	0.484	95.08858	0.299	56.41502	0.272	52.5096	0.328	61.30845
Pb	0.197	37.88468	0.21	38.74542	0.444	87.23002	0.216	40.75466	0.21	40.5405	0.229	42.80376
Ti	0.166	31.92313	0.258	47.60152	0.313	61.49323	0.181	34.1509	0.162	31.2741	0.228	42.61685
V	0.371	71.34627	0.412	76.01482	0.679	133.3991	0.397	74.90556	0.359	69.30495	0.424	79.25238
Zn	1.001	192.5003	1.044	192.6201	1.982	389.3916	1.099	207.3582	1.007	194.4014	1.136	212.3366
Al	109.082	20977.34	124.491	22968.84	188.233	36981.01	116.592	21998.46	107.088	20673.34	126.437	23633.1
Fe	182.412	35079.29	184.081	33963.31	345.171	67813.68	201.313	37983.54	184.336	35586.06	201.085	37586
Ca	61.119	11753.67	64.583	11915.69	105.7	20766.24	64.78	12222.63	57.86	11169.87	62.704	11720.38
Mg	24.4	4692.315	27.015	4984.322	40.851	8025.751	26.468	4993.956	24.182	4668.335	25.87	4835.517
K	9.394	1806.541	12.456	2298.157	14.577	2863.856	8.923	1683.583	8.923	1722.585	11.514	2152.151
Na	0.907	174.4234	1.182	218.0814	1.951	383.3013	1.092	206.0375	0.822	158.6871	1.381	258.131

Results Expressed in mg/L (first column) and mg/kg (second column)

Element	E2-14		E2-15		E2-16		E2-17		E2-18		E2-19	
Ba	0.75	139.1468	0.743	139.9247	0.703	134.9331	0.763	143.1518	0.794	147.8587	0.763	140.2577
Mn	14.544	2698.334	14.683	2765.161	14.328	2750.102	16.184	3036.394	15.999	2979.334	16.405	3015.633
Be	0.008	1.484232	0.008	1.506592	0.008	1.535512	0.009	1.688553	0.009	1.67598	0.009	1.654416
Cd	0.105	19.48055	0.101	19.02072	0.098	18.81002	0.145	27.20447	0.147	27.37434	0.143	26.28683
Cr	0.192	35.62157	0.195	36.72318	0.183	35.12484	0.212	39.7748	0.22	40.9684	0.208	38.23539
Cu	0.254	47.12437	0.275	51.7891	0.226	43.37821	0.249	46.71663	0.249	46.36878	0.251	46.13982
Pb	0.204	37.84792	0.178	33.52167	0.191	36.66035	0.201	37.71102	0.238	44.32036	0.216	39.70598
Ti	0.153	28.38594	0.14	26.36536	0.106	20.34553	0.158	29.64349	0.165	30.7263	0.129	23.7133
V	0.38	70.50102	0.375	70.6215	0.347	66.60283	0.389	72.98301	0.404	75.23288	0.393	72.24283
Zn	0.982	182.1895	0.965	181.7327	0.947	181.7662	1.086	203.7521	1.123	209.1251	1.153	211.9491
Al	116.432	21601.51	115.57	21764.6	106.632	20466.84	117.005	21952.13	122.242	22763.91	116.819	21474.14
Fe	183.888	34116.56	181.858	34248.23	174.591	33510.82	185.986	34894.14	192.092	35771.37	194.97	35840.17
Ca	71.313	13230.63	76.022	14316.77	70.103	13455.5	66.831	12538.63	66.597	12401.69	61.888	11376.5
Mg	27.272	5059.747	26.514	4993.223	23.932	4593.484	24.083	4518.38	26.227	4883.992	25.491	4685.858
K	11.985	2223.565	11.75	2212.807	8.687	1667.374	9.686	1817.258	10.343	1926.073	9.467	1740.262
Na	1.436	266.4196	1.172	220.7157	1.117	214.3959	1.287	241.4631	1.292	240.5962	1.31	240.8094

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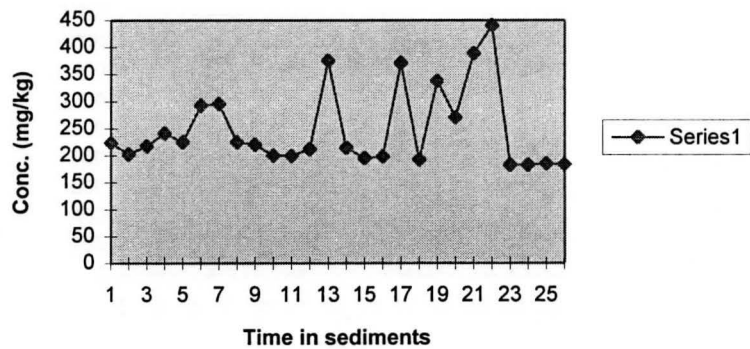
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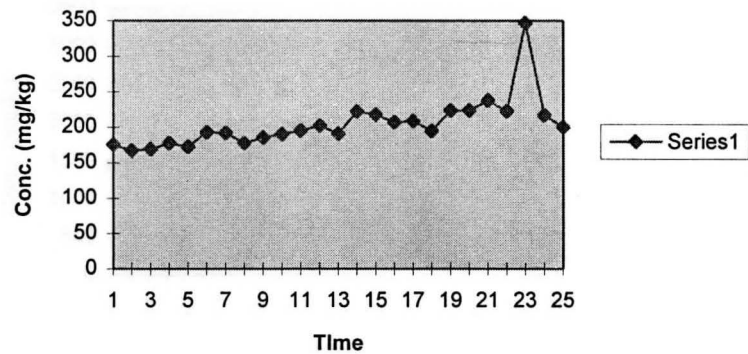
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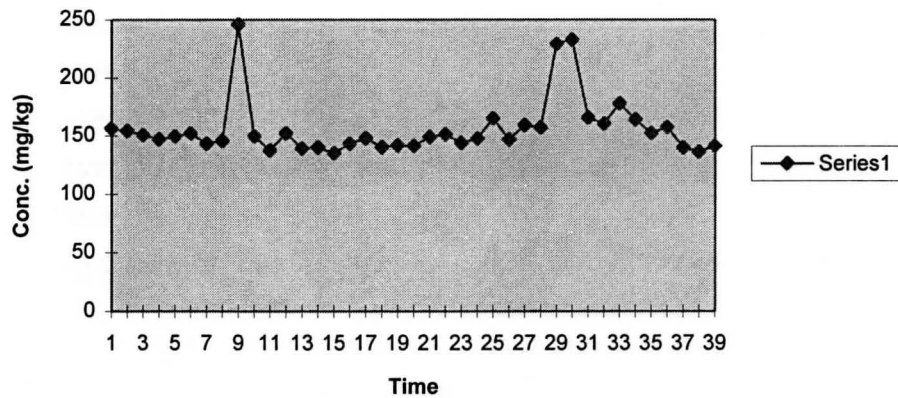
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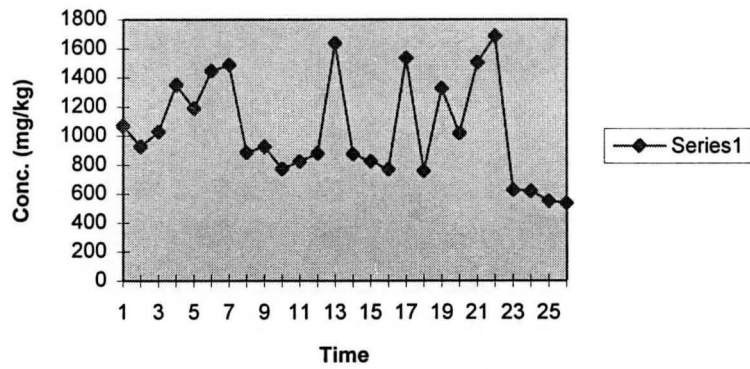
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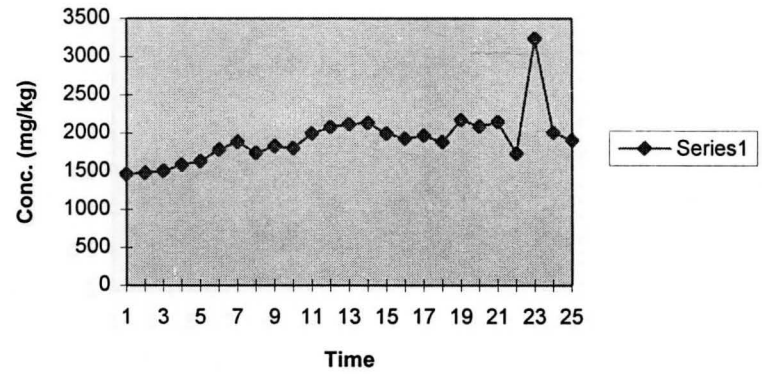
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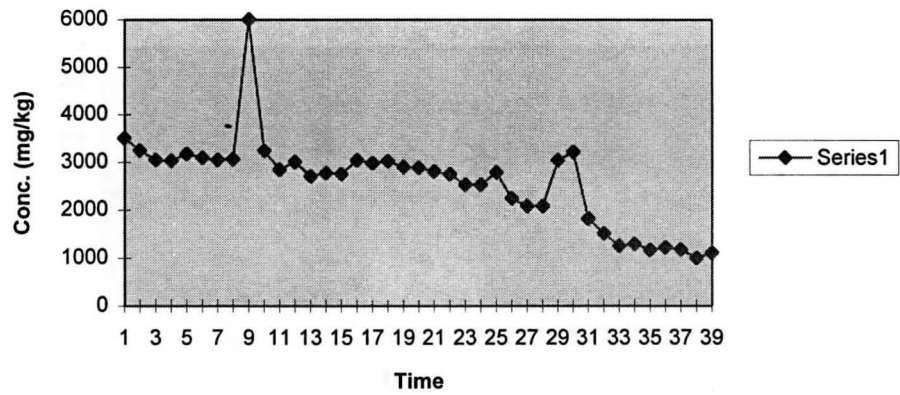
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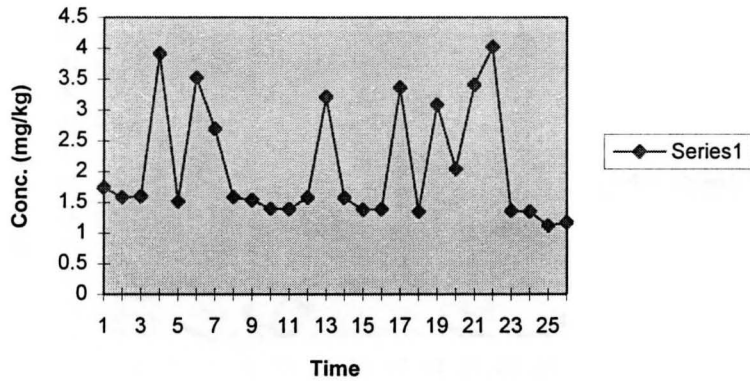
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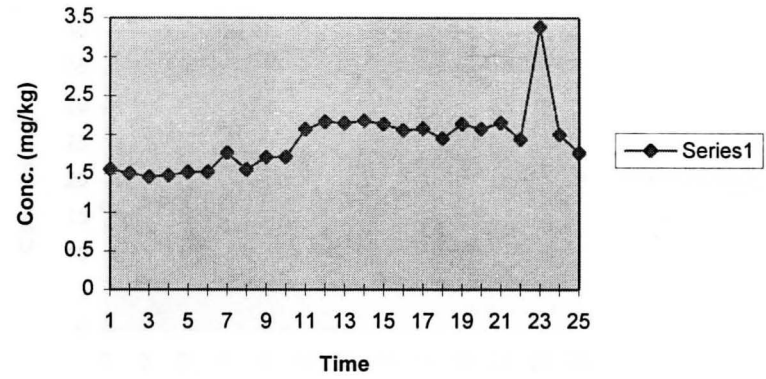
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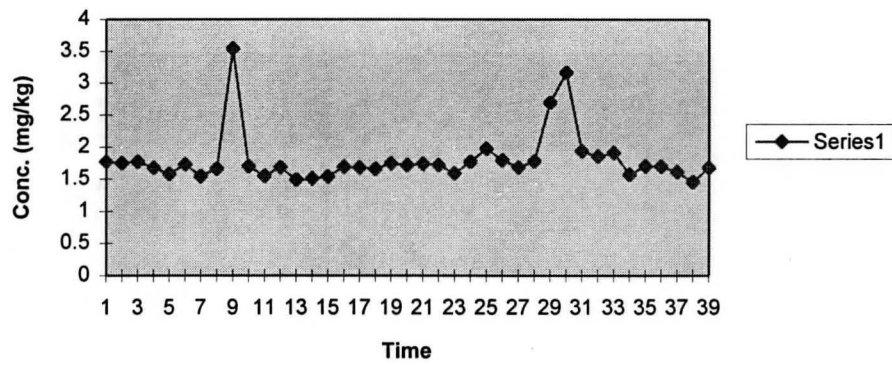
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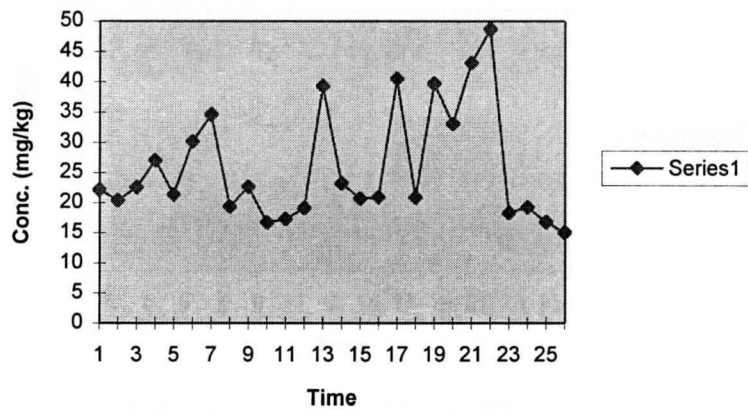
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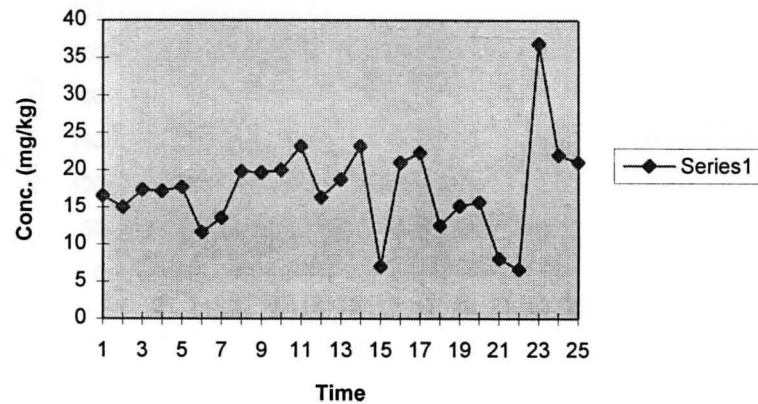
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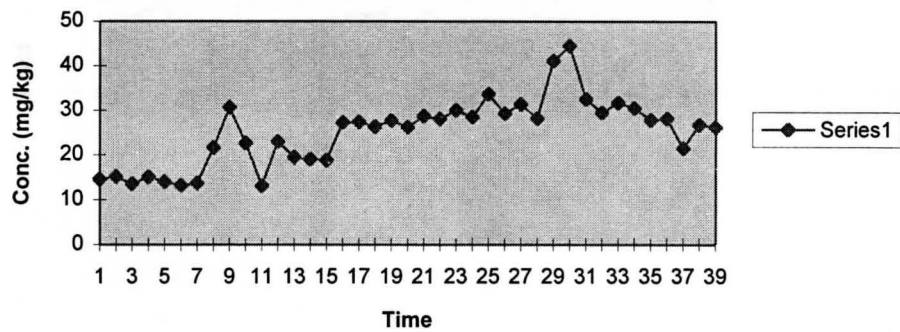
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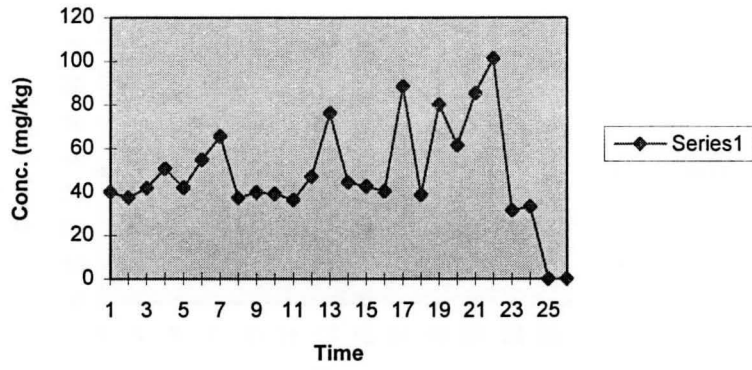
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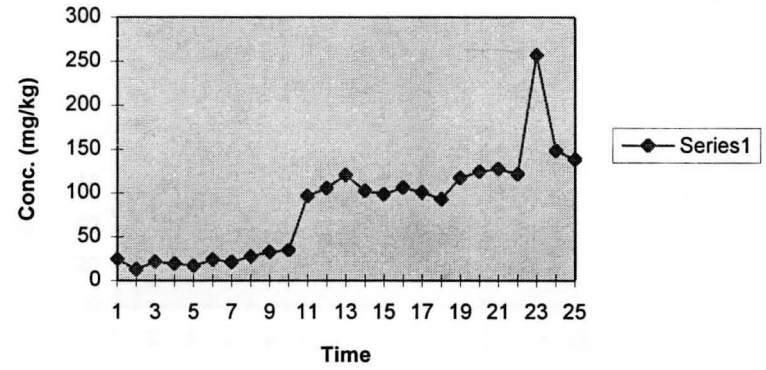
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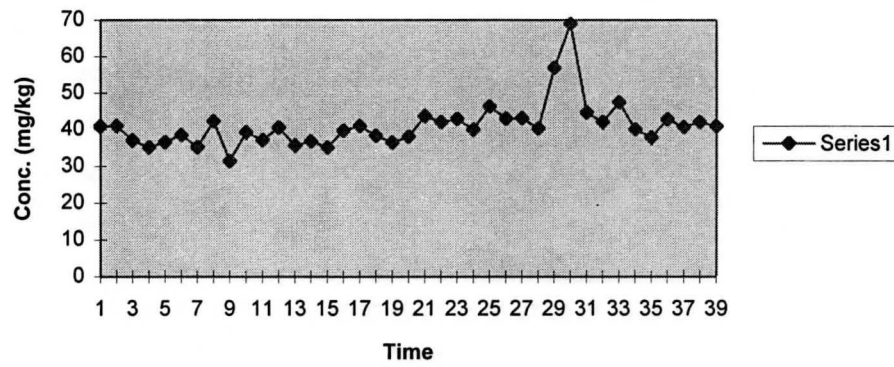
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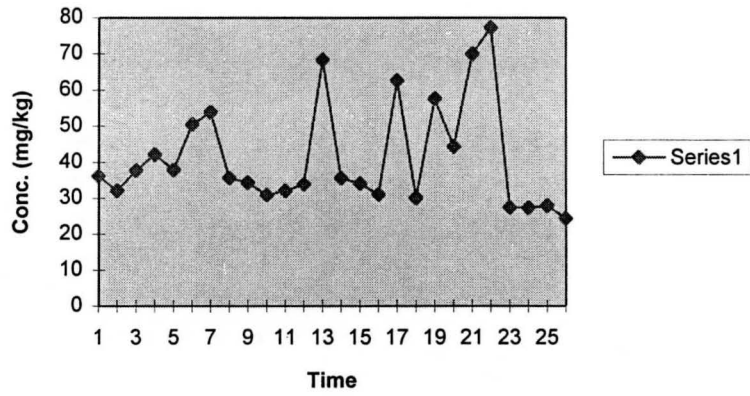
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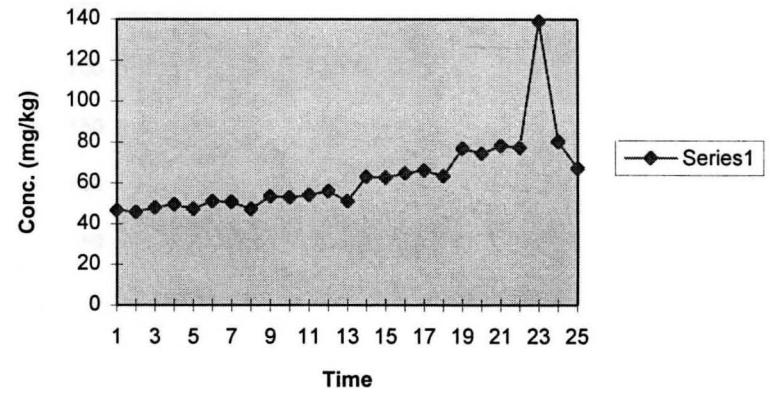
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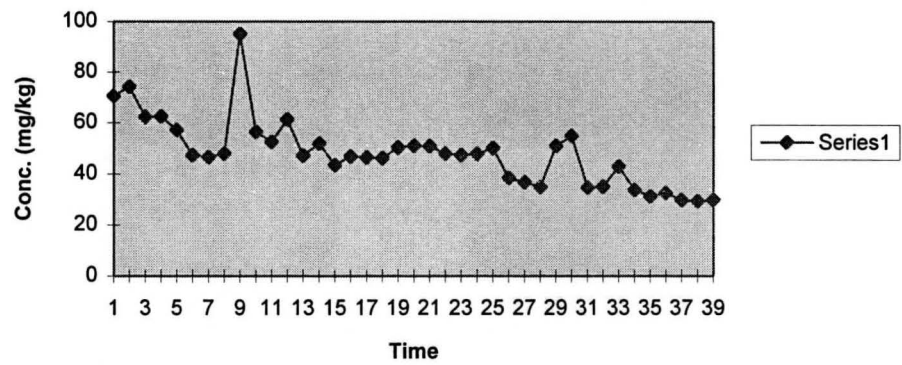
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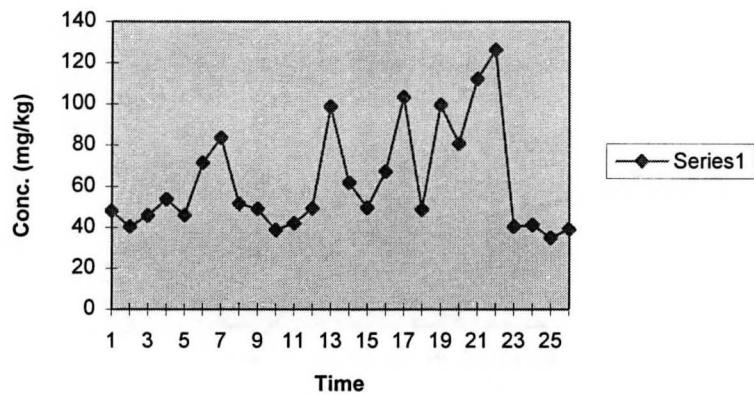
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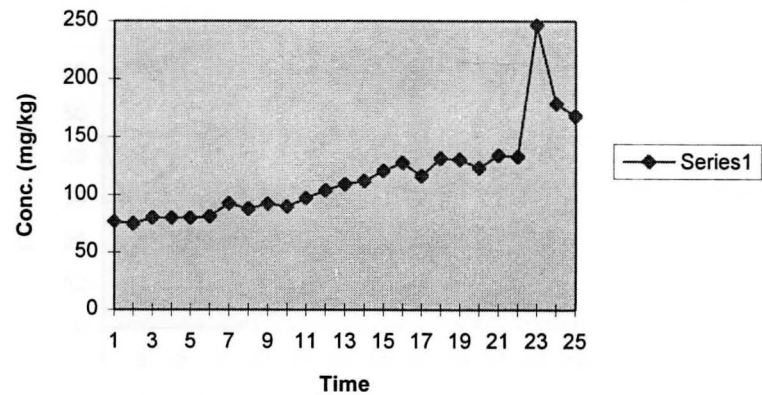
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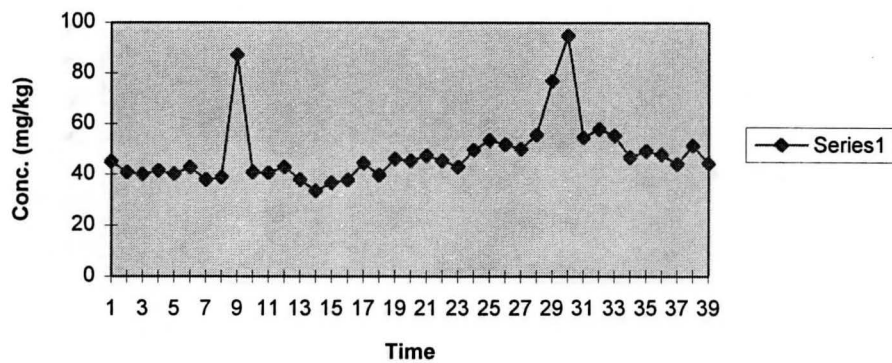
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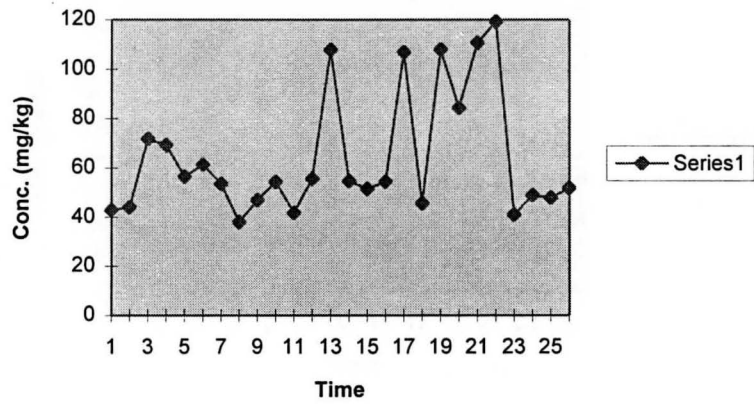
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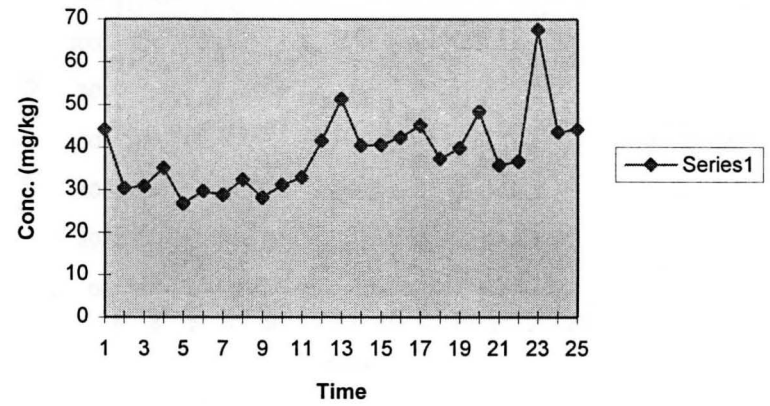
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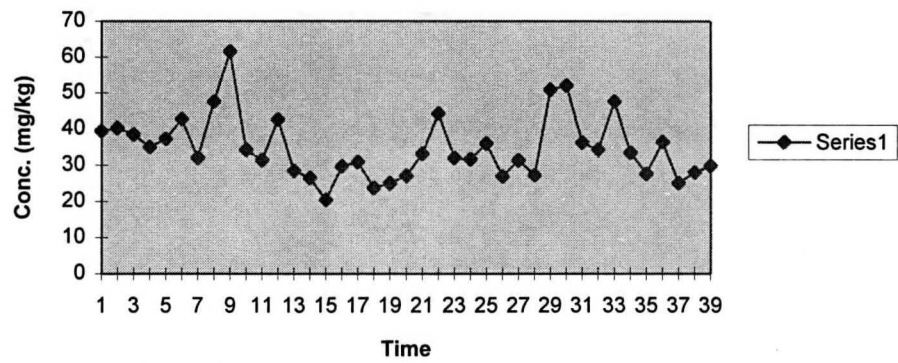
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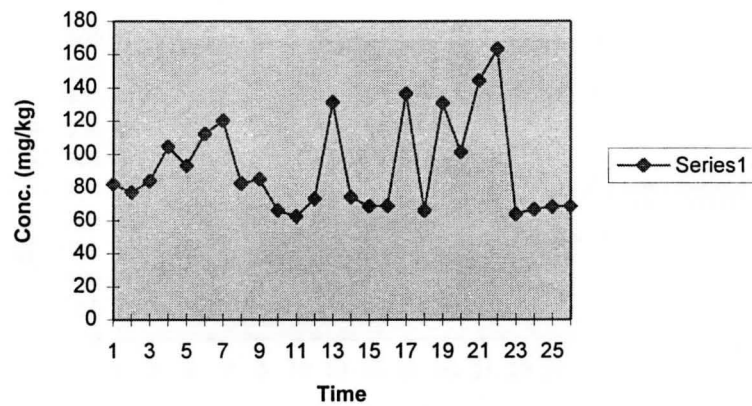
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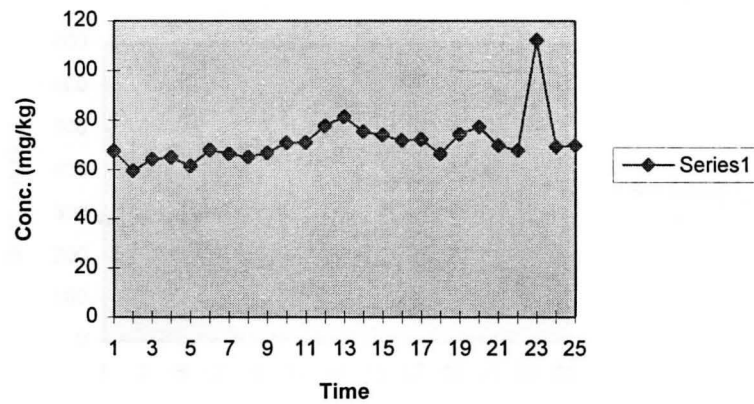
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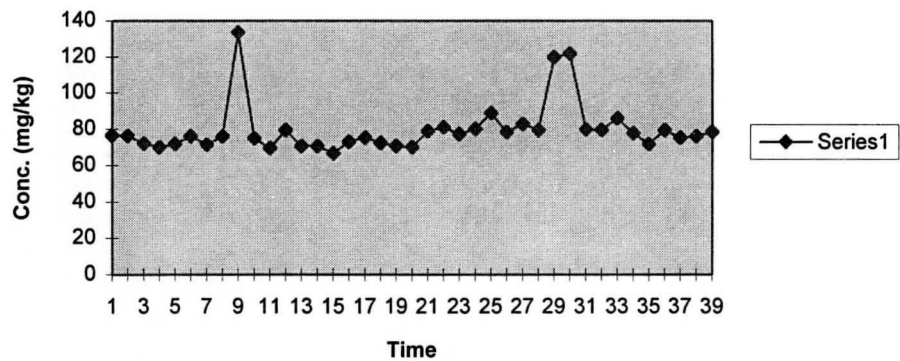
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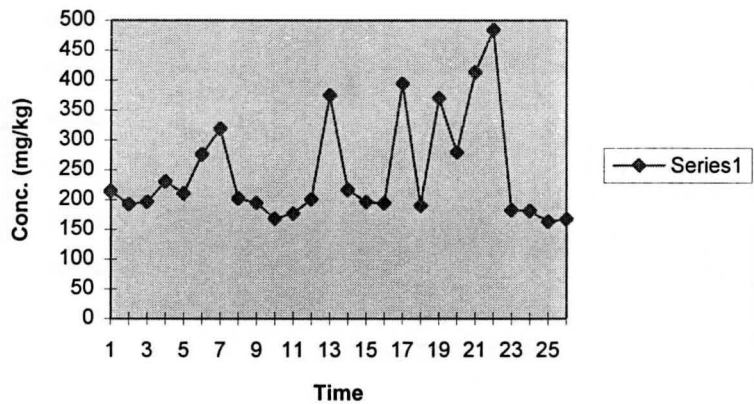
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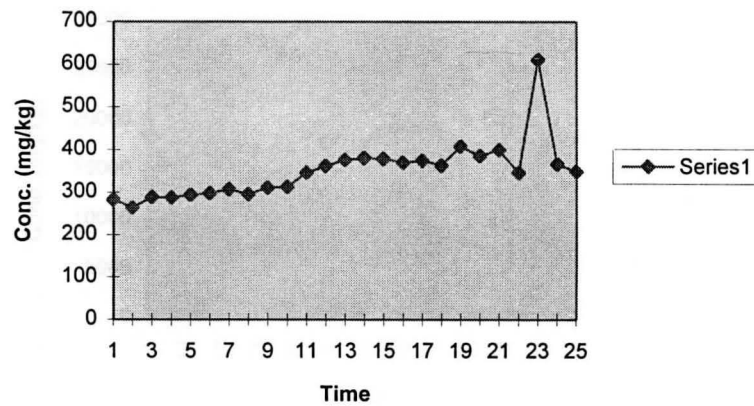
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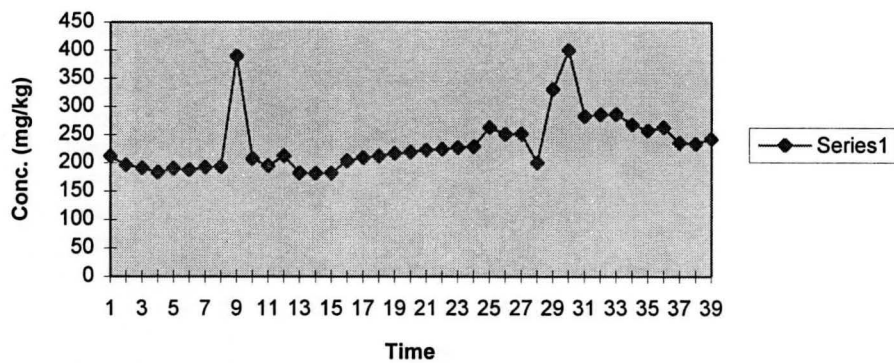
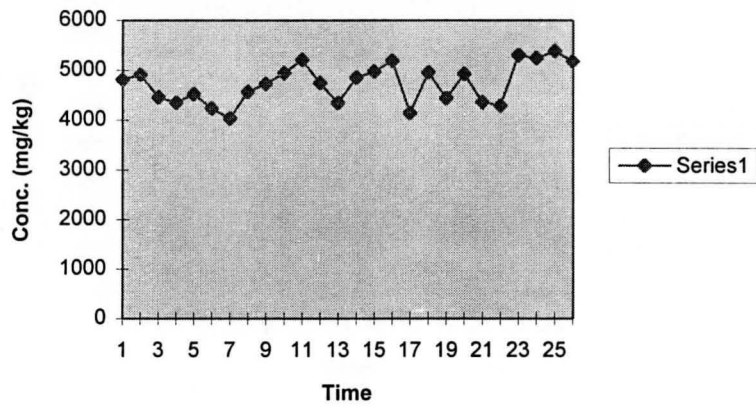Pine Lake Aluminum
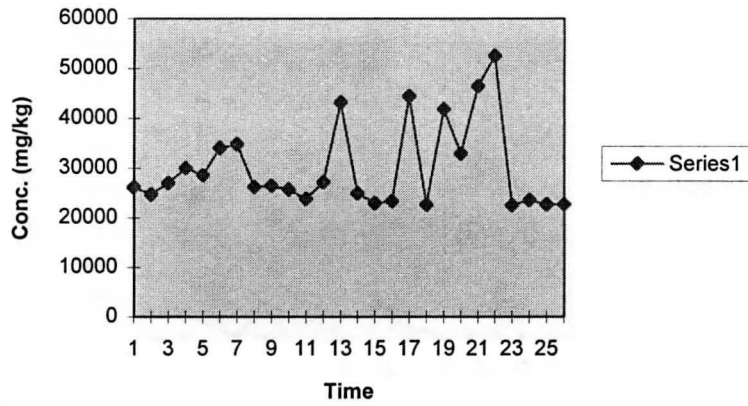
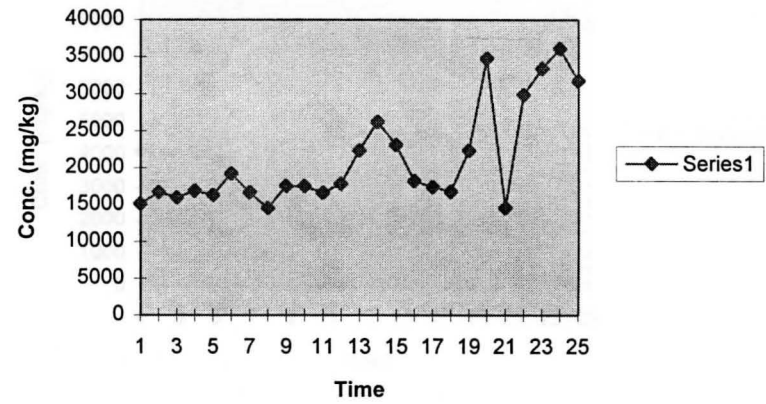Girard Lake Aluminum
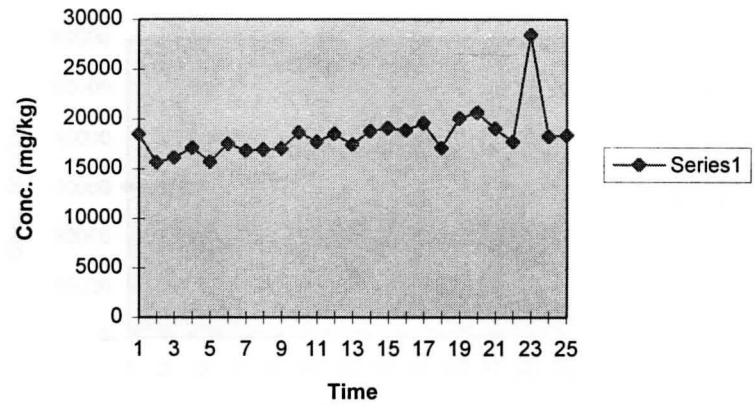
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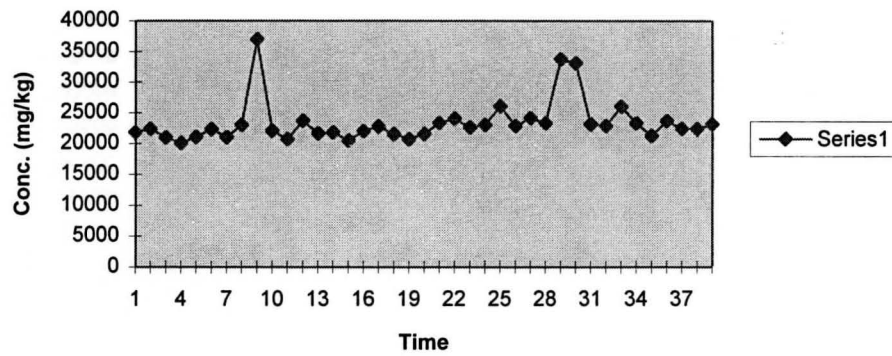
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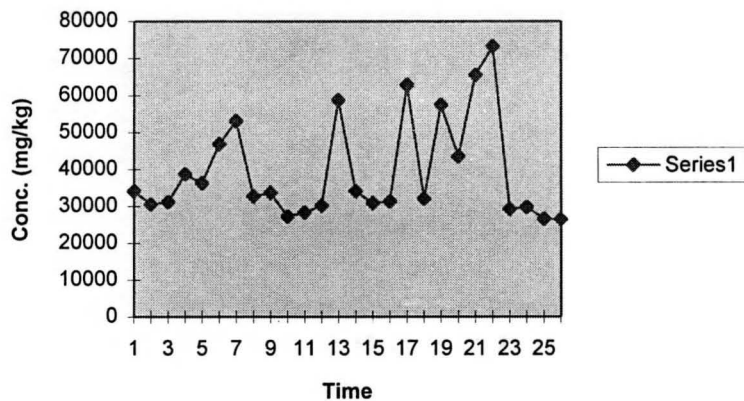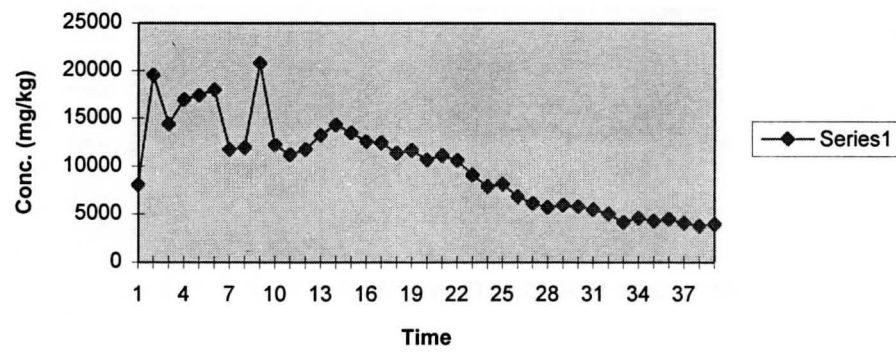
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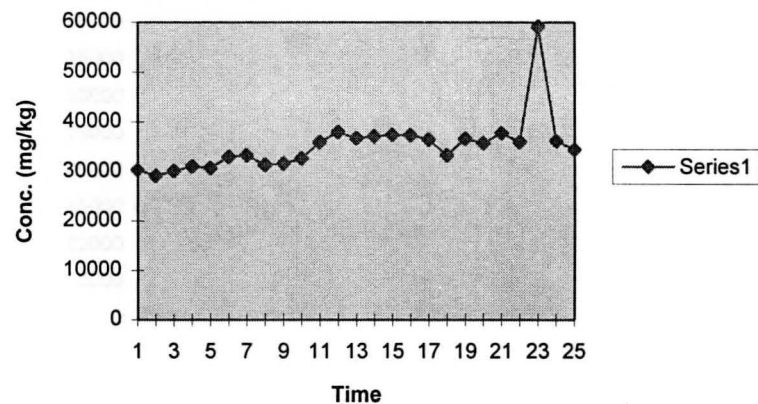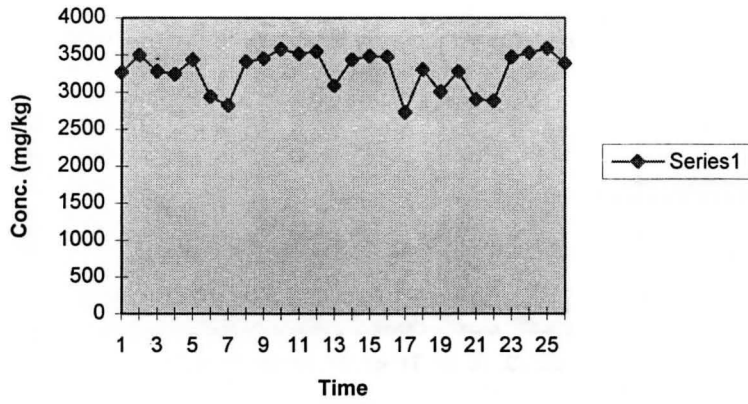
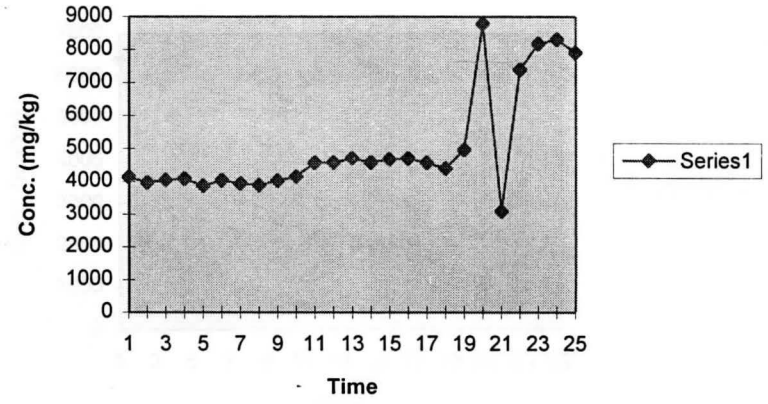**Evan's Lake Iron**
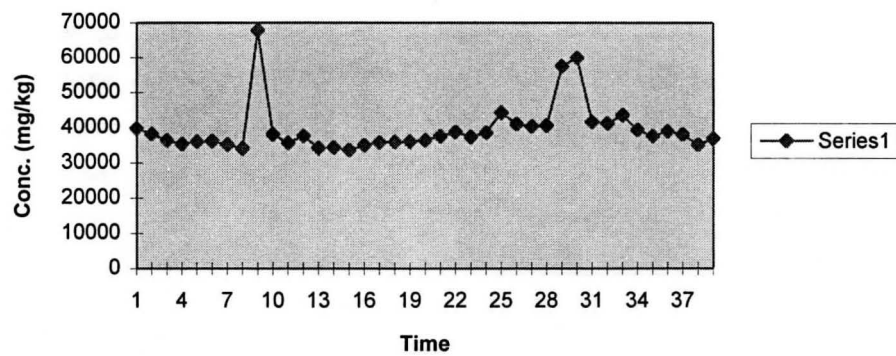
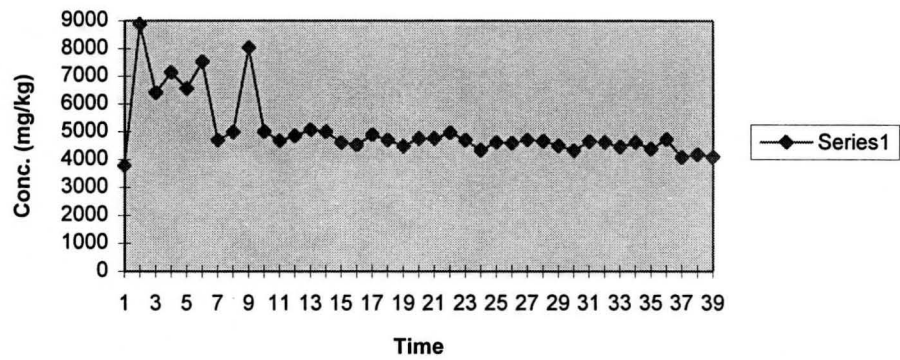**Pine Lake Calcium**

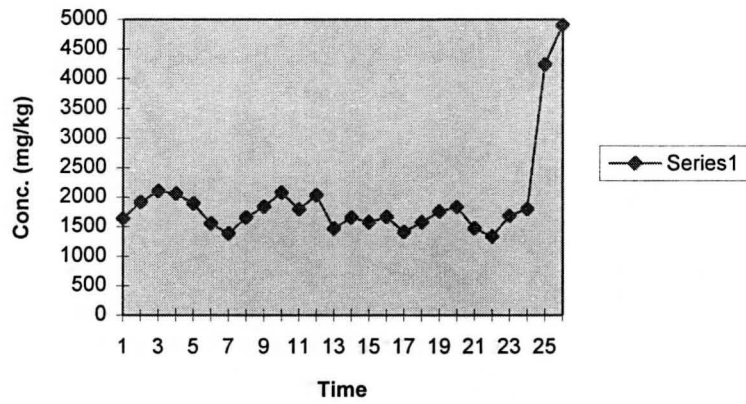**Girard Lake Calcium**
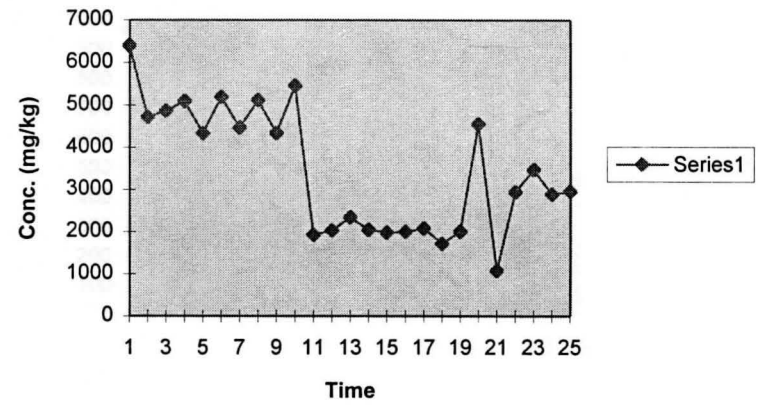
Evan's Lake Calcium

Pine Lake Magnesium

Girard Lake Magnesium

Evan's Lake Magnesium
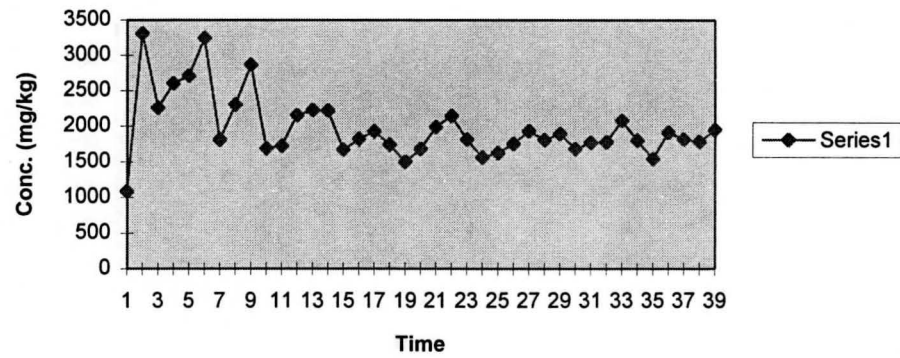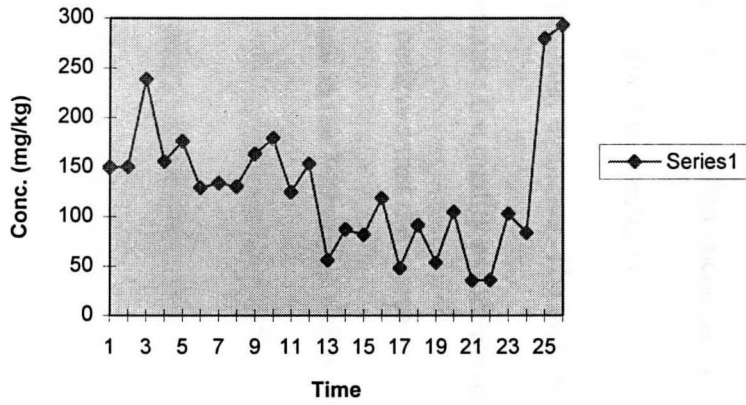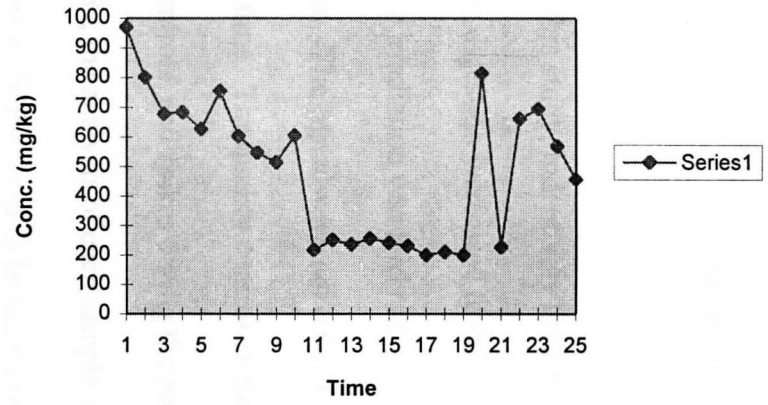
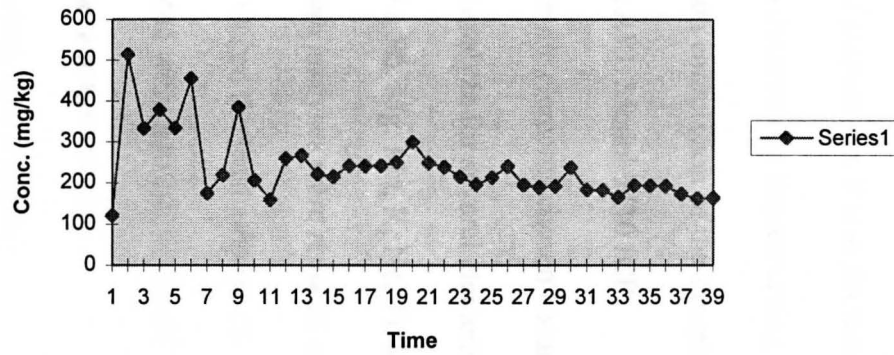Pine Lake Potassium

Girard Lake Potassium

Evan's Lake Potassium

Pine Lake Sodium

Girard Lake Sodium

Evan's Lake Sodium

Chapter Five

Discussion and Conclusions

In this study, Inductively Coupled Plasma-Atomic Emission Spectroscopy and microwave digestion were used to determine elemental concentrations of sediment cores. Microwave irradiation was fairly new but served as an excellent means of sample preparation. The Microwave not only simplified sample preparation, it also decreased digestion time. The quality control of the digestion was overseen by implementing blanks, controls, and spikes during the preparation . Upon completion of the sample preparation, the analysis of each sample was done on an ARL Model 3410 ICP Spectrometer. ICP proved to be the method of choice for the elements chosen because none of the elements were volatile and the system could analyze for several elements at the same time. They were Al, Ba, Be, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, K, Na, Ti, V, Zn.

Interference's often encountered in a multi-element analyses were reduced as much as possible by selecting the emission lines that produced the least amount of overlap with other elements. The instrument was calibrated with certified reference material because the quality assurance of the analysis was a major concern.

It is believed that the increase in elemental (including heavy metals) concentrations in the Mahoning Valley watershed was the result of large scale industrial production. The sediments analyzed in this study were from Evan's, Girard, and Pine lakes. The cores were taken at the deepest part of the lake during the winter. Percent recoveries of the control samples and spiked samples compared to certified values was

well within the accepted range. The only exceptions to this fact were iron and potassium. The samples contained such high levels of these elements that the spikes were not large enough to produce a difference. A plot of each individual element per lake was done to determine if any correlations could be made. The data suggests that Pine Lake on average contains larger amounts of all the elements that were tested. Therefore, it can be assumed that Pine Lake was down-stream or down-wind of the source. Evan's Lake appears to have a major influx of heavy metals around the 6.0 cm region, constituting more recent activity. Girard Lake levels are fairly constant until the 12.00- 13.00 cm region where a large increase is present. Evan's Lake and Pine Lake also have a major input in this area which suggests a increase in industrial production. The concentration of elements in Evan's and Girard lakes are on average comparable to one another. This would suggest that these lakes were further from the source as compared to Pine Lake.

The sediments closer to the surface also give evidence to more recent times. It provides important information about the environment and how it is becoming cleaner and safer. The analysis performed in this study lead to some interesting questions which can be looked at in another study. Further inquiry into this project should focus on finding a more updated version of the microwave digestion method. The CEM Corp. is the originator of this technology and is at the top of the ladder when it comes to research and development of microwave digestion's. It may also prove interesting to look at the reasons that the elements in one lake are more concentrated than the others.

METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0   SCOPE AND APPLICATION

1.1   This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Manganese	Silver	Zinc
Beryllium				

1.2   This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3051.

2.0   SUMMARY OF METHOD

2.1   A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0   INTERFERENCES

3.1   Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5 ± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1   The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power.   Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.

4.1.2   The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3   All electronics are protected against corrosion for safe operation.

4.1.4   The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5   A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit.   The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several signifant safety issues.   First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vesselsequippedres, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened.   This can result in operator exposure to microwave energy.   Use of a unit with corrosion resistant safety devices prevents this from occurring.

> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction.   Pressure is needed to attain elevated temperatures but must be safely contained.   However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures.   Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mecahnisms or containers with PFA-fluorocarbon liners and pressure relief mechanisms are considered acceptable at present.

> Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief

valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2   Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3   Filter paper, qualitative or equivalent.

4.4   Filter funnel, glass or disposable polypropylene.

4.5   Analytical balance, 300 g capacity, and minimum ± 0.01 g.

5.0 REAGENTS

5.1   All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.1.1   Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

5.2   Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1   All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2   All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, sec. 3.1.3 of this manual, for further information.

6.3   Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using athe procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2°C). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be

23 ± 2°C measured to ± 0.05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05°C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2°C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1
$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W)
(W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts
(=4.184)

C_p = the heat capacity, thermal capacity, or specific heat
(cal·g^{-1}·°C^{-1}) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·°C^{-1}) the calibration equation simplifies to:

Eq. 2
$$P = (\Delta T)\ (34.86)$$

> NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.
>
> Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage

circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2   All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3   Sample Digestion

7.3.1   Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and capassembly to 0.001 g prior to use.

7.3.2   Weigh a well-mixed sample to the nearest 0.001 g into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3   Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: All samples known or suspected of containing more than 5-10% organic material should be predigested in a hood for at least 15 minutes.

7.3.4   Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes.   Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels.   When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels.   This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of sample vessels for 10 minutes.   The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5).   The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds.   In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi).   All vessels should be sealed according to the manufacturers recommended specifications.

7.3.4.1 Newer microwave units are capable of higher power (W) that permits digestion of a larger number of samples per batch.   If the analyst wishes to digest more samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4.   That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels.   If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5   At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit.   When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus   sample has decreased by more than 10 percent from the original   w e i g h t, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions.   Once the source of the loss has been   corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3051, as determined by the statistical examination of interlaboratory test results, is located in Tables 1 and 2.

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206 \ x$$

in the long run, where x is one result in $\mu g/g$ (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303 \ x$$

in the long run, where x is the average of two successive measurements in $\mu g/g$ (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

Bias = Amount found - Amount expected.

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

10.0 REFERENCES

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TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN
CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

Element	Repeatability	Reproducibility
Ag	$0.195X^a$	$0.314X$
Al	$0.232X$	$0.444X$
B	12.9^b	22.6^b
Ba	$0.238X$	$0.421X$
Be	0.082^b	0.082^b
Ca	$0.356X$	$1.27X$
Cd	$0.385X$	$0.571X$
Co	$0.291X$	$0.529X$
Cr	$0.187X$	$0.195X$
Cu	$0.212X$	$0.322X$
Fe	$0.257X$	$0.348X$
Mg	$0.238X$	$0.399X$
Mn	$1.96X1/2^c$	$4.02X1/2$
Mo	$0.701X$	$0.857X$
Ni	$0.212X$	$0.390X$
Pb	$0.206X$	$0.303X$
Sr	$0.283X$	$0.368X$
V	$1.03X1/2$	$2.23X1/2$
Zn	$3.82X1/2$	$7.69X1/2$

^{a}Log transformed variable based on one-way analysis of variance.
^{b}Repeatability and reproducibility were independent of concentration.
^{c}Square root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD
BY METHOD 3051

Average Value	Repeatability	Reproducibility
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

All results are in mg/Kg

TABLE 3.
RECOVERY AND BIAS DATA FOR <u>SRM 1085</u> - <u>WEAR METALS IN OIL</u>

Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias ($\mu g/g$)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Ni	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

All values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.

METHOD 3051
(MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS)

```
┌─────────┐
│  Start  │
└────┬────┘
     │
     ▼
┌──────────────┐
│ 7.1 Calibrate│
│ the microwave│
│ equipment.   │
└──────┬───────┘
       │
       ▼
┌──────────────┐        ┌──────────────┐
│ 7.2 Acid wae │        │ 7.3.2 Weigh  │
│ and H₂O rinse│───────▶│ aliquot into │◀──────┐
│ all digestion│        │ the digestion│       │
│ vessels and  │        │ vessel.      │       │
│ glassware.   │        └──────┬───────┘       │
└──────────────┘               │               │
                               ▼               │
                        ┌──────────────┐        │
                        │ 7.3.3 Add    │        │
                        │ concentrated │        │
                        │ HNO₃ cap after│       │
                        │ reaction     │        │
                        │ stopped.     │        │
                        └──────┬───────┘        │
                               │                │
                               ▼                │
                        ┌──────────────┐        │
                        │ 7.3.4 Place  │        │
                        │ sample vessels│       │
                        │ in oven, heat│        │
                        │ according to │        │
                        │ power program.│       │
                        └──────┬───────┘        │
                               │                │
                               ▼                │
                        ┌──────────────┐  ┌──────────┐
                        │ 7.3.5 Allow  │  │ Determine│
                        │ samples to   │  │ reason for│
                        │ cool to room │  │ losses.  │
                        │ temperature. │  └────▲─────┘
                        └──────┬───────┘       │ Yes
                               │               │
                               ▼               │
                        ┌──────────────┐   ◇───┴──────◇
                        │ 7.3.5 Weigh  │  ╱ Has weight  ╲   No    ┌──────────┐
                        │ each vessel  │─▶◇  decreased >  ◇──────▶│ 7.3.6 Place│
                        │ assembly.    │  ╲ 10% from     ╱        │ sample in  │
                        └──────────────┘   ◇ original? ◇          │ acid-cleaned│
                                            ╲────────╱            │ bottle.    │
                                                                  └─────┬──────┘
```

Revision 0

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ARVADA, COLORADO 1-800-372-0122

Appendix B

Certification

PriorityPollutnT™/CLP Inorganic Soils   Quality Control Standards

Catalog № PPS-46   Lot № 228

Parameter	Certified Value	Performance Acceptance Limits™
TRACE METALS PriorityPollutnT™	mg/Kg	mg/Kg
(Catalog No 540)		
aluminum	6070	2730 - 8680
antimony	38.1	11.4 - 68.6
arsenic	65.4	32.0 - 97.4
barium	161	113 - 211
beryllium	122	78.1 - 171
boron	139	66.2 - 211
cadmium	85.4	44.4 - 123
calcium	3710	2340 - 5230
chromium	71.6	38.7 - 101
cobalt	94.2	56.5 - 134
copper	173	98.6 - 251
iron	12500	6380 - 18800
lead	70.4	37.3 - 100
magnesium	2490	1490 - 3590
manganese	298	209 - 402
mercury	1.68	0.806 - 2.62
molybdenum	101	57.6 - 160
nickel	68.5	37.7 - 100
potassium	3250	2010 - 4290
selenium	152	79.0 - 226
silver	89.0	40.5 - 130
sodium	167	71.1 - 262
strontium	82.0	35.7 - 130
thallium	71.8	26.4 - 117
tin	87.5	61.2 - 127
titanium	326	228 - 440
vanadium	105	73.5 - 142
zinc	110	59.4 - 164

For users of internal standards, ERA has determined that scandium is present in this soil at 2.80 mg/Kg and that yttrium is present at 17.7 mg/Kg.

The **Trace Metals Certified Values** are equal to the mean recoveries for each parameter as determined in an interlaboratory round robin study. The standard was digested using Method 3050, SW-846 and the digest analyzed by ICP and atomic absorption spectroscopy.

The **Performance Acceptance Limits (PALs™)** are listed as guidelines for acceptable analytical results given the limitations of the USEPA methodologies commonly used to determine these parameters and closely approximate the 95% confidence interval. The PALs™ are based on data generated by your peer laboratories in ERA's InterLaB™ program using the same samples you are analyzing and data from USEPA methods, WP, WS and CLP interlaboratory studies. If your result falls outside of the PALs™, ERA recommends that you investigate potential sources of error in your preparation and/or analytical procedures. For further technical assistance, call ERA at 1-800-372-0122.

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