

Analysis of Heavy Metal Contamination Soil
Using ICP, GFAA, CVAA
For "Mahoning River Corridor Redevelopment Project"

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TITLE **Analysis of Heavy Metal Contamination Soil
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ABSTRACT**ANALYSIS OF HEAVY METAL CONTAMINATION SOIL
BY ICP, GFAA, AND CVAA
FOR
"MAHONING RIVER CORRIDOR REDEVELOPMENT PROJECT"****QING HONG****Master of Science****Youngstown State University, 1994**

The Mahoning River Corridor Redevelopment Project was formed as a cooperation between Youngstown State University(YSU) and the Ohio Department of Development(ODOD), and the Regional Growth Alliance(RGA) to determine the availability of constructive reuse of the Mahoning River Corridor from the city of Newton Falls in Trumbull County to the Ohio-Pennsylvania State line.

At the request of the Youngstown State University's Youngstown Technology Center(YSU-TDC) a limited environmental study was being performed to determine the level of regulated substances on the project area.

According to the EPA and RCRA Regulations, the analysis should be done using required procedures and methods, such as TCLP for soil sample acid digestion , and ICP, GFAA, CVAA, for sample analysis. The land is considered reuseful if the levels of the

hazardous substances is lower than the RCRA Regulatory Levels.(see Table 8 on page 49)

In this study, hazardous heavy metals were determined for approximately 37 sites and about 165 samples. The techniques such as Inductively-Coupled Plasma Emission, Graphite Furnace Atomic Absorption, and Cold Vapor Atomic Absorption were used for specific element analysis based on their different properties. TCLP was performed for the soil sample leaching and acid digestion.

Eight RCRA Regulatory heavy metals were determined for each sample. They are Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, and Silver. A Model 3410 ICP spectrometer was used for sequential multielement analysis for As, Ba, Cd, Cr, Pb, and Ag with the most sensitive detection limits; CVAA was employed for Hg analysis to increase the sensitivity by reducing the loss of Hg analyte that typically occurs with flame techniques; GFAA was specifically used for Se analysis to avoid the low sensitivity encountered with the ICP method.

The data obtained in this study showed that the concentrations of the metals determined were either below the RCRA Regulatory Levels or undetectable. Sites studied in the project may be suitable for re-use, once further surveying is performed.

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I would like to express my appreciation to the faculty and staff of the Department of Chemistry, especially Drs. James Mike and Elmer Foldvary, for giving all the help and assistance 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
cm	Centi meter
CVAA	Cold Vapor Atomic Absorption
DC	Direct Current
DI H ₂ O	Deionized Water
E°	Ground State Energy Level
E*	Excited State Energy Level
EPA	Environmental Protection Agency
Eh	Redox potential/the negative log of the electron activity
g	Gram
(g)	Gaseous state
GFAA	Graphite Furnace Atomic Absorption
H	Magnetic field unit
ICP	Inductively Coupled Plasma
Int.	Integration
K	Degree in Kelvin
KW	Kilowatt
KΩ	Kilohm
L	Liter
L.Q.D.	Limited Quantitative Detection
mA	Milliampere
mg	Milligram

mg/L	Milligram per liter
MHz	Megahertz
ND	Not detected
nm	Nanometer
ODOD	The Ohio Department of Development
pH	Negative log of hydrogen ion concentration
PMT	Photomultiplier Tube
ppm	Parts per million
psi	Pounds per square inch
RCRA	Resource Conservation and Recovery Act
RF	Radio Frequency
rpm	Run per minute
sec	Second
TCLP	Toxicity Characteristic Leaching Procedure
TDC	YSU Technology Development Corperation
TM	Trade mark
µg/mL	Microgram per milliliter
µL	MicroLiter
V	Volt
YSU	Youngstown State University

Chapter I Introduction

The analysis of soil using TCLP for the determination of heavy metal concentrations is required under RCRA regulations before possibly contaminated lands may be reused. The goal of the Mahoning River Corridor Redevelopment Project is to identify property along the Mahoning River, including steel and other metal manufacturing sites, suitable for reuse. RCRA regulatory heavy metals include Arsenic(As), Barium(Ba), Cadmium(Cd), Chromium(Cr), Lead(Pb), Mercury(Hg), Selenium(Se), and Silver(Ag).

RCRA

The Resource, Conservation and Recovery Act (RCRA) was created in 1976 as a "cradle to grave" law for anyone who generates, stores, handles, transports or disposes of hazardous substances, including heavy metals. An example of the application of RCRA statutes to land reuse is elaborated in "The Mahoning River Corridor Redevelopment Project---Niles N-4 Site,P14".¹ The level of contaminants permitted are dictated by the end use of the property. For example, higher concentrations of heavy metals are tolerated if the property will be residential. This may seem odd but actually is a consequence of the regulations associated with RCRA. The State of Ohio is presently studying legislation termed "Brown Field" regulations that would permit higher concentrations of heavy metals in industrial settings.

TCLP

TCLP stands for Toxicity Characteristic Leaching Procedure. The philosophy of this test is that by subjecting soils to a mildly acidic solution the mobility of toxic

substances contained in the soil will be indicated. The greater the concentrations of these toxic substances in the extraction fluids the greater their mobility and the greater the threat they pose to the environment. These guidelines are intended to help analytical chemists achieve consistent results in their routine analytical work, especially in commercial analytical laboratories. The results obtained by one analytical chemist should be the same as for another within the same laboratory or at different laboratories, within experimental error. They are for guidance only and are not intended to replace sound professional judgment or other regulatory requirements.

The guidelines are presented in the form of laboratory worksheets that can be used to document some of the most important points of the procedure. Two parts are included in the guidelines. Part 1 of the guidelines includes a description of samples appropriate for the procedure and the selection of proper extraction fluids. Part 2 includes the performance criteria for the TCLP extraction procedure for metals, semivolatile organic compounds, and pesticides and herbicides.² In this study, the preparation and selection of the extraction fluids and the soil sample extracting procedure, mentioned in Chapter IV all referred to these guidelines.

Soil

Soil is a complex heterogeneous mixture comprised of mineral and organic solids, aqueous, and gaseous components. It is a dynamic system, subject to short-term fluctuations such as variations in moisture content, pH and redox conditions, and undergoing gradual alterations in response to changes in use management and long-term environmental factors. These changes in soil properties could affect the form and bioavailability of metals, and need to be considered in decisions on the remediation of polluted soils or the use of soils for disposal of waste materials. Soil can show marked spatial variability in physical and chemical properties at the macro and micro-scales,

therefore, thorough sampling methods that consider the variance in properties at any site are needed.

Soil reactivity and pH are the pre-eminent factors controlling the chemical behavior of metals and many other important processes in the soil. Normally, heavy metal cations are most mobile under acidic conditions. The maximum range of pH conditions found in soils is 2-10.5.

The most important chemical processes affecting the behavior and bioavailability of metals in soils are those concerned with the adsorption of metals from the liquid phase onto the solid phase. Several different mechanisms can be involved in the adsorption of metal ions, including cation exchange (or non-specific adsorption), specific adsorption, organic complexation, and co-precipitation.

Heavy Metals in Soils

'Heavy Metals' is commonly adopted as a group name for the metals and metalloids that are associated with pollution and toxicity, but also includes some elements that are essential for living organisms at low concentrations.³ In this study, the term 'heavy metals' will only indicate the essential and non-essential elements, identified as the RCRA regulatory elements.

The soil is open to inputs of heavy metals from many sources, some of the major sources that are of particular concern are:

- (1) The combustion of fossil fuels;
- (2) The disposal of urban and industrial wastes. This is the major source of heavy metal pollutants in the soils analyzed in this study.
- (3) Previous atmospheric pollution from motor vehicles, such as the dispersion of Pb aerosols by using leaded gasolines.
- (4) Agricultural fertilizers and pesticides.

In typical profiles Ag, As, Cd, Hg, and Pb are found distributed throughout the soil as a result of pedogenic processes such as the cycling through vegetation and atmospheric deposition and adsorption by the soil's organic matter. However, recently polluted soils often have higher contents of the pollutant metals in the topsoil because the pedogenic processes have not been operating long enough to effect a redistribution within the soil. In this study, the samples were usually taken at depths of less than two feet, but some soil profiles were also taken.

RCRA Regulatory Heavy Metals in Soils

Arsenic(As)

Arsenic has achieved great notoriety because of the toxic properties of a number of its compounds. Arsenic differs from many of the common heavy metals in that the most organic compounds containing arsenic are less toxic than inorganic ones.³ Over 200 As-containing minerals have been identified. The element As is found associated with many types of mineral deposits, especially, with sulfide-bearing minerals because of the ability of As to bind to S ligands. Therefore, the natural sources of As in soils are mainly as oxysalts and S containing minerals. As(V) and As(III) both exist naturally and the ratio changes with Eh/pH changes. In soil, As is often described as a non-metal, forming covalent compounds or as being found in anionic species. The quantity of soluble As in a soil varies widely with pH. Therefore, the As availability in soils is effected by changes in pH. As a result, the value obtained for the "available" As level in a soil is a function of the extracting agent used. Because of the volatility and chemical properties of As, the difficulty involved in identifying and quantifying the various As species in soils and associated solutions and gases is still a major problem.

Cadmium(Cd)

Cadmium is a relatively rare metal, and is highly toxic to plants and animals.³ The major hazard to human health from Cd is its chronic accumulation in the kidneys. Since the concentration of the metal in uncontaminated soils is usually low, the source of contamination and the behavior of Cd in contaminated soils will be the main concern.

Cadmium pollution of the environment has rapidly increased in recent decades as a result of the rising consumption of Cd by industry. More than half of the Cd ever used in industry was produced in the last 20 years. World production of Cd increased from 11,000t in 1960 to 19,000t in 1985. Its principal uses are: (1) as protective plating on steel; (2) in various alloys; (3) in pigments; (4) as a stabilizer for plastics; (5) in Ni-Cd dry-cell batteries and (6) other miscellaneous uses.

On the surfaces of soil solids, the free ion Cd^{2+} is more likely to be adsorbed than either neutral or anionic species. The free ion, Cd^{2+} , was found present in increasing amounts where the pH of the soil was greater than 6.5. The dynamic equilibrium between Cd in the soil solution and that adsorbed on the solid phase of the soil depends on the pH, the chemical nature of the metal species, the stability of Cd complexes, the binding power of the functional groups and the ionic strength of solutions, and the presence of competing ions. Some aspect of the chemical behavior of Cd in soils can be explained by the hard-soft Lewis acid-base principle. Nevertheless, adsorption processes rather than precipitation appear to control the distribution of Cd between soluble and soil-bound forms at the concentrations normally encountered even in most polluted soils.

Cadmium poses an interesting environmental challenge, since it is not thought to be biologically essential. Any environmental considerations are aimed at reducing its occurrence and lowering its bioavailability.

Chromium(Cr)

Chromium is a d-block transition metal. It occurs in the +3 and +6 oxidation states in the environment, with Cr(III) being the most stable.³ Chromium is produced from the ore chromite, which is a mixed oxide with the general formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ but also contains variable amounts of Mg and Al. Chromium is the seventh most abundant element on Earth. The content of Cr in a soil depends very much on the nature of the parent material. For example, soils formed on serpentine can contain high Cr, Mg and Fe concentrations. Depending on the origin of the soil and pedogenic processes, the surface of the subsoil may be relatively enriched, or may have the same Cr concentration. Chromium-containing effluents are released by the following activities: metal plating, anodizing, ink manufacture, dyes, pigments, glass, ceramics, glues, tanning, wood preserving, textiles, and corrosion inhibitors contained in cooling water. As a result of the latter, soil around coal-fired electricity generators may be slightly enriched with Cr. Also, the dumping of large amounts of pulverized fuel ash on soils leads to large increases in Cr concentrations.

Chromium may exist in a number of oxidation states, but the most stable and common forms are Cr(III) and Cr(VI). If Cr(VI) exists as part of a complex anion, it is more readily extracted from soil and sediment particles and is considered to be the more toxic form. Chromate (CrO_4^{2-}) is in pH-dependent equilibrium with other forms of Cr(VI) such as HCrO_4^- and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), with CrO_4^{2-} the predominant form at $\text{pH} > 6$. Chromium (III), on the other hand, is much less mobile and adsorbs to particulate matter more strongly. The solubility of Cr(III) decreases above pH 4, and above pH 5.5 complete precipitation occurs. Therefore, the acetic acid extraction method found in TCLP is not as satisfactory as for other elements.

In the presence of soil organic matter Cr(VI) is reduced to Cr(III) and the reduction is more rapid in acid than alkali soils. Thus in most soils, the relatively insoluble and less mobile Cr(III) form predominates and it generally occurs as insoluble hydroxides and oxides.

Lead(Pb)

Lead has two stable oxidation states: Pb(II) and Pb(IV), but the environmental chemistry of the element is dominated by the plumbous ion, Pb^{2+} .³ When Pb is released into the environment it has a long residence time compared with most other pollutants. As a result, Pb and its compounds tend to accumulate in soils and are relatively free from microbial degradation, thus they will remain accessible to the food chain and to human metabolism for long periods of time. Pb is a trace element in rocks and soils. Galena, PbS is the major form existing in ores or soils, because Pb has a strong affinity for sulfur.

The several well-known major sources of Pb in soil are mining and smelting activities, sewage sludge (the prominent source of soil Pb in recent years), agriculture and contamination from vehicle exhausts, and the disposal from the industries, probably the major source of Pb in this study. Purves has recognized elevated level of trace elements in urban soils.¹ Urban soils contain mostly acetic acid-extractable Pb.

As results from many studies indicate, lead appears to accumulate naturally in surface strata of soil without regard to the type of soil. In soil, the pH is the main property involved in the immobilization of Pb. In acidic soil Pb is found to be mainly in a cationic form with some organic complexation. In calcareous soils neutral complexes are dominant, together with some cationic lead species. In soil of higher pH, the greater percentage of the Pb is as high-molecular-weight organo-Pb complexes. The resident time of Pb is so long that it can be regarded as permanent in soils. The high Pb concentrations in the environment has posed a potential risk to health. The concentration of Pb in soil has been strictly limited by Departments of the Environment in most countries.

Mercury(Hg)

Hg is among the most toxic elements to man and higher animals. No essential biological function of Hg is known.³ All chemical compounds of Hg are toxic to humans, although Hg^0 may have to be oxidized to ionic forms in order to show toxic effects. Mercury salts show a high acute toxicity, with a variety of symptoms and damages. Some organomercurials, in particular low-molecular-weight alkyl mercury compounds, such as methyl and ethyl mercurys, are considered even more hazardous to humans because of their high chronic toxicity with respect to various, largely irreversible, defects of the nervous system. Methyl mercury is the dominant toxic Hg species in the environment.

The major sources of Hg in land, water and air appear to be the following:

- (1) Mining and smelting of ores, in particular Cu and Zn smelting.
- (2) Burning of fossil fuels, mainly coal.
- (3) Industrial production processes.
- (4) Consumption-related discharges, including waste incineration.
- (5) For soils, in particular, the minerals constituting the rocks forming the soil parent material, and Hg-containing fungicides may sometimes increase substantially the Hg load.

Depending on the redox conditions, Hg may occur in three different valence states, namely as Hg^0 , Hg_2^{2+} and Hg^{2+} , of which Hg^0 and Hg^{2+} are the states normally encountered in soil. Besides the redox potential, pH is also important in determining the chemical behaviors of mercury in soil. In acid solutions, Hg^{2+} is stable at a redox potential above 0.4V, and normally occurs as the HgCl_2 complex. Above pH 7 the complex $\text{Hg}(\text{OH})_2^0$ is the corresponding stable form. Under natural conditions, the release of Hg^0 and possibly also other volatile Hg compounds from soil is probably very significant in the cycling of Hg.

Some properties involving the concentration and distribution of mercury in soils are found to be: (1) Organic soils commonly have higher average Hg contents than

mineral soils; (2) In acidic soils, the correlation between Hg and organic matter content is significant; whereas in neutral soils ($\text{pH} > 6$) where the dominating species are HgOHCl and $\text{Hg}(\text{OH})_2$ rather than HgCl_2 ; (3) In soils with low organic matter contents and $\text{pH} > 6$, Hg appears to be depleted in the surface layer relative to lower strata.

Hg has a very high volatility, and is the only element that has a significant vapor pressure at room temperature. This property of Hg permits the use of the cold vapor atomic absorption technique for analyzing Hg quantitatively. Conversely, the volatility of Hg causes a disadvantage of low sensitivity during the flame or ICP Hg analysis.

Selenium (Se)

Selenium has considerable chemical similarities with S, such similarities result in a number of biological interrelations, and these have been indicated by toxic and deficient responses in both humans and animals.³ Compared with other metals, the Se content of most sewage sludge amended soils is quite low. Se may be found in the oxidation states: II, IV and VI under a variety of conditions in soils. The distribution of Se is dependent on pH and the oxidation-reduction potential. Under conditions where a high oxidation potentials, SeO_4^{2-} appears to be the major contributing species above pH 2. In systems of moderate redox conditions both SeO_3^{2-} and HSeO_3^- are significant contributors to soluble Se concentrations, with biselenite predominating below pH 7.3. Under reducing conditions, soluble Se predominates as HSe^- at $\text{pH} > 3.8$ and as H_2Se^0 below this value.

The distribution of Se in soils indicated that approximately 80% of the total Se occurred in the upper 15cm of the soil profile.⁴

The emission of gaseous Se depends on the temperature and Se concentration in the soil.¹ However, the high volatility of Se brings difficulties to the ICP analyses. Recently, graphite furnace and cold vapor techniques have been used for Se analyses.

Silver (Ag)

Silver is the most reactive of the noble metals, forming three cationic species, Ag^+ , Ag^{2+} and Ag^{3+} , of which only the monovalent form is environmentally significant.³ Laboratory experiments have shown Ag to be one of the most toxic elements to microorganisms and biochemical processes in the soil.

The normal range of Ag in soils varies from < 0.01 to 5mg/kg with an average of 0.1mg/kg . The behavior of Ag in soils is strongly influenced by the prevailing pH and redox conditions, and by interactions with soil organic matter. Ag tends to accumulate in the surface, organic-rich strata of field soil. The mobility of Ag is increased by humus decomposition or by lowering the pH.

Barium(Ba)

Barium is the heaviest of the three common alkaline earth elements: calcium, strontium and barium, and is the least volatile of the three.⁵ Barium constitutes 0.4-0.5% of the earth's crust. The most common barium minerals are barite or baryte, BaSO_4 , and witherite, BaCO_3 . The former is the chief source of barium compounds in the United States. Of the estimated world production of 3 million tons annually of barite, the United States production is about 800,000 tons, chiefly from Missouri and Georgia.

All the soluble compounds of barium are poisonous when taken by mouth. The barium ion is a muscle stimulant. It is very toxic to the heart and may cause ventricular fibrillation.

Methods of Analysis for Heavy Metals in Soils

Techniques of analysis can be broadly categorized into: i. single-element methods, such as atomic absorption spectrometry (AAS); or ii. simultaneous multi-element methods, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES); or iii. X-ray fluorescence spectrometry (XRFS). They can be further categorized into

methods such as AAS, which carry out the analysis in solution, i.e. with dissolved samples, or methods, such as XRF, which analyze solid samples more or less directly. The choice of method for a particular application should take into account those factors as well as their sensitivity, precision and accuracy.

The techniques used in this study will be AAS and ICP. For more details, refer to Chapter III.

Chapter II

Project Background

Project Review

The Youngstown-Warren Metropolitan Area, as with many other northeastern Ohio industrialized communities, has been faced with a decline of its manufacturing employment base throughout much of the 1970's and 1980's. Particularly hard hit was its steel mills that were once many of the most productive in the country. To stabilize its economy and to provide a diversified employment base, the Mahoning valley began to aggressively market itself as a strategic manufacturing and distribution location between the Chicago-midwest market and the east coast. As part of this marketing strategy, the Mahoning River Corridor Development Project was formed as a cooperation between Youngstown State University (YSU, TDC) and the Ohio Department of Development (ODOD), and the Regional Growth Alliance (RGA) to determine constructive reuse of the Mahoning River Corridor from the city of Newton Falls in Trumbull County to the Ohio-Pennsylvania State line.

The YSU Technology Development Corporation (TDC) had compiled a list of thirty-two sites that due to the industrial history of the sites warranted some form of environmental investigation regarding the presence or absence of regulated and/or hazardous substances. The properties are located in several communities along the Mahoning River in Trumbull and Mahoning Counties, Ohio.

At the request of the Youngstown State University's Youngstown Technology Center (YSU-TDC) a limited environmental study was conducted to determine the presence or absence of hazardous or regulated substances on these selected properties identified in the project area.¹

Starting from the summer of 1992, Reid Dulberger, executive director of the RGA, and the YSU TDC began soil testing and carrying out environmental assessments

on the 35-mile stretch of land along the Mahoning River from Newton Falls to the Pennsylvania border, known as the Mahoning River Corridor and shown in Figure 1. The initial two-year study, was funded through a \$175,663 grant by the Ohio Controlling Board, and was known as the Mahoning River Corridor Redevelopment Project.

Local developers estimated that if the extent of contamination was known, the property along the river could be used for industrial, commercial and even residential and recreational developments.⁵

Overview of Sampling and Analytical Procedures

Soil sampling was to be site specific (site names would be left off by the requests from land owner).¹ As a rule, samples were taken at depths of less than two feet. For those sites where historical information was available, sampling location and equipment were chosen accordingly. Samples were placed in labeled, coded containers and transported to the Civil Engineering Environmental Lab where compositing took place. Composites were based upon the original site sampling pattern. No more than ten original samples were agglomerated in any one composite. Properly labeled composite samples were then sent to analytical laboratories in the YSU Chemistry and Biology Departments.

Two major groups of contaminants, heavy metals and organic compounds, were determined. For heavy metals, including (but not necessarily limited to) Se, As, Cd, Cr, Pb, Hg, Ba, and Ag, the analyses were performed in the analytical lab in the Department of Chemistry. For the organic compounds, including PCBs and PAHs, the determinations were performed in the Department of Biology.

For the heavy metals determination, the most appropriate analytical spectroscopic techniques were selected, according to the different properties of the metal to be determined. A relatively precise and sensitive method, ICP-AES, was used for the determination of the RCRA regulated metals: As, Ag, Ba, Cd, Cr, and Pb; excluding Hg

and Se. Analysis for Hg was performed by using the Cold Vapor Analysis method. Determination of Se was accomplished using a Graphite Furnace Atomic Absorption Spectrometer.

Results of the analyses were reported and referenced to current RCRA regulatory standards.¹ If any sample exceeded the RCRA regulatory levels, further analyses were performed, to verify the results. This study analyzed approximately 150 samples from 32 different sites in the Mahoning River Corridor region. The procedure of selecting the best analytical method for the specific element; and the manner in which the data was manipulated for the determination of heavy metal concentrations in the leachates, is part of the EPA protocol SW846 and is known as the TCLP Method.²



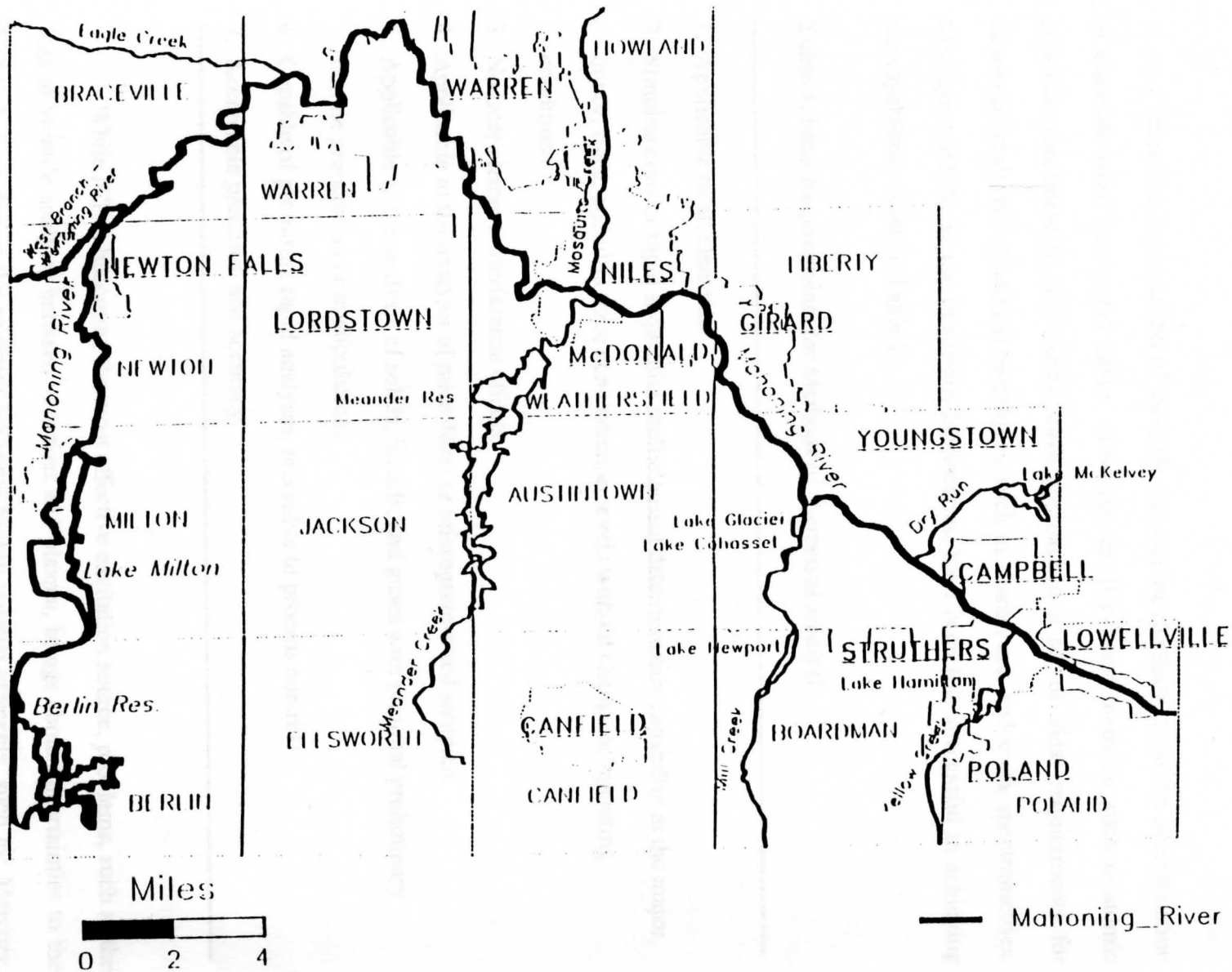


Figure 1 Sketch showing the course of the Mahoning River.

— Mahoning River
 — Tributaries

Chapter III Methodology

There is a large number of methods that may be satisfactory for the determination of elements when they occur alone. However, the ICP-based methods, such as atomic emission spectrometry (ICP-AES), have approached a set of ideal requirements for elemental analysis.⁶ Classical techniques, such as, flame, arc, and spark spectrometries, although currently in use in various laboratories, have been less successful in achieving the capabilities listed in Table 1.

Table 1. Ideal Requirements for Methods of Elemental Analysis

-
1. Applicable to all elements.
 2. Simultaneous or rapid sequential multielement determination capability at the major, minor, trace, and ultra trace concentration levels without change of operating conditions.
 3. No inter element interference effects.
 4. Applicable to the analysis of microliter- or microgram-sized samples.
 5. Applicable to the analysis of solids, liquids, and gases with minimal preliminary sample preparation or manipulation.
 6. Capable of providing rapid analyses; amenable to process control.
 7. Acceptable precision and accuracy.
-

While ICP is becoming the most effective excitation source, problems, such as the loss of volatile analytes between vaporizer and plasma, brings about uncertainties to the ICP technique during the analyses for some highly volatile elements, such as: Mercury, Selenium, etc.. In this study, the RCRA regulated metals: As, Ba, Cd, Cr, Pb, and Ag,

were determined using an ICP-AE Spectrometer. The determination of Se was performed using a Graphite Furnace Atomic Absorption Spectrometer (GFAA). And the determination of Hg used a Cold Vapor Atomic Absorption Spectrometer (CVAA).

Inductively Coupled Plasma Emission Spectrometry

The inductively coupled plasma (ICP) -- atomic emission spectrometry (AES) is a relatively recent development of emission spectroscopy. Although research on its source has been going on since the early 1960s, commercial ICP systems became available only in 1974.^{7,8} In emission spectroscopy, the excitation source transforms the sample from its initial state as solid, liquid, or gas (a liquid state was used in this study.) into a plasma of atoms, ions, and molecular radicals that can be electronically excited. The radiative deactivation of these excited state produces light quanta that are sorted by wavelength in a spectrometer or spectrograph (a scanning monochromator was used in this study); the resulting emission spectrum is detected by either photographic or photoelectric means (in this study, the photomultiplier was used).⁸

Emission spectroscopy is widely used for both qualitative and quantitative analysis. The radiation that is emitted in the emission process is of a particular wavelength(s), depending on the transitions undergone by the valence shell electrons. The wavelengths are usually characteristic of each element, so that it is possible to distinguish radiation of one element from the others, thus the emission spectroscopy is considered as a qualitative technique. With a certain detector, the photocurrent (which is proportional to the analyte emission intensity) is measured directly, is integrated by a capacitor and the capacitor voltage measured, and is converted to a frequency which is counted. The magnitude of the analyte emission is proportional to the analyte concentration and a calibration curve can be obtained directly for standard materials. Then, the standard curves of emission intensities versus concentration can be used to determine the

concentration of unknown. Therefore, the emission spectroscopy can also be used for quantitative analysis.⁸

Using the principles of emission analysis, the function and operation of an ICP-AES is easily understood. Moreover, the development of the excitation source, sorting, and detecting components used in the ICP-AES, makes it more powerful in elemental analysis.

A. Among the most common excitation sources such as: arc, spark and flame, ICP has the highest discharge temperature, 9,000-10,000 K, as compared with about 4,000-7,000 K for arc and spark source, and 2,000-5,000 K for flame.⁹

This extremely high temperature is achieved by the effect of a radio-frequency field on a flowing gas (argon is the most common one used). In Figure 2, the discharge is induced into argon flowing upward through a quartz tube inside a copper coil. The coil is energized by an RF generator operating between about 5 and 75 MHz; typical frequencies are 27 and 41 MHz.⁸ The RF signal creates a changing magnetic field H inside the coil around the flowing argon gas. A changing magnetic field induces a circulating (eddy) current in conducting, argon ions and electrons within the argon gas, causing heat.

Under the high temperature the plasma, the electrons and ions of the plasma are forced by the magnetic field to follow circular paths inside the torch at very high velocities, changing their directions twice during each cycle of the RF power, or 54 million times per second. The electrons and ions meet with resistance to their motion and moving against this resistance raise their temperature. Neutral argon atoms that are continually introduced into the plasma suffer collisions with the charged particles moving about in the plasma, raising their temperature until they too become ionized, thus ensuring the continuity of the plasma. In order to ignite the plasma, an initial supply

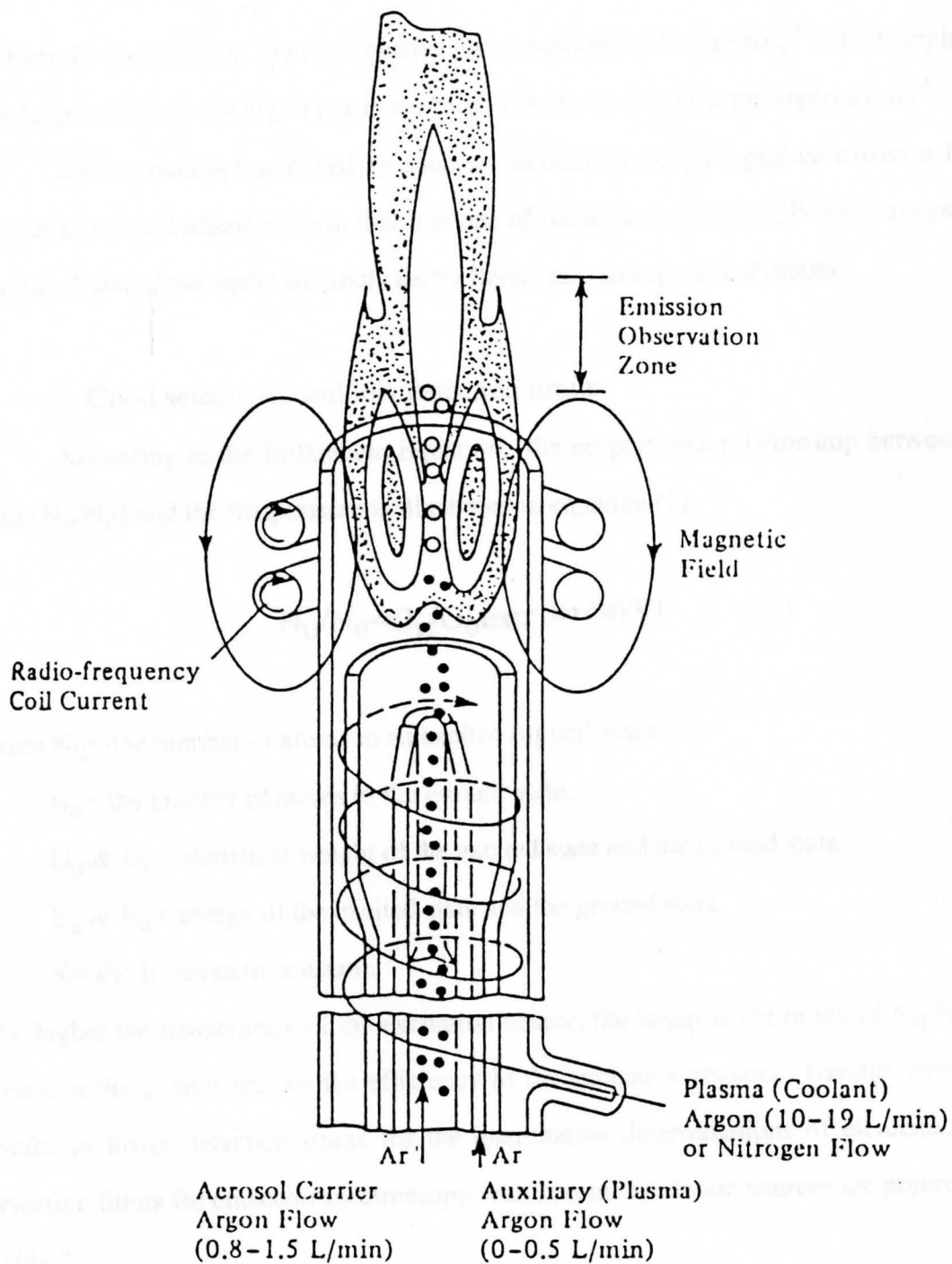


Figure 2 Schematic representation of an inductively coupled plasma discharge. From R. M. Barnes, *Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss.*, 28(4), 383 (1979), by permission of the publisher.

of electrons and ions, or "seed", is needed and generated by the ignitor,¹⁰ which applies a very high voltage to the argon gas in the torch in order to ionize some argon atoms.⁸

The temperature achieved by such an inductively-coupled plasma causes a large number of excited atoms or ions, that it is one of the advantages for ICP-AES analysis as compared with those under the analyses by flame, arc, and spark techniques:

1. Good sensitivity and low detection limits.

According to the Boltzmann Equation, the proportional relationship between the ratio (N_u/N_0) and the temperature is illustrated in equation (1):

$$N_u/N_0 = G_u/G_0 \exp^{-(E_u - E_0)/KT} \quad (1)$$

where N_u = the number of atoms in an excited (upper) state.

N_0 = the number of atoms in the ground state.

G_u & G_0 = statistical weight of the excited state and the ground state.

E_u & E_0 = energy of the excited state and the ground state.

K = the Boltzmann constant.

The higher the temperature of the excitation source, the larger is the ration of N_u/N_0 and therefore the greater will be the efficiency in the excitation process. Greater sensitivity results in lower detection limits for the quantitative determinations of elements. The detection limits for emission spectroscopy with several excitation sources are presented in Table 2:

Table 2. Comparison of Some Experimentally Determined Emission-Spectroscopic Detection Limits ($\mu\text{g/mL}$)⁸

Element	Flame	DCArc	Spark	ICP
Ag	0.02	0.0006	0.2	0.004
As	-----	0.1	5	0.002
Ba	0.001	0.005	0.02	0.00001
Cd	2	0.02	1	0.0002
Cr	0.005	0.01	0.05	0.0008
*Hg	-----	0.07	1	0.01
Pb	0.2	0.05	0.1	0.001
*Se	-----	-----	-----	0.03

The ICP discharge has been found to have both the precision of flame methods and the sensitivity of arc methods.¹¹

2. The ICP discharge provides a rich spectrum for sequential or simultaneous multielement qualitative and quantitative analysis. The spectrum of an element in the ICP discharge is unlike those obtained in the DC arc, a spark, or a flame; and new wavelength tables giving the spectral-line intensities and spectral interferences have been published.⁸

3. Some of the difficulties found in flame, arc and spark techniques are not present in the ICP discharge:

a. Chemical interferences caused by the formation of stable compounds in flames are negligible with the ICP discharge, and thus releasing agents or special conditions are not needed.

b. Ionization interferences that occur in the high temperature source such as the DC arc is minimal in the ICP plasma.

c. By selecting the emission observation height, normally between 1-3cm above the induction coil (Figure 2), the background from the argon continuum and interference from Ar I emission is minimized.

4. A linear calibration curve (over five orders of magnitude) of concentration versus emission intensity is obtained using an ICP due to the reduced interferences as mentioned above.¹²

B. Sequential analysis ICP system gives ICP-AES the power of simultaneous multielemental analysis.

The facility of ICP spectrometry for simultaneous analysis is possibly the capability that originally had the greatest appeal to analysts.¹³ It is perhaps surprising, therefore, that the majority of instrument manufacturers have recently introduced scanning ICP spectrometers. These are designed to measure the elements sequentially, scanning through the spectrum at considerable speed but increasing the time of analysis per sample significantly. The other traditional multielement analysis is performed by using a direct reading, multichannel polychromator (Figure 3).⁹ The polychromator is a simultaneous instrument, that is all the lines are measured at the same time, while definitely having its advantages, such an instrument requires a separate detector for each element of interest. With the introduction of scanning monochromator systems makes the analysis by ICP-AES more flexible, as in theory an almost unlimited range of analytical lines can be used. The ARL Model 3410 ICP-AES used in this study has the potential of analyzing 70 lines with one program and is shown in Figure 4.¹⁰ By using a scanning monochromator, wavelength slewing and scanning is achieved by the rotation of the grating, which moves the spectrum across the exit slit. The grating is moved by a stepper motor that is controlled by a computer. The operation of the stepper motor can be made remarkably precise. Also, there are other reasons for the introduction of scanning ICP systems, including the reduction in cost that can be achieved, as compared to the cost

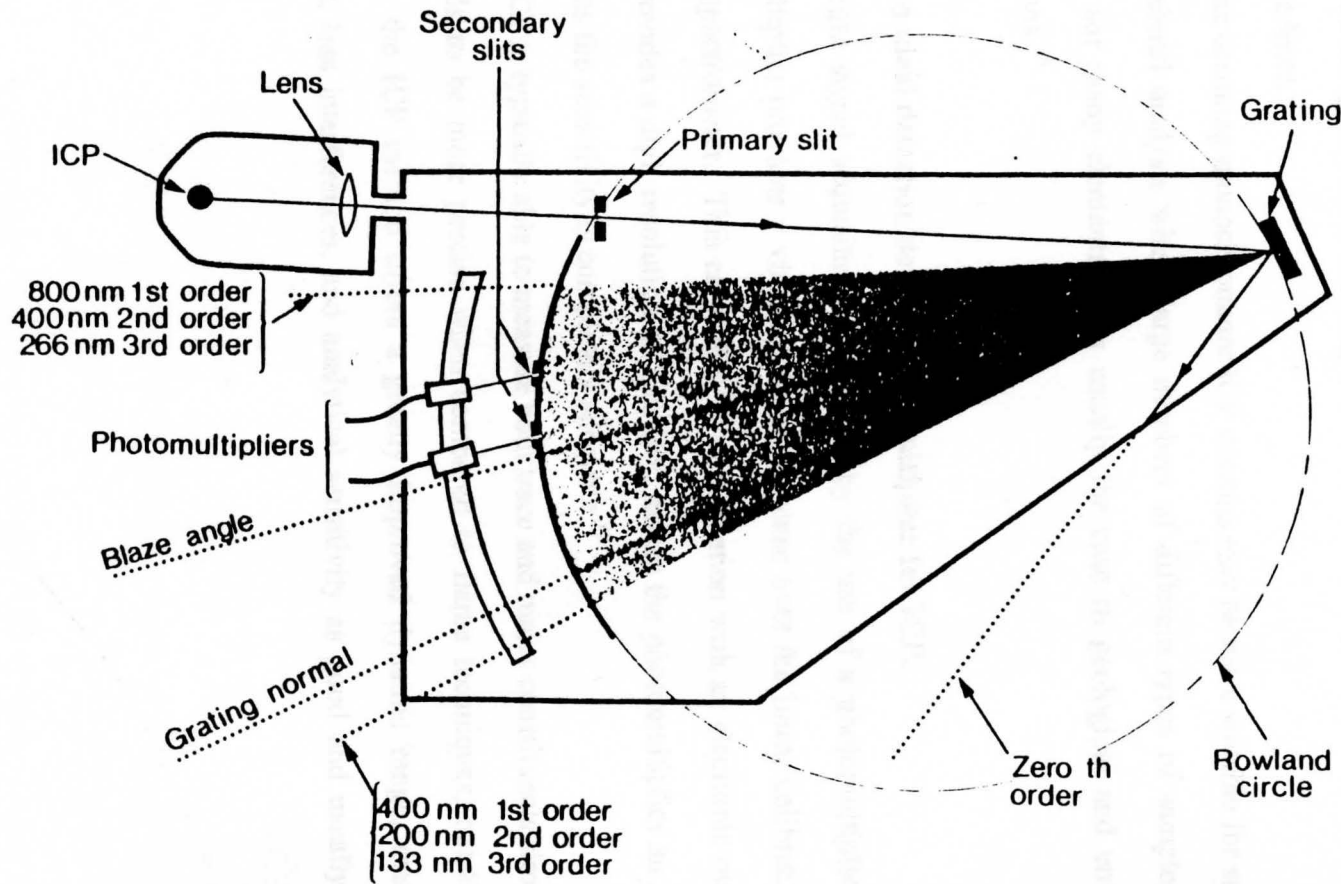


Figure 3. Scale diagram of the optics of a polychromator system in the Paschen-Runge mounting with the grating blazed for maximum reflection of 600 nm in the first order.

of a polychromator system.¹³ One is the reduction of the time spent moving from one element line to the next (slewing). Most users of polychromator systems integrate the analytical signal over a 5-20 second period, and would probably be unable to reduced this to less than a total of 5 seconds. The most recent scanning systems minimize the slew time to as little as 2-3 seconds. Although interferences from spectral overlap certainly do occur in the analysis with a scanning monochromator, they are usually avoided by using alternative lines.

The scanning monochromator ICP systems may be more suitable for simultaneous multielemental analysis where large numbers of different types of samples are to be analyzed for many elements, as is usually the case in geological and environmental applications.¹⁰

C. An ideal detection device-photomultiplier for ICP.

Light signal acquisition is achieved by the use of a photomultiplier tube. The photomultiplier provides a virtually linear response over the linear calibration range of the ICP spectrometer. This capability, in combination with an electronic output system which provides a digit resolution of 1 in 10^6 , makes the photomultiplier an ideal device for ICP, as the sensitivity is completely adequate.¹⁰

ICP is typically able to measure both trace and major constituents simultaneously. ICP tends to be more precise when compared to flame techniques, notably AAS. In addition, the ICP method offers a greatly improved dynamic range, small need for dilutions, less interferences, and analytical sensitivity as good and usually better than AAS.

FOCAL LENGTH NOT REPRESENTED AT SCALE

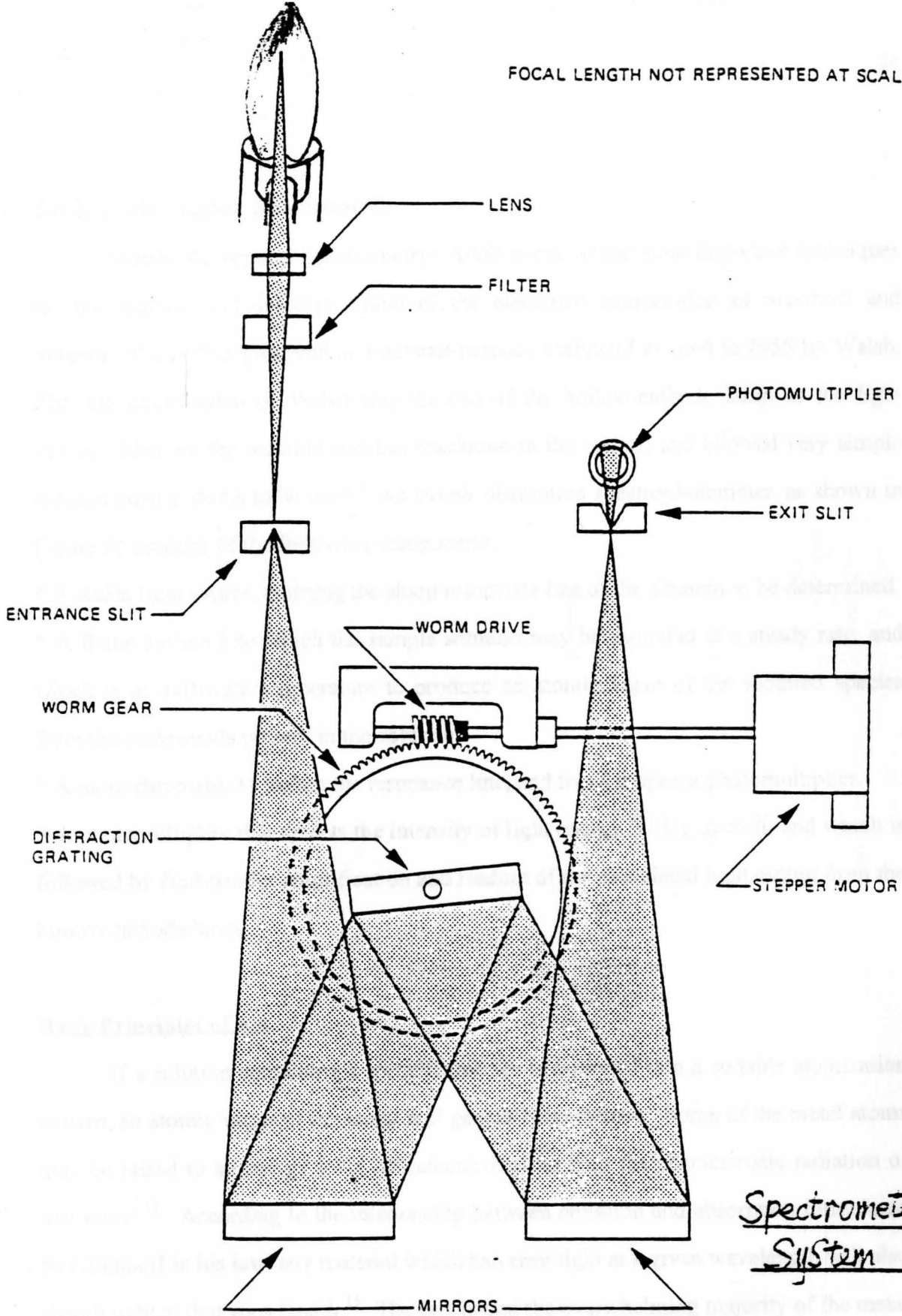


Figure 4 | Schematic Representation of Model 3410 ICPS Spectrometer System

Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is one of the most important techniques for the analysis and characterization of the elemental composition of materials and samples. It was first proposed as a general-purpose analytical method in 1955 by Walsh. The key contribution of Walsh was the use of the hollow-cathode lamp as the light source. This put the required spectral resolution in the source, and allowed very simple measurement systems to be used.⁸ An atomic absorption spectrophotometer, as shown in Figure 5, consists of the following components.

- * A stable light source, emitting the sharp resonance line of the element to be determined.
- * A flame system into which the sample solution may be aspirated at a steady rate, and which is of sufficient temperature to produce an atomic vapor of the required species from the compounds present in the solution.
- * A monochromator to isolate the resonance line, and focus it upon a photomultiplier.
- * A photomultiplier that detects the intensity of light energy falling upon it, and which is followed by facilities for amplification and readout of the modulated light output from the hollow cathode lamp.

Basic Principles of AA

If a solution containing a metallic species is aspirated into a suitable atomization system, an atomic vapor of the metal will generally be formed. Some of the metal atoms may be raised to an energy level sufficiently high to emit the characteristic radiation of that metal.¹⁴ According to the relationship between emission and absorption formulated by Kirchhoff in his law, any material which can emit light at a given wavelength will also absorb light at that wavelength.¹⁵ The fact is that the overwhelming majority of the metal atoms remain in the non-emitting, ground state. If irradiated with light of their

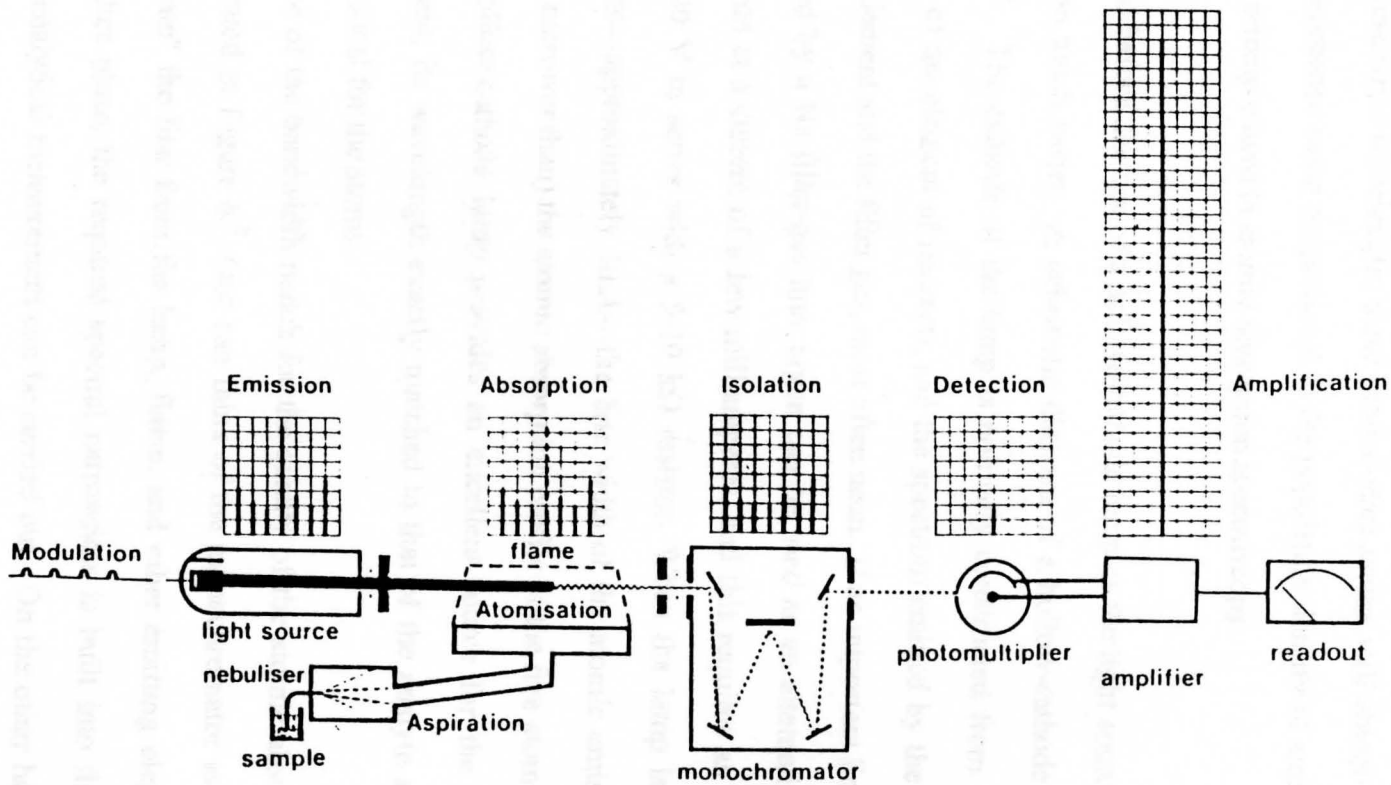


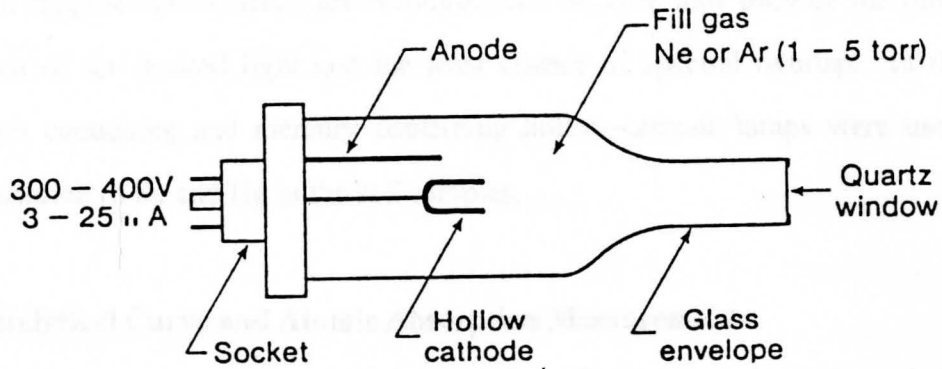
Figure 5. Basic construction of an atomic absorption spectrophotometer

own characteristic resonance wavelength, these ground-state atoms will absorb some of the radiation, the absorbance being proportional to the population density of atoms in the species. This is the principle used in atomic absorption spectroscopy.

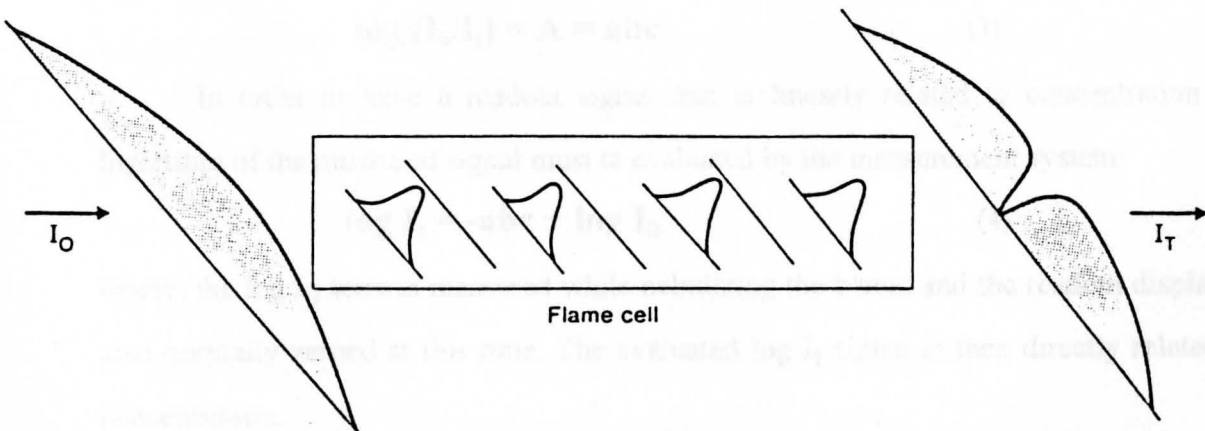
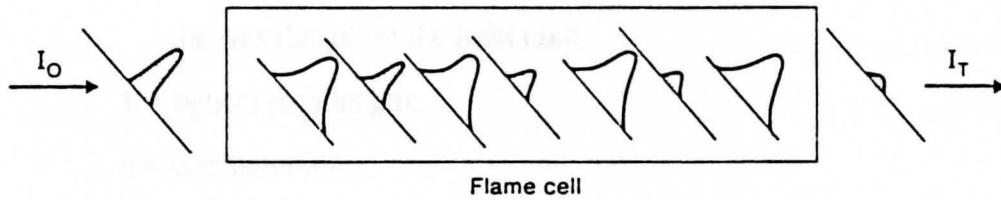
Light Source

As mentioned before, the use of a hollow-cathode lamp as the light source makes the atomic absorption much easier. A schematic diagram of a hollow-cathode lamp is shown in Figure 6.⁸ The cathode of the lamp is normally constructed from a single element (or an alloy of the element of interest), and the spectrum emitted by the lamp is the spectrum of the element and the filler gas, most often neon. If an important line of the element is overlapped by a Ne filler-gas line, argon can be used as an alternative. The lamps are typically run at a current of a few milliamperes, and this requires an applied voltage of 100 to 300 V in series with a 5-10 k Ω resistor. When the lamp is run at relatively low currents---approximately 3mA---the line width of the atomic emission is about the same as (or narrower than) the atomic absorption profile of the free atoms in the flame. Thus, the hollow-cathode lamp provides an excellent source for the atomic absorption measurement, its wavelength exactly matched to that of the analyte and the bandwidth essentially ideal for the atoms.

The importance of the bandwidth match for the quality of the atomic absorption measurement is illustrated in Figure 6.⁸ One can think of the monochromator as being required only to "isolate" the line from the lamp, flame, and other emitting elements. Once this isolation takes place, the required spectral narrowness is built into the line itself, and a sensitive analytical measurement can be carried out. On the other hand, if one started with a continuum source and tried to make the measurement with the same monochromator, the result would be a broad Band of light that even a very strongly absorbing atom concentration in the flame would absorb only a small fraction of that light within the bandpass of the monochromator. This leads to a very insensitive absorption measurement.



Schematic diagram of a hollow-cathode lamp.



Schematic diagram of measurement-bandwidth aspects in atomic absorption spectrometry.

Figure 6

There are a number of multielement hollow-cathode lamps also available. In general, single-element lamps are recommended because they provide the most intense emission of the desired light and the least chance of spectral overlap. In this study, selenium containing and mercury containing hollow-cathode lamps were used for the determination of Se and Hg in the soil samples.

The Analytical Curve and Atomic Absorption Measurements

Ideally, the transmitted intensity I_t of the hollow-cathode lamp through the atomic adsorption system is governed by the Beer-Lambert law in equation (2):

$$I_t = I_0(10^{-abc}) \quad (2)$$

where, I_0 = the intensity of the source radiation absorbed by the sample atoms;

a = molar absorptivity, characteristic of the absorbing species and a function of the wavelength of the light used;

b = optical path length;

c = concentration.

A measurement of absorption can then be obtained and related to concentration, refer to equation (3):

$$\log(I_0/I_t) = A = abc \quad (3)$$

In order to have a readout signal that is linearly related to concentration the logarithm of the measured signal must be evaluated by the measurement system:

$$\log I_t = -abc + \log I_0 \quad (4)$$

where, the $\log I_0$ term is measured while nebulizing the blank, and the readout display is also normally zeroed at this time. The evaluated $\log I_t$ signal is then directly related to concentration.

A typical analytical curve is not exactly linear as predicted by the equation. There are several causes of nonlinearity: including stray light, line broadening,

nonhomogeneities of temperature and nonabsorbing lines within the bandpass of the monochromator.⁸

Atomization Systems

The term atomization refers to the breakdown of a compound to its free atoms. The sensitivity of a determination is directly proportional to the degree of atomization of the element under study in the sample. The success or failure of an analysis is virtually dependent upon the effectiveness of the atomization.¹⁵

The longest practiced, and therefore most widely propagated, method for the dissociation of a sample into atoms in atomic absorption spectroscopy is the spraying of a solution into a flame (as shown in Figure 5).¹⁴ A key disadvantage of flame systems as sources of atomic vapor is the inefficient use of sample by the nebulizer-spray chamber-burner system. Over the last 10 to 15 years, considerable effort has been directed toward the development of "nonflame" atomization systems for atomic absorption spectrometry.

GFAAS

The atomization in graphite furnaces heated by electrical resistance has had the greatest impact in flameless atomization. The early impetus for the development of such flameless systems came from the work of L'vov in 1961. A schematic representation of this system is given in Figure 7.⁸

A fixed sample volume is introduced into the furnace, and after thermal pretreatment, is rapidly atomized. This results in a high, time-dependent signal whose height or area is proportional to the quantity of the element under study.¹⁵

In this study, a GFAAS was employed in the analysis for the heavy metal Se. The sample solution was introduced into the sample container with the sample volume being small, in the microliter range, anywhere from 5 to 100 μL . The sample was then heated by passage of an electrical current, and a three-stage heating program was used:

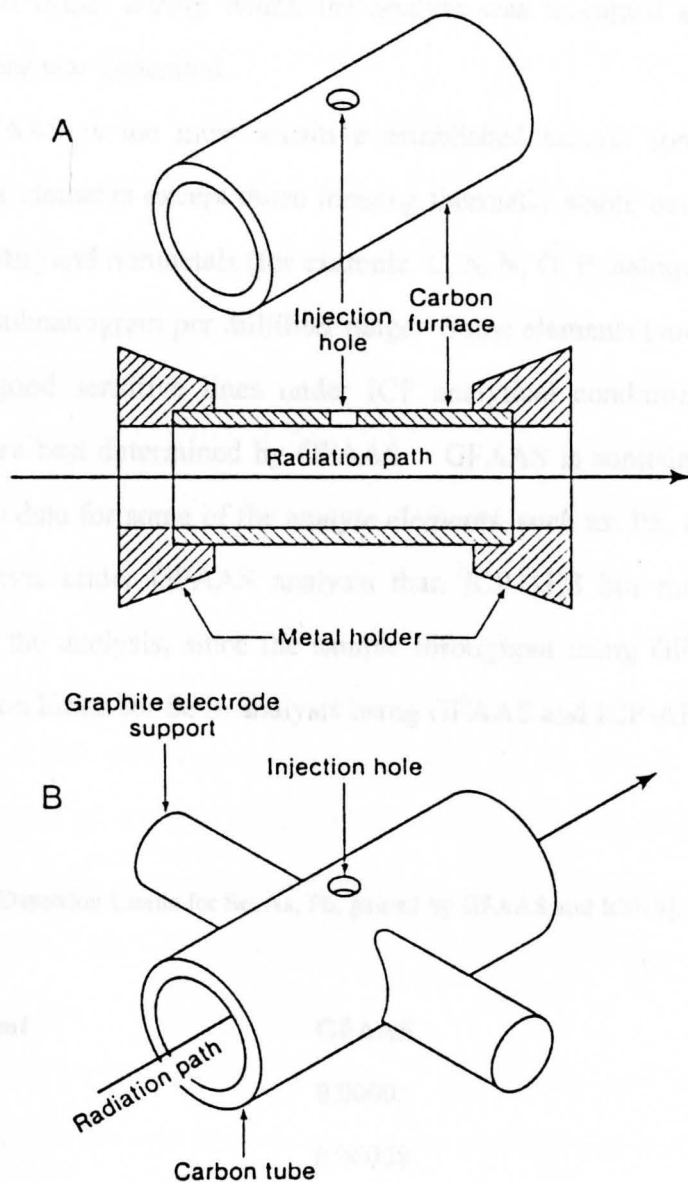


Figure 7 Schematic diagrams of furnace (A) and tube-type (B) electro-thermal atomizers.

(a). drying cycle, during which the solvent was vaporized; (b). ash cycle, during which the objective was to char and "burn off" any organic component in the sample; (c). atomization cycle, during which the analyte was atomized and a transient plume of atomic vapor was generated.

GFAAS is the most sensitive established atomic spectrometric method for a majority of elements except those forming thermally stable oxides and carbides (Ti, Hf, B, rare earths) and nonmetals (for example, C, S, N, O, P, halogens). The detection limits are in the subnanogram per milliliter range. Some elements (such as Se, As, etc.) that do not have good sensitive lines under ICP analytical conditions because of their high volatility are best determined by GFAAS. GFAAS is sometimes used only to provide comparison data for some of the analyte elements, such as: Pb, As, etc. which have more sensitive lines under GFAAS analysis than ICP-AES but much longer time will be needed for the analysis, since the sample throughput using GFAAS is extremely slow. The detection limits for Se in analysis using GFAAS and ICP-AES are presented in Table 3:

Table 3. The Detection Limits for Se, As, Pb, gained by GFAAS and ICP-AES(mg/L)¹⁶

element	GFAAS	ICP-AES
Se	0.00005	0.03
As	0.00008	0.03
Pb	0.000007	0.025

II/(2). CVAAS

A special method has also been developed for the determination of mercury. Mercury is the only common metal that has an appreciable vapor pressure at room

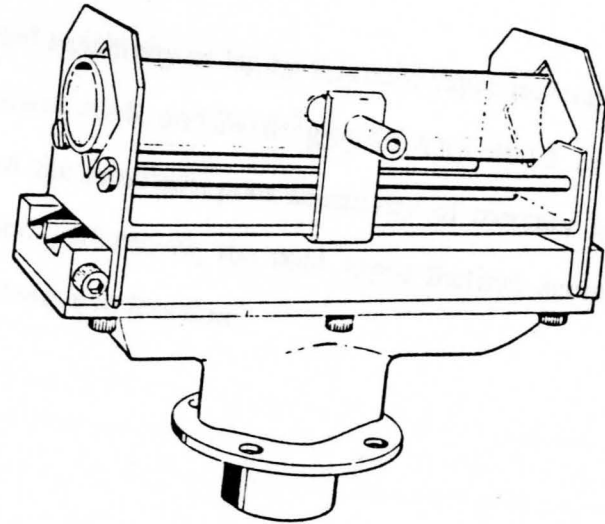
temperature and that does not require the application of energy by the cell in order to convert the analyte to atoms.¹⁷

The determination of mercury at trace levels is readily accomplished by cold-vapor atomic absorption spectrophotometry. In this technique, a mercury ion in solution is reduced by a chemical reducing agent (such as 5% stannous chloride in hydrochloric acid, which was used in this study; 40% hydrazine hydrate; or 5% sodium borohydride), and then the free mercury atoms are flushed from the reaction vessel into a quartz cell mounted in the optical path of an AA spectrophotometer.

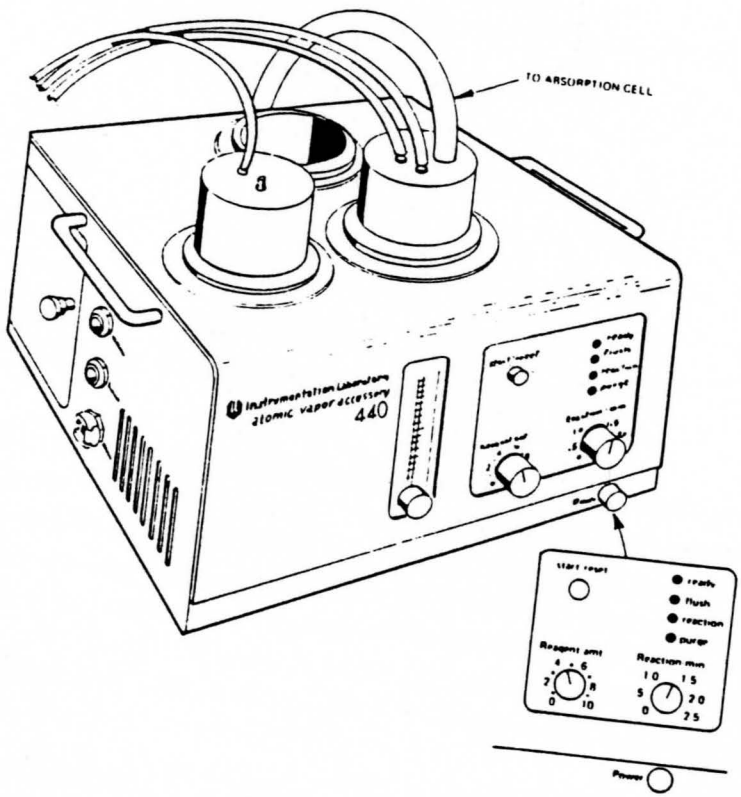
The atomization system, named "Atomic Vapor Accessory (IL440)" used for the cold-vapor method, consists of two parts: the vapor generator and the absorption cell. This system is shown in Figure 8.¹⁸ The vapor generator consists of the system's electronic circuitry, operational controls, peristaltic pump, system plumbing, and an enclosure. The IL440 has three recessed protective wells to hold Fleaker vessels: the right rear for the reaction Fleaker cap, the left front for the Fleaker containing reducing agent, and the right front (which has a stirring motor) for the reaction Fleaker. The absorption cell is made of quartz and designed to fit onto the standard burner head. The cell is closed on both ends with quartz windows that are transparent to radiation at the wavelength (253.7nm) of the mercury line that is used for the assay. The cell is mounted on the burner head shown in Figure 8.

A mercury hollow-cathode lamp is used as the source of radiation. After the vapor has passed through the cell, and the measurement has been completed, the mercury is flushed from the system into a hood.

In this study, a digestion procedure was performed because the existence of organically bound Hg is suspected in the soil sample extraction leachates. The digestion was carried out by using a mixed nitric/sulfuric acid in a BOD flask, an oxidizing agent (5% KMnO_4) was used to oxidize the Hg^0 or Hg_2^{2+} to Hg^{2+} since Hg^{2+} is the only stable form of Hg in the solution.



(A) Mercury Vapor Cell



(B) The IL440

Figure 8

Expected sensitivity of Hg by this cold vapor technique is $2 \times 10^{-9} \text{g}$; however, it is $1.4 \times 10^{-4} \text{g}$ by flame AAS, and $2 \times 10^{-7} \text{g}$ by GFAAS, and $1.2 \times 10^{-5} \text{g}$ by ICPS¹⁶. Thus, this method avoided the relatively poor sensitivity of mercury in either the Flame-AAS or ICP-AES method. Moreover, the cold vapor method achieved better sensitivity than Furnace AA technique in less time.

Standard solutions for the calibration of AAS
 The standard solutions were prepared by adding 1.0, 2.0, 5.0, 10, and 20 mL of a 1.0 mg/L Hg standard solution to 100 mL of a 0.1% KI solution. The standard solutions were prepared in Table 4.

Table 4. The Concentrations of Each Component in the Standard Solution Used for Calibration

Component	Concentration (ppm)
Hg	1.0
KI	10
Fe	10
Cd	10
Pb	10
Cu	10

Blank for calibration: 1.0 mg/L HgO and 10 mg/L KI.

The results and data are given in the following table. According to the ICA
 (International Council for Harmonization of Technical Requirements for Pharmaceuticals
 in Human Use) (ICH Q1A, Federal Register, Vol. 49, No. 27, Tuesday, March 29, 1984,
 1367-1368), the following parameters were initially evaluated for (1)
 determination of the percent solids (if the percent solids is greater than or equal to 0.5
 percent, additional steps are necessary); (2) determination of the particle size (should
 be appropriate for the intended use); (3) determination of which of the two
 extraction methods is preferred (see b & c following)

After finishing the preliminary evaluation, a 10g (wet and dried phases) sample was
 dissolved and extracted with 100 mL of appropriate solvent and 1 mL of appropriate
 reagent. The extract was then dried (by the use of a rotary evaporator) to obtain a
 solid residue. The residue was then weighed and re-dissolved in 10 mL of appropriate
 solvent. The extract was then placed in a vial and stored at 19 to 25 °C. Following
 the extraction, the sample was filtered through a 0.45 µm glass fiber filter. Reagent grade

Chapter IV

Procedures and Results

Calibration and sample solution preparations

Preparations for the analysis on ICP

1. The calibration solution containing As, Ba, Ag, Cd, Cr, and Pb; and blank used for sequential multielement analysis on ICP was acquired from Fisher Scientific (Fair Lawn, NJ). The concentration of each content was given in Table 4:

Table 4. The Concentration of Each Component in the Standard Solution Used for Calibration

Constituent	Concentration(ppm)
Ag	5
As	5
Ba	10
Cd	5
Cr	10
Pb	10

Blank for calibration contained HNO₃ and DI H₂O only.

2. Sample and blank solution preparations for analysis. According to the TCLP extraction method (Refer to Federal Register/Vol.55, No.61/Thursday, March 29, 1990/Rules and Regulations. P11862-11877), samples were initially evaluated for (1) determination of the percent solids (if the percent solids is greater than or equal to 0.5 percent, additional steps are necessary); (2) determination of the particle size (should be approximately 1mm in diameter or less); (3) determination of which of the two extraction fluids should be used for sample extraction.(see b & c following)

After finishing the preliminary evaluation, a 50g (solid and liquid phases) sample was obtained and transferred into an extractor bottle and to this was added 1.0L of appropriate extraction fluid. The extractor bottle was closed tightly (Teflon tape was used to ensure a tight seal), and secured in a rotary agitation device, and rotated at from 28 to 32rpm for 18±2 hours. The extraction took place at room temperature, from 19 to 25 °C. Following the extraction, the sample was filtered through a new glass fiber filter. Reagent grade

HNO₃ was added to the liquid phase from the filtration to achieve a final concentration of 1% and then stored at 4°C until the time of analysis.

b. Extraction Fluid Preparation

(1) Extraction Fluid #I-----5.7mL Glacial Acetic Acid was added to 500mL DI water in a 1.0L volumetric flask. Then 64.3mL of 1N NaOH(40g of NaOH/1Lwater) was added to the flask and the resulting solution was diluted to a final volume of 1L with DI water. The pH of this fluid was 4.93±0.05.

(2) Extraction Fluid #II-----5.7 mL of Glacial Acetic Acid was diluted with DI water to a volume of 1.0 Liter. The pH of this fluid was 2.88±0.05.

These two extraction fluids were checked each time for proper pH everytime before using. Any fluid was discarded when the pH was not within the above specifications.

c. Selection of Extraction Fluids

In this study, 1.25g of solid was transferred into a 125mL beaker, 25mL DI water was added and the beaker was covered with a watchglass, stirred vigorously for 5 minutes using a multiple magnet magnetic stirrer. Then the pH was measured.

If the pH was < 5.0, extraction fluid#1 was used;

If the pH was > 5.0, 0.9mL 1N HCl was added, slurried briefly, covered with a watchglass, heated to 50°C, and held at 50°C for 10 minutes. Then, the solution was cooled to room temperature and the pH was measured again.

If the pH was < 5.0, extraction fluid#1 was used.;

If the pH was > 5.0, extraction fluid#2 was used.

d. Blank solutions for quality assurance were prepared using the appropriate extraction fluid selected for the sample. Reagent grade HNO₃ was added until the final concentration of nitric acid in the extraction fluid was 1%HNO₃. The heavy metal concentration was subtracted from the values given for the samples.

Preparations for the analysis on GFAAS.

1. Calibration standard solutions: 1000ppm Se in 1% (v/v) HNO₃ standard was obtained commercially from Fisher Scientific (Fair Lawn, NJ). To avoid any matrix effects on the analysis, standard additions of successively larger increments of analyte to the sample were made.
2. Sample solutions and blank for the analysis: the same solutions for both the sample and blank were used as that used for ICP analysis.

In the analysis, a 25 µL aliquot of sample was placed directly into the cylindrical furnace cuvette and analyzed according to the conditions described below in Table 5:

Program Variables

ICP Analysis

Initially, a task file was generated to conduct an analysis with the ICP spectrometer. Once named, variables such as elements to be analyzed, their wavelength of emission, the PMT sensitivity, and integration times were entered as in Table 6. In addition, the number and content of standard solutions must be entered. One of these solutions was a blank. The concentration of each component was noted. If the element to be analyzed was not present in a solution the label N/A was used.

Table 6. Variables Used in the ICP Analysis

Element Symbol	Line Lib. Wavelength	L.Q.D.	PMT Attn.	Int. Time	Line Lib. Interferences
Ag	328.068	0.0100	8	1.0	Fe Mn V
Ba	455.403	0.0020	5	0.5	Cr Ni Ti
Cd	214.438	0.0100	10	1.0	Al Fe Pt
Cr	267.716	0.0150	10	1.0	Fe Mn Pt V
Hg	194.227	0.0500	10	1.5	Al V
Pb	220.353	0.1000	10	1.0	Al Cr Pd Sn
Se	196.090	0.2500	10	1.5	Al Fe Pd
As	189.042	0.2000	8	1.0	
As	193.759	0.1250	10	1.5	Al Fe V
Cd	226.502	0.0150	10	1.0	Fe Ni
Cr	205.552	0.0100	10	1.0	Al Cu Fe Ni
Pb	226.999	0.1000	10	1.0	Al Cr Pd Sn
Ag	338.289	0.0500	8	1.0	Cr Ti
Se	203.985	0.4000	10	1.5	Al Cr Fe Mn

The choice of which emission line to be employed was guided by several criteria. First spectral interferences are quite possible. The sample matrix will determine spectral interferences. For example, many chromium lines are either totally or partially overlapped by iron emission lines. Often to analyze a steel sample, the intensity of iron at the chromium wavelength must be known. This is termed interfering element correction. Secondly the intensity of the element emission may determine its analytical value. If the element exists only in trace amounts, an extremely sensitive spectral line may be necessary. The opposite situation also may occur where an insensitive line is used for a very concentrated sample. It may be advisable to use more than one emission line for each element being detected.

First the ICP torch was lit and allowed to stabilize for at least five minutes. Then the monochromator was calibrated such that the number of steps of the diffraction grating's stepper motor to scan between the "zero" angle and the argon triplet at 345.61 nm was noted. This count was measured three times and averaged. The ratio of steps to wavelength (in steps/nm) was recorded in memory. The instrument was then capable of

stepping to any other wavelength by relating the number of steps required to this ratio. To further refine the number of steps needed to reach an elemental emission line, a solution containing from one to ten mg/mL of the elements of interest was aspirated into the torch. Next, the monochromator was driven by the number of steps anticipated to reach a chosen element. If a peak was found the instrument indicated the difference between the number of steps and the actual number of steps necessary to reach the maximum of the element peak. If prompted the instrument would use this value whenever this line was employed.

Once initial instrument "set-up" has been performed, a standard was aspirated and the number of photons striking the PMT were counted and recorded. Next any additional elements, standards, and blanks were measured. In the case of multi-point calibrations for many elements, this may be a lengthily process. When finished, the photon counts were "fitted" to the best representative curve. Calibration curves may be drawn and inspected. At this point the instrument was ready to analyze unknown samples.

GFAAS Analysis

In graphite furnace atomic absorption spectrometry spectral interferences are seldom observed. Therefore the most sensitive line was employed for analysis. However, chemical interferences are more prevalent. Due to the more extensive study of GFAAS operating parameters, the lamp, graphite curve, temperature program, the addition of Pd matrix modifier and PMT, were operated as specified in the manufacturer's procedure for Se analysis.

CVAAS Analysis

The Atomic Absorption and Cold Vapor attachment was operated as specified by the manufacturer. The lamp and PMT settings were such that maximum light throughput occurred with minimum noise. The argon carrier gas flow rate and sample and reagent volumes were specified by the manufacturer. Some attempts to change these values resulted in less sensitivity and were abandoned.

III. Results

Results of the heavy metal analyses are summarized in (Table 7). All of the heavy metal levels in 165 samples from about 33 different sites were below the RCRA Regulatory Levels (Table 8). The sites where samples were selected were left off by land owner's request.

**Table 7. Mahoning River Corridor
Heavy Metals Results**

Results Expressed in mg/L

SAMPLE	Ag	Ba	Cd	Cr	Hg	Pb	Se	As
1	0.049	11.4	0.827	4.88	0.006	1.29	ND	0.120
2	0.051	18.1	0.208	1.37	ND	1.04	ND	0.0864
3	0.055	7.35	0.890	4.95	0.003	2.32	ND	0.113
4	ND	0.631	ND	ND	ND	ND	ND	ND
5	ND	0.742	ND	ND	ND	ND	ND	ND
6	ND	0.774	ND	ND	ND	ND	ND	ND
7	ND	0.771	ND	0.018	ND	ND	ND	ND
8	ND		ND	0.031	ND	ND	ND	0.269
9	ND	0.745	0.044	0.027	ND	0.013	ND	ND
10	ND	0.727	0.039	0.018	ND	ND	ND	ND
11	ND	0.888	0.041	0.027	ND	0.448	ND	ND
12	ND	0.370	0.040	0.026	ND	ND	ND	ND
13	ND	0.816	0.043	0.020	ND	0.103	ND	ND
14	ND	1.296	0.032	0.031	ND	ND	ND	ND
15	ND	0.984	0.034	0.029	ND	ND	ND	0.134
16	ND	0.555	ND	ND	ND	ND	ND	0.136
17	ND	0.488	ND	ND	ND	ND	ND	ND
18	NS	0.514	ND	0.017	ND	ND	ND	ND
19	ND	0.353	ND	ND	ND	ND	ND	ND
20	ND	0.443	ND	ND	ND	ND	ND	ND

21	0.613	ND	ND	ND	ND	ND	ND	ND
22	ND	0.398	ND	0.015	ND	0.429	ND	ND
23	ND	0.469	ND	ND	ND	ND	ND	ND
24	ND	0.554	ND	ND	ND	ND	ND	ND
25	ND	0.735	ND	ND	ND	ND	ND	ND
26	ND	0.292	ND	ND	ND	ND	ND	ND
27	ND	0.445	ND	ND	ND	ND	ND	ND
28	ND	0.946	ND	ND	ND	ND	ND	ND
29	ND	0.653	ND	ND	ND	ND	ND	0.236
30	ND	0.968	ND	ND	ND	ND	ND	ND
31	ND	0.847	ND	ND	ND	ND	ND	ND
32	ND	0.65	ND	ND	ND	ND	ND	0.29
33	ND	0.63	0.02	ND	ND	ND	ND	0.20
34	ND	0.78	0.02	ND	ND	ND	ND	ND
35	ND	2.19	ND	ND	ND	0.10	ND	0.28
36	ND	0.65	ND	0.47	BD	0.14	0.41	0.62
37	ND	0.11	ND	0.05	ND	0.15	0.45	0.62
38	ND	1.44	ND	0.04	ND	ND	ND	0.32
39	ND	0.86	ND	ND	ND	ND	ND	0.34
40	ND	0.81	ND	ND	ND	ND	ND	ND
41	ND	1.06	ND	0.03	ND	ND	ND	0.45
42	ND	0.54	ND	ND	ND	ND	ND	ND
43	ND	0.31	ND	ND	ND	ND	ND	ND
44	ND	0.41	ND	ND	ND	ND	ND	ND
45	ND	0.85	ND	ND	ND	ND	ND	ND
46	ND	0.67	ND	ND	ND	ND	ND	ND
47	ND	0.74	ND	ND	ND	ND	ND	ND
48	ND	0.56	ND	ND	ND	ND	ND	ND
49	ND	1.14	ND	0.32	ND	ND	ND	ND
50	ND	0.98	0.02	ND	ND	0.13	ND	0.24

51	ND	0.29	0.02	ND	0.18	0.17	ND	0.31
52	ND	ND	ND	0.03	0.10	0.18	ND	0.31
53	ND	1.74	ND	0.33	ND	0.21	ND	0.28
54	ND	0.85	ND	ND	ND	ND	0.49	ND
55	ND	0.63	ND	ND	ND	ND	ND	ND
56	ND	0.74	ND	ND	ND	ND	ND	ND
57	ND	0.69	ND	ND	ND	ND	ND	ND
58	ND	4.01	0.07	0.16	ND	0.45	0.46	0.57
59	ND	0.62	ND	ND	ND	ND	ND	ND
60	ND	0.52	ND	ND	ND	ND	ND	ND
61	ND	0.51	ND	ND	ND	ND	ND	ND
62	ND	0.69	0.02	ND	ND	ND	ND	0.28
63	ND	0.58	0.02	ND	ND	ND	ND	0.28
64	ND	0.45	0.27	0.08	0.18	0.17	ND	0.40
65	ND	0.31	0.02	ND	ND	ND	ND	0.30
66	ND	1.09	0.02	ND	ND	ND	ND	0.24
67	ND	0.53	0.02	ND	ND	ND	ND	0.38
68	ND	0.49	ND	ND	ND	ND	ND	ND
69	ND	0.80	ND	ND	ND	ND	ND	ND
70	ND	0.53	ND	ND	ND	ND	ND	ND
71	ND	2.00	ND	ND	ND	ND	ND	0.25
72	ND	1.00	ND	ND	ND	ND	ND	0.37
73	ND	1.36	ND	ND	ND	ND	ND	0.41
74	ND	1.16	ND	ND	ND	ND	ND	0.37
75	ND	1.62	ND	ND	ND	ND	ND	0.41
76	ND	1.15	ND	ND	ND	ND	ND	0.39
77	ND	0.39	ND	ND	ND	ND	ND	ND
78	ND	0.6	ND	ND	ND	ND	ND	0.14
79	ND	0.39	ND	ND	ND	ND	ND	ND
80	ND	0.30	ND	ND	ND	ND	ND	N

81	ND	0.75	ND	ND	ND	ND	ND	ND
82	ND	0.45	ND	ND	ND	ND	ND	ND
83	ND	0.45	ND	ND	0.08	ND	ND	ND
84	ND	0.84	ND	ND	ND	ND	ND	ND
85	ND	1.10	ND	ND	ND	ND	ND	ND
86	ND	0.58	0.02	ND	ND	ND	ND	0.29
87	ND	1.05	0.02	ND	ND	ND	ND	0.26
88	ND	0.48	ND	ND	ND	ND	ND	0.32
89	ND	0.34	0.02	ND	ND	ND	ND	0.41
90	ND	0.37	0.04	ND	ND	0.11	ND	0.24
91	ND	1.07	0.03	ND	ND	0.29	ND	0.35
92	ND	0.41	0.03	ND	ND	ND	ND	0.35
93	ND	0.82	0.02	ND	ND	0.13	ND	0.38
94	ND	1.48	0.02	ND	ND	0.21	ND	0.49
95	ND	0.22	0.02	ND	ND	ND	ND	0.31
96	ND	0.86	0.02	ND	ND	ND	ND	0.33
97	ND	0.41	0.03	ND	ND	0.17	ND	0.25
98	ND	1.41	0.02	ND	ND	ND	ND	0.21
99	ND	0.95	0.02	ND	ND	ND	ND	0.30
100	ND	0.71	0.02	ND	ND	0.38	ND	0.34
101	ND	0.84	0.02	ND	ND	0.12	ND	0.36
102	ND	0.91	0.02	ND	ND	0.12	NS	0.25
103	ND	2.63	0.03	0.13	ND	3.31	ND	0.25
104	ND	1.60	0.03	0.04	ND	0.38	ND	0.28
105	ND	1.52	ND	0.06	ND	0.25	ND	0.30
106	ND	0.20	ND	ND	ND	ND	ND	0.21
107	ND	0.56	ND	ND	ND	0.11	ND	0.26
108	ND	1.32	ND	0.05	ND	0.24	0.26	0.45
109	ND	0.50	ND	ND	ND	ND	ND	ND
110	ND	0.85	ND	ND	ND	ND	ND	ND

111	ND	0.44	ND	ND	ND	ND	ND	ND
112	ND	0.87	0.02	ND	ND	ND	ND	ND
113	ND	0.37	ND	ND	ND	ND	ND	0.18
114	ND	0.72	ND	ND	ND	ND	ND	ND
115	ND	0.77	ND	ND	ND	ND	ND	ND
116	ND	0.59	ND	ND	ND	ND	ND	ND
117	ND	0.57	0.02	0.15	ND	ND	ND	ND
118	ND	1.21	ND	ND	ND	ND	ND	0.22
119	ND	1.02	0.02	ND	ND	ND	ND	0.26
120	ND	0.58	0.02	ND	ND	0.11	ND	0.26
121	ND	1.29	0.02	ND	ND	ND	ND	0.45
122	ND	1.11	0.02	ND	ND	0.11	ND	0.26
123	ND	1.09	0.02	ND	ND	ND	ND	0.35
124	ND	ND	ND	ND	ND	0.14	ND	ND
125	ND	0.49	0.02	ND	ND	ND	ND	ND
126	ND	0.74	ND	ND	ND	ND	ND	ND
127	ND	0.46	ND	ND	ND	ND	ND	ND
128	ND	0.71	ND	ND	ND	ND	ND	ND
129	ND	0.44	ND	ND	ND	ND	ND	ND
130	ND	0.553	ND	0.022	0.233	ND	ND	0.338
131	ND	0.621	ND	0.013	ND	ND	ND	0.352
132	ND	0.585	0.014	0.017	ND	ND	ND	0.360
133	ND	0.379	ND	0.022	ND	ND	ND	0.543
134	ND	0.516	ND	0.019	ND	ND	ND	0.345
135	ND	0.480	ND	ND	ND	ND	ND	0.374
136	ND	0.731	ND	0.026	ND	ND	ND	0.521
137	ND	0.708	ND	0.016	ND	ND	ND	0.441
138	ND	0.720	ND	0.021	ND	ND	ND	0.360
139	0.010	0.846	0.034	0.035	ND	0.173	ND	0.639
140	ND	0.770	ND	0.030	ND	0.106	ND	0.587

141	0.010	0.809	ND	0.027	ND	ND	ND	0.433
142	0.011	0.518	ND	0.031	ND	ND	ND	0.426
143	0.013	0.515	ND	0.034	ND	ND	ND	0.448
144	0.011	0.629	ND	0.031	ND	ND	ND	0.455
145	0.014	0.593	ND	0.039	ND	ND	ND	0.463
146	0.017	0.468	ND	0.052	ND	0.109	ND	0.646
147	ND	0.261	ND	0.027	0.199	ND	ND	0.382
148	ND	0.154	ND	ND	0.068	ND	ND	0.335
149	ND	0.051	ND	0.040	0.083	0.117	ND	0.575
150	ND	0.636	0.028	0.049	0.065	0.145	0.487	0.652
151	ND	0.313	ND	0.012	ND	ND	ND	0.464
152	ND	0.592	ND	0.045	0.071	0.130	ND	0.611
153	ND	0.518	0.010	0.050	0.072	0.133	ND	0.617
154	ND	1.191	ND	ND	ND	ND	ND	0.305
155	ND	1.525	0.155	0.018	0.176	ND	ND	0.393
156	ND	0.712	0.161	0.021	0.173	ND	0.269	0.875
157	ND	1.005	ND	ND	ND	ND	ND	0.317
158	ND	1.010	ND	ND	ND	ND	ND	0.341
159	ND	0.615	ND	ND	ND	ND	ND	0.341
160	ND	0.190	ND	0.021	ND	ND	ND	0.382
161	ND	0.727	0.043	0.119	0.073	0.148	0.487	1.186
162	ND	0.363	ND	0.018	ND	ND	ND	0.399
163	ND	0.654	0.018	0.018	ND	ND	ND	0.423
164	ND	0.322	ND	0.018	ND	ND	ND	0.382
165	ND	0.650	ND	ND	ND	ND	ND	0.290

Table 8.

RCRA Regulatory Levels for the above Heavy Metals are as follows:

Metal	Concentration (mg/L)
Silver (Ag)	5.0
Barium (Ba)	100.0
Cadmium (Cd)	1.0
Chromium (Cr)	5.0
Mercury (Hg)	0.2
Lead (Pb)	5.0
Selenium (Se)	1.0
Arsenic (As)	5.0

Chapter V

Discussion and Conclusions

In this study, Inductively Coupled Plasma Emission Spectrometry was used as an effective means for the analysis of most RCRA regulatory heavy metals, such as: As, Ag, Ba, Cd, Cr, and Pb. The multielement interferences were reduced by selecting the appropriate line for each element at which the least interference from the other elements occurred. In addition a second line was used to confirm the results. The relative ease of operation exhibited by ICP-AES provided many advantages for the determination of specific elements in a large series of samples of the same type. The analysis of quality assurance certified reference materials showed that the ARL Model 3410 ICP provided results that were in reference range.

The selection of the analytical technique GFAAS for the determination of Selenium brought a low detection limit of about 10^{-11} g and good reproducibility for the specific element analyzed. However, the temperature programming for the ashing, pyrolysis, and atomization of blanks, standards, reference materials, and samples was time consuming.

The unique property of mercury---that it is the only metal exhibiting considerable vapor pressure at room temperature---and that it does not react with atmospheric oxygen have made the determination of this element with cold-vapor Atomic Absorption technique possible. The detection limits obtained by this method amounted to about 10^{-10} g mercury. Therefore, the technique has the sensitivity needed to accurately determine the very low mercury concentrations encountered in soil samples. One disadvantage of this technique was the oxidation and concentration determination steps were both very time consuming. Some error was introduced during the sampling, extraction, and instrument operation. However, the determinations were sufficiently accurate to provide land reuse planners information regarding the suitability of lands situated along the Mahoning River for possible reuse.

If further investigations are planned, it would be advantageous to find one technique and one piece of equipment that would be able to determine all RCRA metals at one time with only one instrument. Such an instrument might be an ICP/mass spectrometer. Initial studies at other institutions have indicated that all RCRA metals could be determined with such a piece of equipment at the concentration specified by the RCRA regulations.

The TCLP soil sample extraction method used in this study brought a lot of convenience for the large series of similar sample analysis. Matrix spikes were added to the extraction fluids and determined to verify the techniques in this study.

According to RCRA Regulatory Levels for the heavy metals studied, many of the results for some of the heavy metals were less than detection levels. Some of them, although detected, were still less than Regulatory Levels. The results in the Table 7 covered a total of 165 samples selected from about 37 different sites belonging to the Mahoning

River Corridor Redevelopment Project region mentioned in the previous section. The results obtained from this study suggest that the re-use of these lands may be possible. Further analyses of other lands along the Mahoning River Corridor is recommended.

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