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Optimization of Microwave-Assisted Acid Digestion Method for Determination of Trace Elements in Coal and Coal Fly Ash

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OPTIMIZATION OF MICROWAVE-ASSISTED ACID DIGESTION METHOD FOR DETERMINATION OF TRACE ELEMENTS IN COAL AND COAL FLY ASH

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Master of Science

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Dejan Savic

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OPTIMIZATION OF MICROWAVE-ASSISTED ACID DIGESTION METHOD FOR DETERMINATION OF TRACE ELEMENTS IN COAL AND COAL FLY ASH

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OPTIMIZATION OF MICROWAVE-ASSISTED ACID DIGESTION METHOD FOR DETERMINATION OF TRACE ELEMENTS IN COAL AND COAL FLY ASH

Dejan Savic June 24, 2008 65 Pages

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Abstract

In most of the analytical and environmental laboratories today inductively coupled plasma (ICP) is a method of choice for analysis of trace metal elements present in coal and coal combustion products. This method requires use of liquid samples, so all coal and coal combustion products must be digested prior to analysis by ICP. Traditionally an open-air hot-plate acid digestion method published as ASTM D6357-04 was used to extract all trace metal elements into solution. Recent development of microwave systems designed for digestions under extreme acidic conditions and high temperatures and pressures shifted focus toward more rapid and precise microwave-assisted digestion of samples. A number of papers have been published involving research efforts toward development of quantitatively satisfying digestion methods. However, there is still no published ASTM or EPA method for microwave-assisted digestion of coal and coal combustion products. The goal of this research is compare the recoveries obtained by using hot plate method with results obtained by microwave-assisted digestion, as well as to attempt to optimize method conditions for latter.

I. INTRODUCTION

A. Coal Fundamentals[1,2]

Coal is type of fossil fuel that consists of organic matter from prehistoric times, chemically altered under high pressures and long exposure. It formed in swamp ecosystems where oxidation and biodegradation is prevented by water and mud. Because of tectonic shifts and movements in the Earth crust, these swamp areas are often buried sometimes to enormous depths. The high pressure environment combined with the heat from the Earths interior transformed the organic matter by altering its chemical nature. First it was transformed into peat and the peat was then refined into coal of different types. Coal we encounter today ranges in color from brown to black; it is in general a sedimentary rock, but in the case of anthracite it can be regarded as metamorphic rock due to longer exposure and elevated pressure. Time scales for creation of different types of coal vary much. A peat deposit can be created in as little as 9000 years, while anthracite requires millions of years to form.

Traditionally, different types of coal are divided into two major groups – low-rank coals and high-rank coals – based on maturity, carbon content, and energy/moisture content. Carbon content of low-rank coal ranges from 25% to 50% while high-rank coal can have from 50% to 98%. First stage of coal formation is called peat. Approximately 60% of the worlds swamp areas are peat. Due to very high water content and the presence of lots of non-carbon materials peat is not as energy-rich as brown coal and limited to local small-scale heating. The next stage in coal formation is lignite, often called the brown coal. It is considered the lowest rank of coal with carbon content from 25% to

35% and heat content from 10-20 MJ/kg. Other characteristics of lignite are the brownish-black color and very high moisture content, in a range of 66%, as well as high ash content. Because of this lignite is almost exclusively used for steam-electric power generation.

Sub-bituminous coal is the next form of low-rank coal. Its carbon content can range from 35% to 45%. While the moisture content is not as high as in lignite, sub-bituminous coal usually contains 20%-30% of moisture. The heat content ranges from 20-28 MJ/kg on as-received basis. Lower sub-bituminous coal is dark brown, soft, and crumbly; the higher one is relatively strong, hard, and black. Like lignite, sub-bituminous coals are primarily used for steam-electric power generation. The main source of sub-bituminous coal in the United States is Powder River Basin (PRB) in Wyoming.

Bituminous coal is considered the high-rank coal. It is a hard type of coal that contains a tar-like substance called bitumen. Bituminous coal is a sedimentary rock formed by compression and heating of peat for an extensively long period, so its main constituents are macerals vitrinite and exinite. Carbon content of bituminous coals ranges from 60% to 80%, and its heating value ranges from 24-35 MJ/kg. The color of most bituminous coals is black with well defined bands of bright and dull material. Bituminous coals themselves are divided into several groups based on moisture, ash, and volatile content, as well as the plasticity. Highest ranking coals are used for coking and steel making. Low ash and sulfur coals are the best choice for power generation since they do not produce much boiler slag and they do not require as much effort to scrub the flue gases to remove particulate matter.

Anthracite coal is the highest of the metamorphic rank, with carbon content ranging from 92% to 98%. Despite its lower calorific content, anthracite has the lowest amount of impurities compared to all other coals. Anthracite ignites with difficulty and burns with a short, blue, and smokeless flame. However, barely 1% of coals found in nature are classified as anthracite. It was primarily used as a domestic fuel because it burns cleanly with little soot. Its high market value and scarcity makes anthracite a bad choice for commercial power plant use.

B. Coal Combustion Process and Its Products[1,2]

Coal is primarily used for electricity and heat production through a process of combustion. Approximately 40% of worlds need for electricity is satisfied by coal. Typical coal fired power plant will burn pulverized coal in a furnace with a boiler. Heat generated in a furnace will convert boiler water into steam which is used to spin turbines that turn generators and produce electricity. Just like any other type of fossil fuel, coal combustion results in generation of carbon dioxide (CO_2), nitrogen oxides (Nox), and various amounts of sulfur dioxides (SO_2). SO_2 will readily react with oxygen to produce the sulfur trioxide, which, in turn, reacts with water to form sulfuric acid; released into the atmosphere, sulfuric acid will return as acid rain. Most power plants today, however, are equipped with scrubbing systems that use limestone to trap the SO_2 and in that way stop formation of acid rains. On the other hand, coal fired power plants are still believed to be one of the primary sources of carbon dioxide emissions and reasons for global warming, even though modern power plants utilize a variety of techniques to limit the harmfulness of their waste products and improve the efficiency of burning.

Major coal combustion products include fly ash, bottom ash and a boiler slag, and flue gas desulfurization (FGD) materials. All these products contain various heavy metals that can present serious danger if released to the environment. While most of these harmful elements are present in trace or ultra-trace levels, enough coal is burned on a daily basis for significant accumulation in the environment.

Fly ash is the finely divided mineral residue resulting from the combustion of coal in electric generating plants. It consists of inorganic, incombustible matter present in the coal that has been fused during combustion into a glassy, amorphous structure. In most of the power plants, fly ash particles are collected by electrostatic precipitators (ESP fly ash) or filter bags. Fly ash is mostly consisted of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3), and is hence a suitable source of aluminum and silicon. Chemical properties of fly ash will largely be influenced by the type of coal that is burned.

Bottom ash is the coal combustion product that consists of non-combustible particles with traces of combustibles embedded in forming clinkers and sticking to hot side walls of furnace during the furnace working. The clinkers fall by themselves into the water or sometimes by poking manually, and get cooled. FGD slurry and gypsum are products of flue gas desulfurization process. It is the current state-of-the art technology used for removing sulfur dioxide from the exhaust flue gases. As a result of stringent environmental protection regulations regarding SO_2 emissions that have been enacted in a great many countries, SO_2 is now being removed from flue gases by a variety of methods:

- Wet scrubbing using slurry of sorbent, usually limestone or lime, to scrub the gases.
- Spray-dry scrubbing using similar sorbent slurries.
- Dry sorbent injection systems.

For a typical coal-fired power station, FGD will remove 95% or more of the SO_2.

Depending on the type of sorbent slurry used, different types of product will remain after FGD process. Wet scrubbing with a limestone or lime will result in production of calcium sulfite ($CaSO_3$), while reaction with magnesium hydroxide will result in production of magnesium sulfite ($MgSO_3$). Some FGD systems go even further to oxidize the produced $CaSO_3$ slurry and form gypsum ($CaSO_4 * 2H_2O$).

C. Major, Minor, and Trace Elements in Coal and Its Combustion Products[3]

It already well known that coal, and subsequently its combustion products, contain almost all elements in the Periodic Table. Based on their respective concentrations these elements are divided into three groups:

- Major elements (carbon, nitrogen, hydrogen, oxygen, and others with contents in excess of 1% or 10,000ppm)
- Minor elements (Al, Ca, Fe, K, Mg, Na and Si with contents between 1% and 0.1%)
- Trace elements (all the remaining elements with contents below 0.1%m/m or 1000ppm).

These elements, bound in coal, are mobilized during coal burning and may be released either associated with particles or as vapors. From an environmental perspective, trace elements have attracted more attention than the major and minor constituents; within a context of progressively more stringent regulation of pollutant discharges from coal fired power plant, there is a need for information on the trace element content of coal and coal derived residues. The US Clean Air Act Amendments (CAAA) of 1990 identified 11 trace elements and their compounds commonly found in coal as potentially 'hazardous air pollutants' (HAPs): Be, Cr, Mn, Co, Ni, As, Se, Cd, Sb, Hg and Pb.

Davison and Clarke (1996) in their review "Trace Elements in Coal" noted that partitioning or distribution of trace elements in the various products of coal combustion and the chemical state in which they exist (mode of occurrence) are probably the most important pieces of information needed to fully understand the coal combustion process in whole and its potential impact on the environment[3].

Clarke and Sloss (1992) devised a diagram which summarized and classified the trace elements by their partitioning behavior; it divided them into three groups[3]. Elements of the first group are concentrated in the more coarser residues such as bottom ash or slag like manganese, or they show no preference between bottom ash and fly ash (Be, Co, Cr, Ni). This can be explained by the fact that elements of this group do not vaporize significantly during combustion. Group two elements are more concentrated in the particulates, and they are also enriched on the fine grained particle which is explained by the volatilization/condensation mechanism; during combustion volatile species are vaporized, and later as temperature falls, these species condense out of the vapor phase onto the surface of ash particle. Group three elements, namely mercury and selenium, are readily volatilized and have the ability to stay in the gas phase. It is important to notice that all three groups overlap reflecting variations in operating conditions and modes of occurrence.

The mode of occurrence includes such information as whether or not the element forms its own specific mineral, whether it is dispersed within a particular host mineral or maceral, with what fraction of the coal the element is associated, in which state of oxidation the element occurs and so on. This is potentially the most important aspect of research into the observed partitioning of trace elements during combustion, and there is a need for better techniques to determine those modes of occurrence. Most of the evidence collected so far points to trace elements being part of the mineral matter with the organic/inorganic difference being mainly a reflection of particle size. Most important mineral phases found in coal are: sulfides, aluminosilicates and silicates, carbonates, and oxides and hydroxides. Coals also contain many accessory minerals. Based on the affinity toward particular minerals, elements are often described as chalcophiles, or those with strong affinity toward sulfur, and lithophile, or those with strong affinity for oxygen and are typically associated with aluminosilicate minerals.

D. Instrumental Methods and Quantitative Analysis of Coal[3]

Currently there are many different analytical methods employed in studying the trace, as well as major and minor, elements in coal and coal combustion products. Different types of atomic absorption techniques, such as flame AAS, graphite furnace AAS, or hydride generation AAS are readily utilized to analyze coal and its combustion products. Last one, HgAAS, is particularly useful in determination of elements that form volatile hydrides such as As, Se, Sn, Sb, Te, and Bi. Another AAS method – cold vapor AAS – is very useful for determination of mercury in coal and coal combustion products. Other analytical techniques include, but are not limited to: atomic fluorescence spectroscopy, mass spectroscopy, proton-induced gamma/X-ray emission, and X-ray fluorescence. Last one, XRF, is a very good technique because sample preparation is fairly easy and fast, it is multi-element capable, possesses a high precision and reproducibility, and short measuring times. However, it is more suited for analysis of ash samples than coals because trace elements are more concentrated in ash than in parent coal. Another problem is that element in coal matrix can cause absorption or enhancement of secondary X-rays.

The most often used method in analysis of trace elements in coal is atomic emission spectroscopy. In AES the sample is excited to produce visible line spectra characteristic of the elements present. Concentrations of the elements present are determined by comparing the intensities of the line spectra obtained against the spectra from standards. One AES method, inductively coupled plasma, has been applied to quantitative analysis of trace elements more than any other. In ICP-AES excitation is achieved by high temperature plasma, usually argon, flowing in a quartz tube surrounded by an induction coil. Advantages of using an ICP include its ability to identify and quantify all elements, except argon, in a very short period of time and requires a fairly low amount of sample. Since many wavelengths of varied sensitivity are available for determination of any one element, the ICP is suitable for all concentrations from ultra-trace levels to major components; detection limits are generally low for most elements with a typical range of 1 – 100 g/L. In coal analysis ICP is the technique of choice for Be, V, Cr, Mn, Ni, Cu, Zn, Sr, Y, Ba, and also Al, P, K, Ca, Ti, and Fe. Detection limits of ICP source is comparable or better than other atomic spectral procedures; at 10 ppb level or less more elements can be detected with plasma excitation than with any other emission or absorption method.

Unfortunately there are many disadvantages that must be considered when choosing ICP for analysis of trace elements. For ICP determinations, the general types of interferences that may be encountered are spectral, physical, and chemical, especially at low analyte concentrations.

Spectral interferences are the result of overlap of the spectral line from another interfering element, unresolved overlap of molecular band spectra, or background shift from various sources. To some extent they can be accounted for by using inter-element correction factors. These interferences can be caused by many different elements for different analytes. Some specific interferents of concern include aluminum, boron, calcium, iron, potassium, sodium, and magnesium. They are usually found at much larger concentrations than other target analytes which increases the likelihood of interelement matrix effects. Physical interferences that affect ICP are mainly associated with solids that can interfere with sample transport into nebulizer. In addition the presence of high concentrations of salts may also interfere with sample analysis by deposition on the nebulizer.

The one of the most important problems that affects ICP analysis lies in the fact that only solutions can be analyzed. It means that coal samples as well as almost all combustion products must be dissolved prior to analysis. The most commonly used method for ICP analysis of trace elements in coal and its combustion products is ASTM

D6357. This method instructs ashing of the sample at 500°C prior to open-air acid digestion[4]. The digestion is performed on a hot plate in Teflon beakers. The method suggests using 0.2-0.5g of ashed sample, dissolving it in aqua regia and hydrofluoric acid, and boiling it to dryness at 150°C. The solution is then removed from the hot plate, allowed to cool, and then rinsed with DI water and also 1 mL of concentrated nitric acid is added. The contents are heated again at 100°C until the sample is completely in the solution. However, digestion coal and CCPs often results in solids remaining after the procedure is completed. The last step in this method is filtration of samples and dilution to 100 mL.

This procedure proved to be unsatisfying for determination of many trace elements, especially the more volatile ones like mercury, selenium, antimony, and arsenic. Ashing at 500°C itself can result in loss of some of these samples. Other potential factors for losing the trace elements are the heating in open-air conditions, and in some cases filtration of samples. Another disadvantage of this method is the time required to prepare the samples; it takes approximately four hours to complete the ashing of samples, and digestion of 20 samples usually requires 3-4 hours.

E. The Objectives of the Research

In the last decade use of the microwave oven for digestion needs became increasingly popular. In fact, the use of the closed vessel microwave assisted digestion systems under high temperature and pressure has now become routine. Compared to the more traditional method mentioned above, this procedure allows shorter digestion times and good recoveries, even for some volatile elements. Furthermore, it requires smaller amounts of acids, reduces risk of external contamination, which in turn, results in improved detection limits and the overall accuracy. Microwave digestion inherited some disadvantages from open air digestion; most of these problems, however, are associated with usage of HF. So far researchers attempted to optimize the method in many different ways; some research has been done to determine the need for HF. It has been found that for digestion of coal addition of HF is not necessary, and its absence will not result in poorer recovery of trace elements[5]. However, for fly ash, addition of HF proved to be necessary.

The objective of this study is to try to understand differences in mineral composition of coals and fly ashes, and based on that modify and further improve microwave digestion methods for various substances. In that process we will attempt to modify several key parameters – time, temperature, sample mass, which can be described as a ratio between sample and acid, as well as the effect of hydrofluoric acid usage – and observe the results. We will use two available NIST standards, namely SRM 1633b fly ash and SRM 1635 sub-bituminous coal standard, to validate our method and help us observe changes in results obtained. Data gathered by microwave-assisted acid digestion will be compared to the data gathered by following ASTM published open-air acid digestion method.

In addition, we will also apply the same digestion conditions to three different types of coal, namely Texas lignite, PRB sub-bituminous, and Illinois bituminous, and observe possible differences.

II. EXPERIMENTAL

A. Instrumentation

In this study two instruments were primarily used: Prodigy High Dispersion ICP-AES (Teledyne Leeman Labs, Hudson, NH), and Ethos EZ microwave digestion system (Milestone, Shelton, CT). Both of the instruments will be described in detail, including background theory, operation principles, and relevant parameters used in this study.

A-1. Inductively Coupled Plasma – Atomic Emission Spectrometry[6]

The basis of atomic emission spectroscopy relies on a fact that species excited to higher electronic states will shortly after excitation go through a process of relaxation and produce ultraviolet and visible line spectra that can be very useful for qualitative and quantitative elemental analysis. There are several different types of atomizers used to convert components of sample to atoms and simple elementary ions, and excite a fraction of those species to higher energy levels. Plasma is one of the sources used for atomization that we focused on in this study; other sources used for this purpose are electric arc and electric spark. These types of emission spectrometry offer several advantages compared to more traditional flame and electrothermal adsorption methods: lower interelement interference as a result of significantly higher temperatures, simultaneous detection of dozens of elements under the same set of excitation conditions, detection of low concentrations of elements that tend to form refractory compounds. Emission spectra from above mentioned sources are highly complex. This can be considered as an advantage if qualitative information is needed. However, in terms of quantitative analysis this complexity will result in increased probability of spectral interferences. In addition, these methods require more expensive optical equipment than those used in flame or electrothermal methods. Considering both advantages and disadvantages, atomic absorption and emission methods appear to be complementary. Plasma is an electrical conducting gaseous mixture containing a significant concentration of cations and electrons with net charge approaching zero. The most often used gas for creating plasma is argon whose ions are capable of absorbing sufficient power to form an external source in order to maintain the temperature at a level at which further ionization sustains plasma indefinitely. Typical inductively coupled plasma source is called a torch (Figure 1).

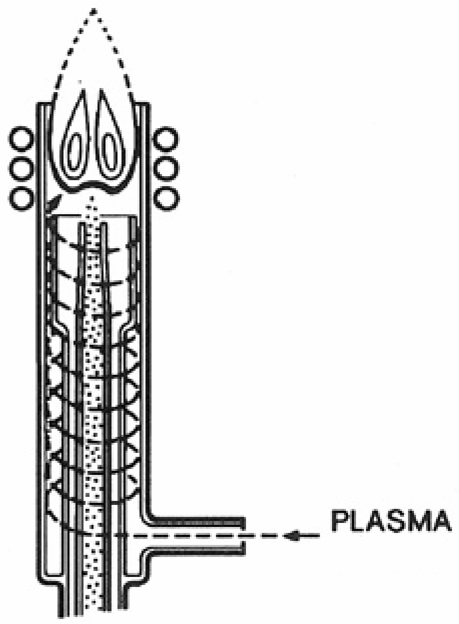

Figure 1. A typical ICP torch design.

The diameter of the large tube is approximately 2.5 cm and it is surrounded by concentric quartz tubes through which argon gas stream flows. The top of the torch is surrounded by a water-cooled induction coil that is powered by a radio-frequency generator capable of producing 0.5 to 2 kW of power at about 27 or 41 MHz.

Ionization of flowing argon is initiated by a spark, and resulting ions and their electrons will interact with the fluctuating magnetic field produced by the induction coil on top. This interaction causes the ions and electrons within the coil to flow in the closed annular paths with ohmic heating created as a consequence of the resistance to this movement.

Liquid samples are carried into the torch by argon flowing at 0.3 to 1.5 L/min through the central quartz tube. Samples are introduced into this flow by pumping from a sample container with a peristaltic pump. The important part of the sample introduction system is the nebulizer. The word “nebulizer” is derived from the Latin “nebula,” meaning mist and is defined as an instrument for converting a liquid into a fine spray. The pneumatic nebulizer is literally an instrument for converting a liquid into a fine spray that uses a gas as the driving force. The most popular types of ICP pneumatic nebulizers are concentric, fixed cross-flow, and high solids. Another important sample introduction part is a spray chamber. The most common types of spray chambers used today are the Scott double-pass and the cyclonic. The purpose of the spray chamber is to remove droplets produced by the nebulizer that are >8 μm in diameter. Important considerations here include the wash-in time, wash-out time, stability, and sensitivity. The drainage characteristics are important in part due to pressure changes that can occur during drainage. It is important that the drainage process continues smoothly and without interruptions. The analyst might observe faster wash-in and wash-out times with the cyclonic design. The chamber material of construction, chamber surface area, volume, and flow pattern as well as the sample matrix and the chemistry of the element influence the wash-out times. In addition, the analyst might observe faster wash-out times with glass construction than with polymers due in part to better wetability of the glass (lack of beading).

Typical plasma has a very intense, white, nontransparent core topped by a flamelike tail. The core which extends a few millimeters above the tube is made up of a continuum upon which is superimposed the atomic spectrum for argon. 10-30 mm above the core continuum fades and plasma is optically transparent. Spectral observations are usually made at a height of 15-20mm above the induction coil. The background radiation in this region is free of argon lines and well suited for analysis. Even though the temperature cross section of plasma is relatively uniform, various regions of plasma will not have exactly the same temperature. The area within the RF-coil can reach the temperatures of 10,000 K. Temperature in the region of 5-15 mm above the coil is usually between 7000-8000 K. Going toward the top of the plasma and away from the coil, the temperature gradually drops to 6000 K. By the time sample atoms have reached the observation point, they have resided for about 2ms at temperatures ranging from 6000 to 8000 K which will result in more complete atomization and less interference. As a consequence of relatively uniform temperature of the plasma, self-absorption and self-reversal effects are not encountered which results in linearity of calibration curves over several orders of magnitude of concentration.

Plasma emission spectrometers currently in use today are slowly approaching the characteristics of ideal spectrometers. Most of the spectrometers are able to encompass the entire ultraviolet and visible spectrum ranging from 170 to 800 nm. Some of them are even equipped for vacuum operation which helps extending the ultraviolet region to 150-

160 nm. This is important for determination of several elements that have emission lines in this region such as phosphorus and sulfur. There are several different instruments for emission spectroscopy in use today, but most widely used is the simultaneous multichannel type designed to measure the intensities of emission for a large number of elements at the same time. Multichannel emission spectrometer in the system used in this study is an array-based system. This type of system can employ either charge-injection or charge-coupled devices as detectors (Figure 2).

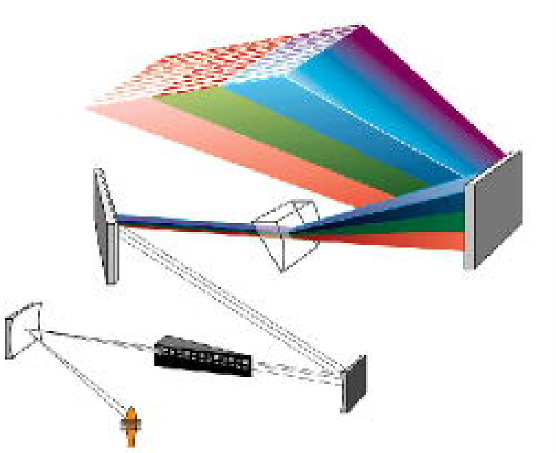

Figure 2. Echelle spectrometer with a charge-injection detector.

The charge-injection detector uses calcium fluoride prism to sort the spectral orders that are subsequently formed by the echelle grating. A toroidal camera mirror is used to focus the slit images onto the transducer surface. In order to eliminate dark currents in the transducer elements, the unit is housed in a liquid nitrogen cryostat. A set of 39 detector elements, called a read window, is used to monitor each spectral line.

The charge-coupled instrument is a more recently developed device. It is a device with two echelle systems and two charge-coupled detectors, one designed for detection of lines in 150-375 nm region, and the other for 375-800 nm region. After entering the spectrometer via slit, the radiation is dispersed by an echelle grating and consequently falls on a Schmidt cross-disperser element that separates the orders of the ultraviolet radiation and also separates the ultraviolet and visible optical beams. Two dispersed beams are then focused onto the surface of two detector elements. The detector systems consist of numerous subarrays fabricated on silicon chips with each subarray being custom positioned so that three to four major emission lines for each of 72 elements fall on its surface. Although there are only 224 of these array segments in the system, multiple lines fall on many of the subarrays so that several thousand lines can be monitored simultaneously.

In theory, all metallic elements can be determined by plasma emission spectroscopy, while for determination of phosphorus, nitrogen, sulfur, and carbon vacuum spectrometer setup is necessary because the emission lines for these elements lie below 180nm. In addition, most of the elements have several prominent lines that can be used for identification and determination purposes. Intensity information for these lines can be found in several different publications, so suitable line for any element can be easily found. The selection of best line for a given element will also depend on a sample matrix and other elements present that can increase likelihood of overlapping lines.

Calibration curves for plasma emission spectroscopy most often consists of a plot of the signal intensity as a function of analyte concentration. For most of the elements it is possible to obtain linear calibration curves, but some of them will have nonlinear curves. A major cause of nonlinearity is self-absorption in which the output signal is reduced by the absorption by nonexcited species in the medium. Self-absorption becomes a problem mostly with high concentration elements, and causes the calibration curve to bend toward x-axis. Nonlinearity can also rise due to erroneous background corrections.

Detection limits of several important elements for Prodigy High Dispersion ICP Spectrometer published by the manufacturer Teledyne Leeman Labs are presented in (Table 1).

Table 1. Detection Limits of Several Elements on Prodigy ICP-AES

Element	**Detection Limits (ug/L)**
Ag	0.3
Al	0.2
As	1.5
Au	1
B	0.1
Ba	0.03
Be	0.01
Bi	2
Ca	0.01
Cd	0.05
Ce	2
Co	0.2
Cr	0.15
Cu	0.3
Fe	0.1
K	0.3
Li	0.06
Mg	0.01
Mn	0.03
Mo	0.5
Na	0.15
Ni	0.3
P	2
Pb	0.8
S	5
Sb	2
Se	2
Si	1.4
Sr	0.01
Ti	0.1
Tl	2
V	0.2
W	2
Zn	0.2
Zr	0.3

A-2. Ethos EZ Milestone Microwave Digestion System[7]

The Ethos series lab-stations are high-performance microwave instruments for faster sample preparation of trace metals for AA, ICP, and ICP-MS analysis. This type of microwave oven is rugged and designed specifically for work in harsh acidic environments. The chassis is made of corrosion-resistant stainless steel and interior cavity together with inside of the door is coated with 5 layers of polytetrafluoroethylene (PTFE), a type of perflourated plastic, to prevent the deterioration from aggressive acid used for digestion. Milestone engineers have designed a door based on the "moving wall" principle used in high pressure autoclaves. The door is mounted on spring-loaded high impact steel bars. If there is a sudden pressure increase, the door moves out a fraction of an inch to release the excess pressure, then reseals. An integrated safety switch cuts off microwave power in the event of pressure release.

Figure 3. Parts of Ethos EZ sample vessel

Milestone microwave unit employs re-sealable type of digestion vessels (Figure 3). Vessels are placed in a sample rotor and secured with a calibrated torque wrench for uniform pressure, to prevent leaks and ensure that the patented pressure-relief spring operates to spec. If the operating pressure exceeds the vessel limits, a patented spring device allows the vessel to open and close instantaneously, bringing the internal pressure down to a containable level. Unlike other release designs, this spring releases only the excess pressure, allowing valuable sample (including volatile elements) to remain in the vessel. These vessels are designed to operate under pressures up to 1500psi. The unit is capable of running a maximum of ten samples per run. The microwave unit used in this study was also equipped with in-vessel temperature control for a standard reference vessel that can operate at temperatures up to 300ºC. In addition, Ethos EZ is equipped with EasyControl monitoring system that allows the user to monitor the temperature of reference vessel and input energy throughout the digestion procedure and easily set up digestion parameters such as ramp and hold time, temperature, and maximum energy input.

B. Standards and Reagents

Ultra high purity deionized water with resistivity of 18.2 MΩ.cm (Synergy Water System, Millipore, Bedford, MA) was used throughout the whole experimental work done on this study including: preparation of working standards, dilution of digested samples, and cleaning of digestion vessels and other equipment that was used. In addition to rinsing with ultra-pure water, digestion vessels were cleaned with trace metal grade nitric acid diluted to 10%.

The standard working solutions were prepared by dilution of multi-element standard blend (Spex CertiPrep, Metuchen, NJ). This multi-element standard blend contained most elements of interest at 10 mg/L, and some elements, such as Fe, Na, Mg, K, Ca, Sr, at 1000 mg/L level. Dilution was performed with the same mixture of acids and water as the one used for digestion of samples in order to imitate the matrix of analyzed samples.

Acids used for digestion of samples were: nitric, hydrofluoric, and hydrochloric acids. All acids used were trace metal grade acids and all produced by Fisher Scientific (Pittsburgh, PA). Concentration of nitric acid was 65%-70%, with boiling point of 122ºC and vapor pressure of 25 bar at 225ºC. It is an oxidizing acid that forms with all elements except: Au, Pt, Al, B, Cr, Ti, and Zr. Concentration of trace metal grade hydrofluoric acid was 47%-51%, with boiling point of 108ºC and vapor pressure of 25 bar at 240ºC. Hydrofluoric acid is a non-oxidizing acid used for decomposition of silicates. Trace metal grade hydrochloric acid had a concentration range 34%-37%, with a boiling point of 84ºC and a vapor pressure of 25 bar at 205ºC. Hydrochloric acid will form soluble chlorides with all elements except Ag, Hg, and Ti. It will also dissolve salts of weaker acids, such as carbonates, phosphates, and borates. However, it is not capable of dissolving oxides of the following elements: Al, Be, Cr, Sb, Sn, Si, Ti, and Zr.

C. Experimental Procedures

This section will contain parts; in the first part experimental procedures used in this study will be explained. In the second part we will focus on similar research efforts done by several other research groups.

C-1. Experimental Procedures Used in This Study

The first part of this research involved digestion of samples using the traditional open-vessel hot-plate method published by the American Society for Testing and Materials as method number ASTM D6357-04 - “Standard Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Absorption Spectrometry”. All coal samples were prepared following the ASTM D2031-04 method named “Standard Practice for Preparing Coal Samples for Analysis”, while ash samples are used as received.

The method used for digestion of samples requires sample preconcentration by ashing[4]. Enough coal or ash sample was measured out in order to yield approximately 0.5 g of ash that was then transferred into an open 50-mL quartz or high-silica crucible. The crucible was placed in a cold muffle furnace and temperature control adjusted so that the furnace reaches a temperature of 300°C in 1 h and then 500°C in the second hour. A temperature of 500°C was maintained for a minimum of 2 h. Ashing is considered complete when no visible evidence of carbonaceous material remains. Samples were then cooled to room temperature under conditions that minimize the absorption of water. The next step instructed by method was dissolution in acid mixture. 0.2000 to 0.5000 g of the thoroughly blended ash prepared in the previous step was placed into a 100- or 200-mL Teflon beaker. 20 mL of freshly prepared aqua regia (3:1 mixture of hydrochloric and nitric acid) and 20 mL of concentrated hydrofluoric acid was added to the beaker. The beaker was placed on a hot plate that had been adjusted to 130 to 150°C. The mixture was heated to dryness. After the solution has evaporated, the beaker walls were rinsed with deionized water and heated again to dryness. The beaker was removed from the hot plate and cooled to room temperature. 1 mL of concentrated nitric acid and 20 mL of ultra pure water was added and heating was resumed on a hot plate at 90 to 100°C until the sample was in the solution. The method also advises that if some residue remains after 1 h of heating, it may be ignored; trace elements are considered to be quantitatively extracted at that point. Beakers were then removed from the hot plate and the solution was allowed to cool down to room temperature. Cool solution was then filtered into 100-mL volumetric flask and diluted to volume with ultra pure water. The solution was then transferred to a HDPE bottle to avoid adsorption of lead during storage.

The second part of this research involved digestion of the same samples used in the previous part, but this time closed-vessel microwave digestion system was employed instead of hot-plate. Since there are no published ASTM or EPA methods for microwave assisted digestion of coal and fly ash samples, as a starting point we chose two different procedures published by Milestone in their “Application Notes” handbook that came with the instrument. One method was used for digestion of coal samples and the other for fly ash digestion.

The method for coal digestion was a two step process that called for a digestion of approximately 0.2g of sample in 8 mL of nitric acid with temperature ramp to 180ºC in first 5 min. and hold at 180ºC for another 10 min. Samples were then taken out of the microwave and cooled to room temperature. 2 mL of hydrofluoric acid was added and samples were digested again with ramp to 220ºC in first 5 min. and hold at 220ºC for another 10 min. After that, samples were allowed to cool down, transferred to 50 mL plastic vials with screw caps, and diluted to the 50 mL mark.

A one step procedure for fly ash digestion involved measuring out approximately 0.2g of sample into a digestion vessel and adding 10 mL of ultra pure water, 6 mL of nitric acid, 2 mL of hydrochloric acid, and 2 mL of hydrofluoric acid. Samples were ramped to 220ºC in the first 10 min. and then held at the same temperature for another 40 min. Similarly, samples were allowed to cool down, transferred to 50 mL plastic vials with screw caps, and diluted to the 50 mL mark.

Also as a part of this study, we attempted to tweak and optimize both of these methods by modifying the following key parameters: time, temperature, ratio of sample mass to acid volume, and amount of hydrofluoric acid added. Thus, this second part of the study can be divided into four subsections.

A total of ten coal samples were used in this study and they are: NIST SRM 1635 sub-bituminous coal standard used for method validation, three Illinois bituminous samples (labeled as C-B1, C-B2, C-B3), three Powder River Basin sub-bituminous samples (C-SB1, C-SB2, C-SB3), and three lignite coals (C-L1, C-L2, C-L3). All nine samples were collected by ICSET during summer and fall 2007, from three different locations. In the first step we examined the effect of changing ratio of sample mass to acid volume. In three different digestion runs, 0.2 g, 0.1 g, and 0.05 g samples were measured out and dissolved in the same acid mixture described above using the same digestion times and temperatures. In the second part of the experiment, in two separate runs, digestion temperature of the first step was increased to 200ºC and 220ºC, respectively. All other parameters were held constant. In the third part of experiment, in two separate runs, digestion time of both steps was increased from 15 min. to 25 and 35 min, respectively while other parameters were held constant. The fourth part of the study involved examination of changes caused by the amount of hydrofluoric acid present. In two separate runs, amount of HF was decreased from 2 mL to 1 mL and 0 mL, respectively.

A total of ten fly ash samples were used in this study and they are: NIST SRM 1633b fly ash standard used for method validation, three fly ash samples obtained by burning Illinois bituminous coal (labeled as FA-B1, FA-B2, FA-B3), three Powder River Basin sub-bituminous fly ash samples (FA-SB1, FA-SB2, FA-SB3), and three samples obtained by burning lignite coal (FA-L1, FA-L2, FA-L3). All samples were treated similarly to coal. In the first step we examined the effect of changing ratio of sample mass to acid volume. In three different digestion runs, 0.2 g, 0.1 g, and 0.05 g samples were measured out and dissolved in the same acid mixture described above using the same digestion times and temperatures for fly ash. In the second part of experiment, in two separate runs, digestion temperature of the first step was first increased from 220ºC to 230ºC and then decreased to 200ºC. All other parameters were held constant. In the third part of the experiment, in two separate runs, digestion time was increased from 50 min. to 60 and 70 min, respectively while other parameters were held constant. The fourth part of the study involved examination of changes caused by the amount of hydrofluoric acid present. In two separate runs, the amount of HF was decreased from 2 mL to 1 mL and 0 mL, respectively. All this information is summarized in the Table 2 below. Table 3 contains the information on parameters used on the Prodigy ICP-AES instrument, and Table 4. is the published list of trace elements present in both standard reference materials (SRM's).

Table 2. Microwave-Assisted Digestion Parameters

FLY ASH

Initial Conditions: Weight: 0.2g; Acids: 6mL HNO_3, 2mL HCl, 2mL HF, 10mL H_2O; Digestion Program: 10min. ramp to 220ºC then 40min. hold at 220ºC.

Method	Run 1	Run 2	Run 3
Weight (g)	Initial Conditions	0.1	0.05
Temperature (ºC)	~||~	Ramp/hold at 230	Ramp/hold at 200
Time (min)	~||~	10 Ramp/50 Hold	10 Ramp/60 Hold
Hydrofluoric Acid (mL)	~||~	1	0

COAL

Initial Conditions: Weight: 0.2g; Acids: 8mL HNO_3, 2mL HF; Digestion Program: (1)5min. ramp to 180ºC/15min. hold at 180ºC; (2)5min. ramp to 220ºC/15min. hold at 220ºC.

Method	Run 1	Run 2	Run 3
Weight (g)	Initial Conditions	0.1	0.05
Temperature (ºC)	~||~	(1)Ramp/hold at 200 (2)Ramp/hold at 220	(1)Ramp/hold at 220 (2)Ramp/hold at 220
Time (min)	~||~	(1) 25; (2) 25	(1) 35; (2) 35
Hydrofluoric Acid (mL)	~||~	1	0

Table 3. Important ICP-AES parameters

ICP Parameters	**Set Values**
RF Power	1.2 kW
Coolant Flow	20 L/min
Auxiliary Flow	0.4 L/min
Plasma View	Dual (60s Axial and 10s Radial View)
Nebulizer Pressure	37 psi
Nebulizer Type	HF Resistant
Spray Chamber Type	HF Cyclonic Type
Sample Uptake Rate	1.1 mL/min
Calibration Standards Used	In ppm: 0.00625, 0.0125, 0.0250, 0.05, 0.1, 0.0625, 0.125, 0.250, 0.5, 1 for most of the elements (except Fe, Na, K, Mg, Ca, Sr; they are present in 10X higher concentrations)

Table 4. Published concentrations of trace elements in two NIST SRMs[8]

Element	Fly Ash SRM 1633b(ppm)	Coal SRM 1635(ppm)
Aluminum	15.05±0.27*	0.32*
Antimony	(6)	(0.14)
Arsenic	136.2±2.6	0.42±0.15
Barium	709±27	NA
Cadmium	0.784±0.006	0.03±0.01
Calcium	1.51±0.06*	NA
Chromium	198.2±4.7	2.5±0.3
Cobalt	(50)	(0.65)
Copper	112.8±2.6	3.6±0.3
Iron	7.78±0.23*	0.239±0.005*
Lead	68.2±1.1	1.9±0.2
Magnesium	0.482±0.008	NA
Manganese	131.8±1.7	21.4±1.5
Mercury	0.1431±0.018	0.0109±0.001
Nickel	120.6±1.8	1.74±0.1
Potassium	1.95±0.03*	NA
Selenium	10.26±0.17	0.9±0.3
Silicon	23.02±0.08	NA
Sodium	0.201±0.003*	0.24*
Strontium	1041±14	NA
Thallium	(5.9)	NA
Thorium	25.7±1.3	0.62±0.04
Uranium	8.79±0.36	0.24±0.02
Vanadium	295.7±3.6	5.2±0.5
Zinc	(210)	4.7±0.5

* Values given as mass fractions (%); Values in parenthesis are noncertified values.

C-2. Similar Research Efforts Done by Other Groups

There are numerous ongoing research efforts focused on optimization and improvement of sample preparation for ICP analysis. Most of them are concerned with completeness of digestion procedure, length and time consumption, pretreatment conditions, and use of hydrofluoric acid.

Hassan, et al. used several different standard reference materials, namely urban particulate matter, and six CANMET materials, to examine and modify US EPA method 3051 for microwave assisted digestion of sediments, sludges, soils, and oils which specifies a 10 min total digestion time and a sample mass of up to 500 mg combined with 10 mL nitric acid[9]. The research was simultaneously performed in two laboratories, Health Canada and Environment Canada, using two different microwave digestion systems and different ICP-MS instruments. They found that recoveries of all elements improved by increasing the digestion time and by decreasing the sample mass to acid volume ration recommended by US EPA method 3051. They also compared two digestion methods, one with nitric acid alone, and other with nitric and hydrochloric acid mixture, for quantitative determination of 10 elements (V, Cr, Fe, Ni, Cu, Zn, As, Al, Pb, and U) and found that nitric acid alone was enough to quantitatively extract all the elements but Al and Cr. Nitric/hydrochloric mixture also resulted in similar recoveries for most of the elements, with exception of Al and Zn which showed improved recoveries compared to the extraction by nitric acid alone. However, recoveries for Al and Cr were still low compared to the certified values which can probably be attributed to the presence of incompletely dissolved Al and Cr silicate compounds.

Ohki, et al. investigated the effect of hydrofluoric acid addition on microwave assisted digestion procedure for determination of several trace metals in coal using ICP-AES[5]. By testing five certified reference materials, BCR-180, BCR-040, NIST-1632b, NIST-1632c, and SARM-20, they found that the two-stage digestion without HF (HNO_3+H_2O_2 was used) was very effective for the analysis by ICP-AES measurement. According to their findings, optimum method for digestion of coal was the two-stage digestion without HF; coal was digested with a mixture of HNO_3+H_2O_2 (first processing), followed by the further addition of the fresh mixture, and then the second stage was performed. They also claim that the addition of HF to the digestion system caused a great depression in the recoveries of Al, Ca, and Mg, and that the two stage digestion improved the metal recoveries, especially for minor and trace metals, compared to recoveries in the one-stage digestion. The possibility of “HF memory effect” was diminished by the use of a set of vessels which had never been contacted with hydrofluoric acid. After optimizing the method, they also analyzed 24 different Japanese standard coals. Very good agreements were reported between the concentrations of Al, Ca, Fe, and Mg measured by their optimized method and those of Japanese Industrial Standard method.

In a separate study Ohki, et al. performed microwave-acid digestion followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS), and hydride generation atomic absorption spectrometry (HGAAS) were examined the extraction of various elements in coal and coal fly ash (CFA)[10]. Eight certified reference materials (four coal samples and four CFA samples) were tested. The 10 elements (As, Be, Cd, Co, Cr, Mn, Ni, Pb, Sb, and Se), which are described in the Clean Air Act Amendments (CAAA), were especially considered. They found that for coal, the HF-free MW-AD followed by ICP-AES was successful in the determination of various elements except for As, Be, Cd, Sb, and Se. These elements (except for Sb) were well-determined by use of GFAAS (Be and Cd) and HGAAS (As and Se). For CFA, the addition of HF in the digestion acid mixture was needed for the determination of most elements, except for As, Sb, and Se, for which the HF-free MW-AD was applicable. The use of GFAAS (Be and Cd) or HGAAS (Sb and Se) resulted in the successful determination of the elements for which ICP-AES did not work well.

Herod, et al. performed an evaluation of two digestion methods used to extract 17 elements (Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Mo, Cd, Sn, Sb, Ba and Pb) from coal and coal ash, obtained as standard reference materials[11]. An acid digestion method in open vessels using sulfuric, hydrofluoric, perchloric and nitric acid was compared with a sealed microwave digestion method using nitric acid only. They found that the microwave method with nitric acid only cannot break down silicates, which harbor many trace elements, but can extract As and Se quantitatively. On the other hand, volatile elements such as As and Se might be lost during the open vessel digestion; therefore, they concluded that the closed vessel digestion is the method of choice. The comparison with certified values for reference materials showed that a number of factors must be considered when choosing which one is the more suitable digestion technique:

1. the acid attack must include hydrofluoric acid to dissolve the silicate-enriched ash matrix completely since, except for Se and As, none of the other elements studied here is completely extracted from the matrix by HNO_3 alone;

2. the loss of volatile elements has to be expected during the open vessel acid digestion and an alternative preparation, involving closed vessels such as in the microwave attack, is often preferable for these elements (As and Se);

3. the final solutions must be suitable for the ICP-MS instrument (total dissolved solid kept low and possible interferences mainly due to the use of HCl or $HClO_4$ avoided); the total solid to final solution dilution factor has to be kept minimal to allow the determination of some elements present in coal at very low level. For the small sample size of 10 mg, a dilution factor of 1000 has proved necessary to quantify several elements (Ni, Cu, Mo, Sb and to some extent Zn).

III. RESULTS AND DISCUSSION

The results are presented in five subsections. The first subsection will cover the data obtained by ASTM D6357-04 digestion method, and the following four are variations of microwave-assisted method. The data is presented in the form of graphs for easier visualization of recovery trends, as well as in the form of tables where standard deviations and confidence levels are calculated. In the following text term “high concentration element” will be used for elements that are present in parts per million level (>1 ppm), and term “low concentration elements” for elements present in parts per billion level (<1 ppm). Also, for elements present in parts per million levels, good recovery is based on criterion used by majority of researchers; recovery in range between 90% - 110% is considered good, while everything outside is considered poor. For elements in parts per billion levels determination of good or poor recovery will be based on standard deviation calculations and confidence levels (95% confidence level). The calculations of confidence levels are performed by using published table of student’s ‘t’ values and following formula:

$$t(calculated) = \frac{|x - known.value|}{s} \times \sqrt{n}$$

where ‘s’ is the measured standard deviation, ‘n’ is the number of observations (3 repetitions are done for each standard), and ‘x’ is the average or mean of 3 repetitions. The t(calculated) is then compared with t(table) at 95% confidence level to determine if the difference is significant. Since we did 3 repetitions, number of degrees of freedom will be: n-1 = 3-1 = 2, and t(table) at 95% confidence level for 2 degrees of freedom is

4.303. If t(calculated) is greater than 4.303 then the result is considered to be significantly different than known value.

A. ASTM Method D6357-04 Digestion

The hot-plate digestion was performed following the step by step instructions published by the ASTM. The results for two standard reference materials obtained by subsequent ICP-AES analysis are presented in next four figures. From the data we can see that this method is much better suited for digestion of fly ash samples rather than coal. The recoveries of more volatile trace elements such as As and Pb, as well as Co, Cu, Fe, and Mn obtained for NIST 1633b fly ash standard were remarkably well.

The recovery of Cr was slightly below the 90% level, and since the published value for Cr is not certified we were not able to calculate the confidence level. The poor recovery was observed for Ni and Se, 61.91% and 71.83%, respectively. At 95% confidence level these elements are found to be significantly different form published value. The results are presented in Figure 4 and Table 5.

Recoveries obtained for coal standard were less satisfying. Only recovery of Cu and Ni was in 90%-110% range and there was no significant difference at 95% confidence level. This loss of more easily volatile elements in coal may be due to the preconcentration ashing step used in this method as well as the open-vessel conditions under which digestion was performed. The results for all other coal and fly ash samples are given in Table 5. below.

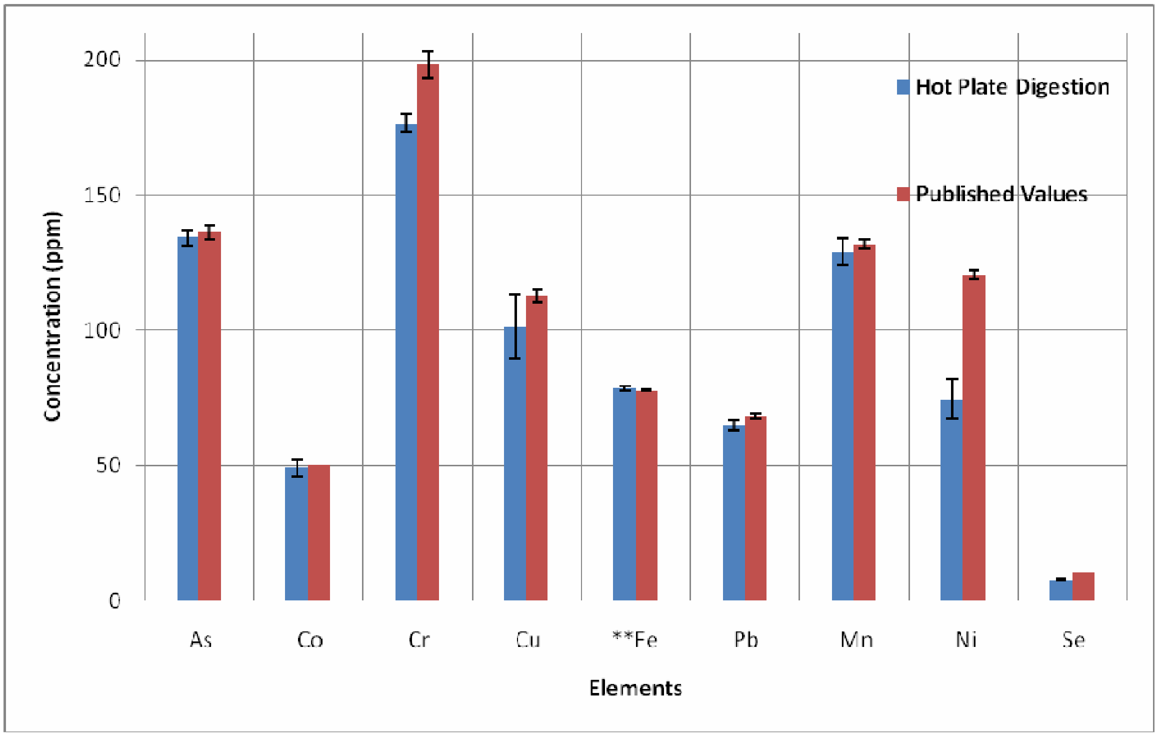

Figure 4. Hot plate digestion of NIST 1633b fly ash SRM.
(**Fe concentration is divided by thousand to fit the graph)

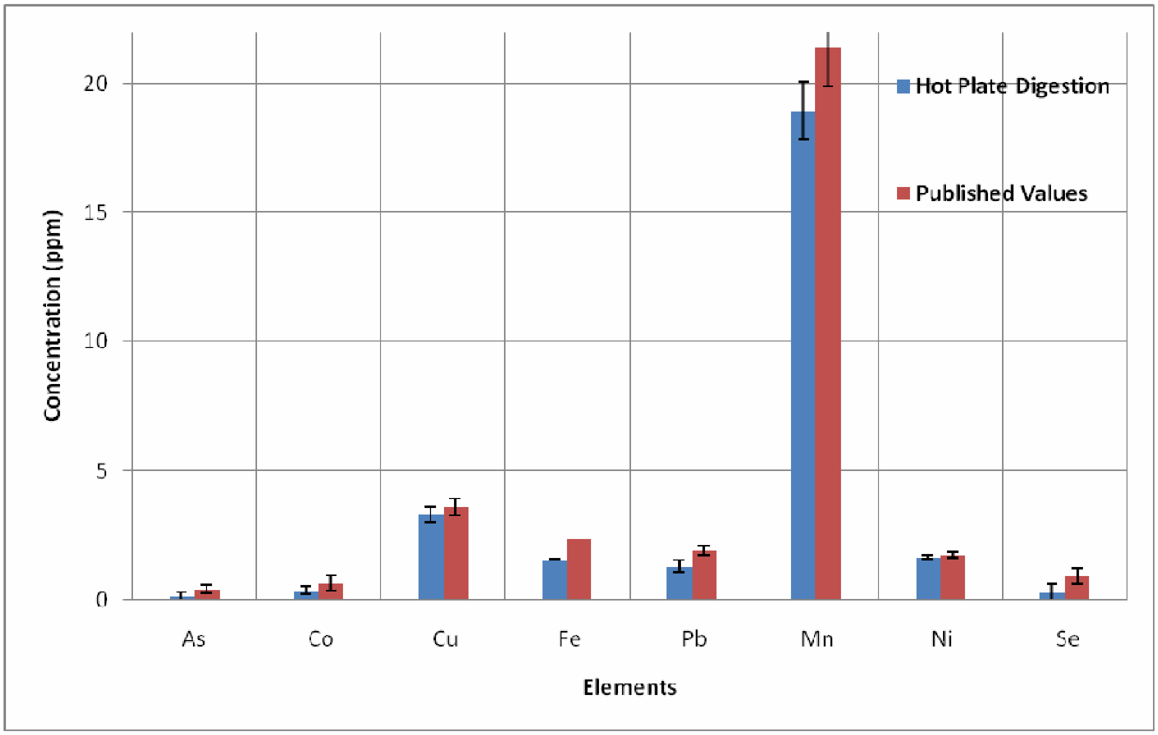

Figure 5. Hot plate digestion of NIST 1635 coal SRM.
(**Fe concentration is divided by thousand to fit the graph)

Table 5. ASTM D6357-04 digestion recoveries for fly ash and coal standards.

FLY ASH

Element	Our Value	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	134.33 ± 2.87	136.20 ± 2.60	98.63	1.128	no
Co	49.21 ± 3.18	50.00	98.42	--	--
Cr	176.49 ± 3.27	198.32 ± 4.70	88.99	11.569	yes
Cu	101.15 ± 11.83	112.80 ± 2.60	89.67	1.706	no
**Fe	7.86 ± 0.89	7.78 ± 0.23	101.08	0.163	no
Pb	64.99 ± 1.69	68.20 ± 1.10	95.29	3.294	no
Mn	128.79 ± 5.03	131.80 ± 1.70	97.72	1.034	no
Ni	74.66 ± 7.36	120.60 ± 1.80	61.91	10.812	yes
Se	7.78 ± 0.30	10.26 ± 0.17	75.83	14.511	yes

COAL

Element	Our Value	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	0.13 ± 0.17	0.42 ± 0.15	31.83	2.859	no
Co	0.37 ± 0.18	0.65 ± 0.30	56.92	2.728	no
Cu	3.30 ± 0.30	3.60 ± 0.30	91.57	1.779	no
**Fe	1.56 ± 0.01	2.39 ± 0.01	65.47	173.057	yes
Pb	1.30 ± 0.23	1.90 ± 0.20	68.42	4.460	yes
Mn	18.95 ± 1.11	21.40 ± 1.50	88.57	3.824	no
Ni	1.65 ± 0.06	1.74 ± 0.10	94.83	2.800	no
Se	0.25 ± 0.37	0.90 ± 0.30	28.15	3.021	no

(**Fe concentration is divided by thousand to match the graph)

B. Microwave-Assisted Digestion

B-1. Microwave-Assisted Digestion: Optimization of Sample Mass/ Acid Volume Ratio

This part of the study was based on reducing the sample mass to acid volume ratio. According to original method 0.2 g was the sample mass suggested to be used for digestion. In next two runs sample mass was reduced to 0.1 g and 0.05 g, respectively. The results obtained for NIST 1633b fly ash standard are shown in Figure 6, and complete data in Table 6. In the case of As, Co, Cr, and Ni decreased sample weight resulted in somewhat poorer recovery, while in the case of Se, Mn, and Pb this modification resulted in a better recovery. In most cases, results obtained by microwave assisted digestion of fly ash were comparable to the results obtained by hot-plate digestion.

The results obtained for NIST 1635 coal standard is shown in Figure 7, and complete data in Table 6. In the case of As, Co, Se decreased sample weight resulted in significantly poorer recovery; with 0.05g of sample used As and Co were not detected at all. In the case of Fe, Mn, and Co this modification resulted in slightly better recovery. The results show that recovery of elements with concentrations in lower parts per million range significantly decreased, while recovery of elements with higher concentrations improved with sample weight reduction. In most cases, results obtained by microwave assisted digestion of coal were comparable to the results obtained by hot-plate digestion.

The procedure was also performed for different types of ash and coals collected at three different power plants. The effect of reducing sample weight relative to the volume of acids used on elemental recovery in fly ash samples was comparable to that of NIST 1633b. The observed recoveries are presented in Figure 8. below. Reduction in sample mass resulted in poorer recovery of As and Cr for all three types of fly ash samples, subbituminous, lignite, and bituminous. Also the recovery of Pb in fly ash sample that comes form bituminous coal decreased with reducing sample weight; however, Pb recovery for other two types of fly ash samples improved. Drastical increase in Mn recovery was observed for fly ash sample that comes form bituminous coal.

The recovery of elements in three different types of coal samples is given in Figure 9. The elemental recovery and the effect of sample weight reduction in subbituminous coal sample followed the same trend observed for NIST 1635; poorer recovery was observed for low concentration elemets (As, Co, Se) while improvement was observed for higher concentration elements (Cu, Fe,Mn). However, the highest recovery for high concentration elements was observed when 0.1g of sample was used, with the exception of recovery of Mn in bituminous coal sample. From the figure below we can also note that no Se was detected in bituminous coal sample. This problem occurred for all the bituminous coal samples digested using microwave digestion method.

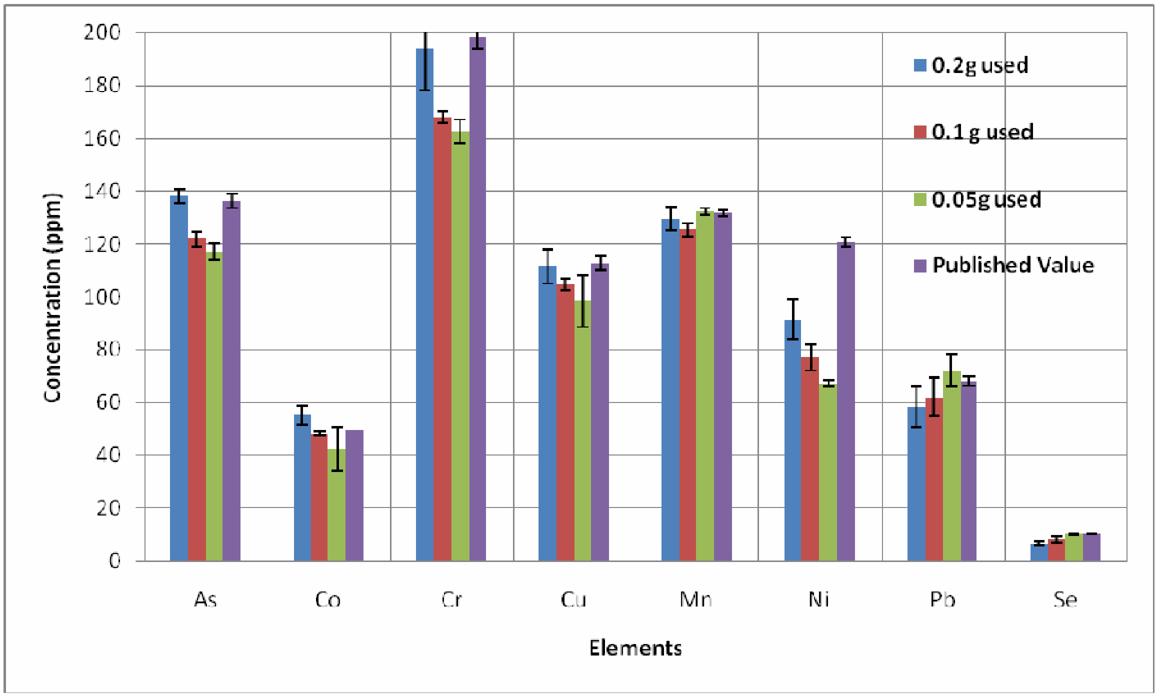

Figure 6. The effect of sample weight reduction for NIST 1633b fly ash SRM.

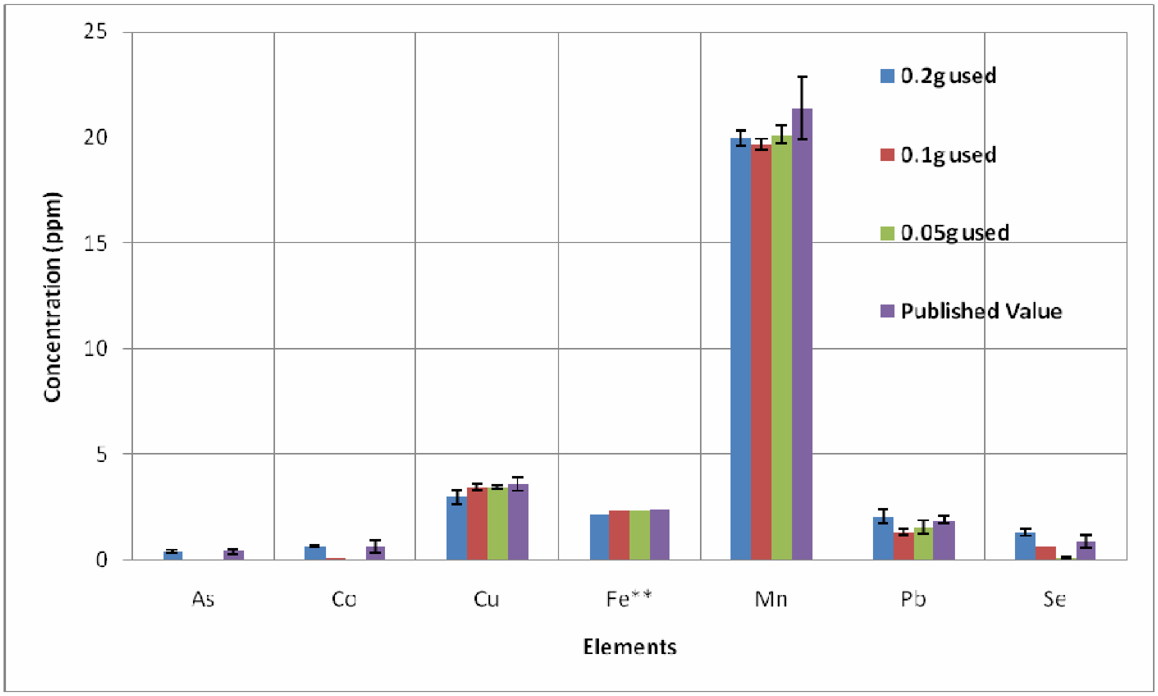

Figure 7. The effect of sample weight reduction for NIST 1635 coal SRM.
(**Fe concentration is divided by thousand to fit the graph)

Table 6. The effect of weight reduction for NIST 1633b fly ash and NIST 1635 coal SRM

FLY ASH

Element	Our Value (0.2g, 0.1g, 0.05g)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	138.06 ± 2.72	136.20 ± 2.60	101.37	1.182	no
Co	55.20 ± 3.56	50.00	110.40	--	--
Cr	193.61 ± 15.30	198.32 ± 4.70	97.62	0.533	no
Cu	111.59 ± 6.42	112.80 ± 2.60	98.92	0.328	no
Mn	129.56 ± 4.60	131.80 ± 1.70	98.30	0.844	no
Ni	91.48 ± 7.51	120.60 ± 1.80	75.85	6.720	yes
Pb	58.30 ± 7.61	68.20 ± 1.10	85.49	2.253	no
Se	6.88 ± 0.67	10.26 ± 0.17	67.02	8.707	yes
As	121.84 ± 2.71	136.20 ± 2.60	89.45	9.185	yes
Co	48.30 ± 0.63	50.00	96.60	--	--
Cr	167.92 ± 2.30	198.32 ± 4.70	84.67	22.933	yes
Cu	104.62 ± 2.12	112.80 ± 2.60	92.75	6.670	yes
Mn	125.56 ± 2.46	131.80 ± 1.70	95.26	4.398	yes
Ni	76.96 ± 4.78	120.60 ± 1.80	63.82	15.817	yes
Pb	62.09 ± 7.21	68.20 ± 1.10	91.04	1.468	no
Se	8.31 ± 1.05	10.26 ± 0.17	81.02	3.202	no
As	117.01 ± 3.07	136.20 ± 2.60	85.91	10.815	yes
Co	42.42 ± 8.31	50.00	84.85	--	--
Cr	162.76 ± 4.51	198.32 ± 4.70	82.07	13.655	yes
Cu	98.57 ± 9.85	112.80 ± 2.60	87.38	2.502	no
Mn	132.33 ± 1.38	131.80 ± 1.70	100.40	0.662	no
Ni	67.21 ± 1.52	120.60 ± 1.80	55.73	60.884	yes
Pb	72.12 ± 6.28	68.20 ± 1.10	105.75	1.081	no
Se	10.09 ± 0.42	10.26 ± 0.17	98.33	0.713	no

COAL

Element	Our Value (0.2g, 0.1g, 0.05g)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	0.39 ± 0.08	0.42 ± 0.15	92.90	0.628	no
Co	0.69 ± 0.01	0.65 ± 0.30	105.95	6.686	yes
Cu	2.99 ± 0.33	3.60 ± 0.30	83.12	3.227	no
**Fe	2.17 ± 0.01	2.39 ± 0.01	90.92	42.739	yes
Mn	19.97 ± 0.37	21.40 ± 1.50	93.33	6.651	yes
Pb	2.05 ± 0.32	1.90 ± 0.20	107.98	0.830	no
Se	1.33 ± 0.16	0.90 ± 0.30	147.74	4.602	yes
As	0.07 ± 0.01	0.42 ± 0.15	15.87	106.000	yes
Co	0.12 ± 0.00	0.65 ± 0.30	18.36	227.429	yes
Cu	3.46 ± 0.13	3.60 ± 0.30	96.05	1.844	no
**Fe	2.31 ± 0.01	2.39 ± 0.01	96.78	13.620	yes
Mn	19.67 ± 0.24	21.40 ± 1.50	91.92	12.571	yes
Pb	1.33 ± 0.14	1.90 ± 0.20	69.98	7.126	yes
Se	0.65 ± 0.02	0.90 ± 0.30	72.67	20.131	yes
As	0.00 ± 0.00	0.42 ± 0.15	0.00	--	--
Co	0.00 ± 0.00	0.65 ± 0.30	0.00	--	--
Cu	3.46 ± 0.08	3.60 ± 0.30	96.06	2.924	no
**Fe	2.33 ± 0.02	2.39 ± 0.01	97.52	4.321	yes
Mn	20.11 ± 0.42	21.40 ± 1.50	93.96	5.310	yes
Pb	1.58 ± 0.29	1.90 ± 0.20	83.23	1.915	no
Se	0.13 ± 0.03	0.90 ± 0.30	14.74	40.250	yes

(**Fe concentration is divided by thousand to match the graph)

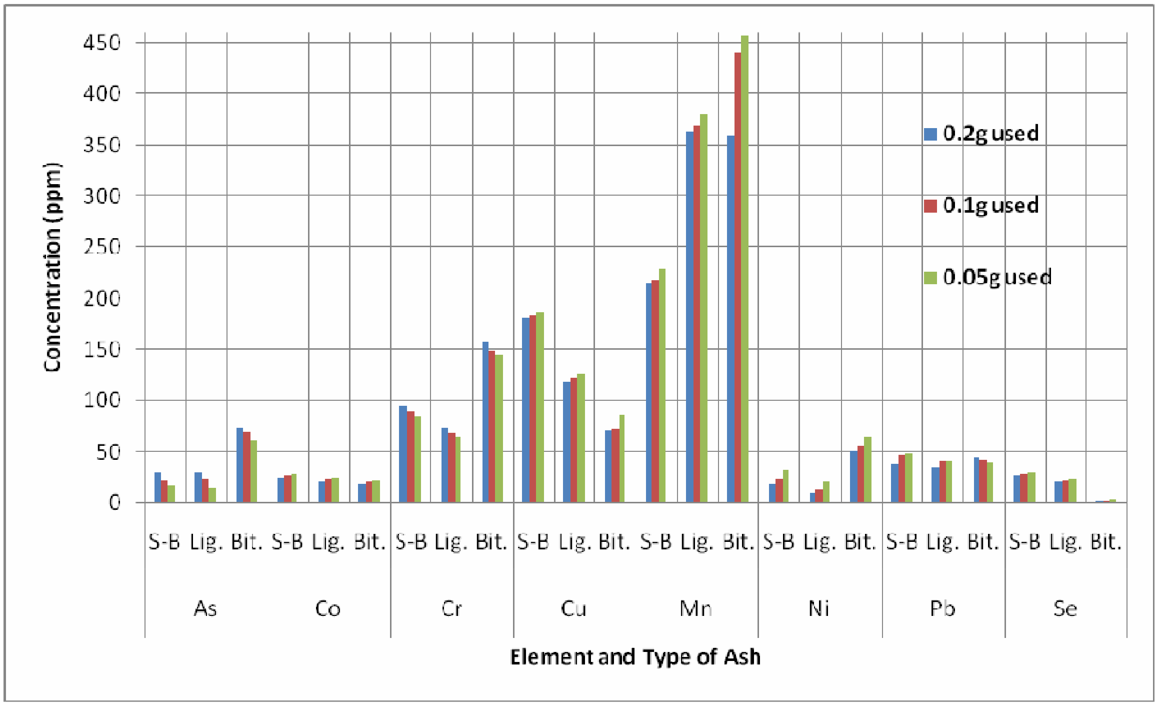

Figure 8. The effect of sample weight reduction for different types of ash.

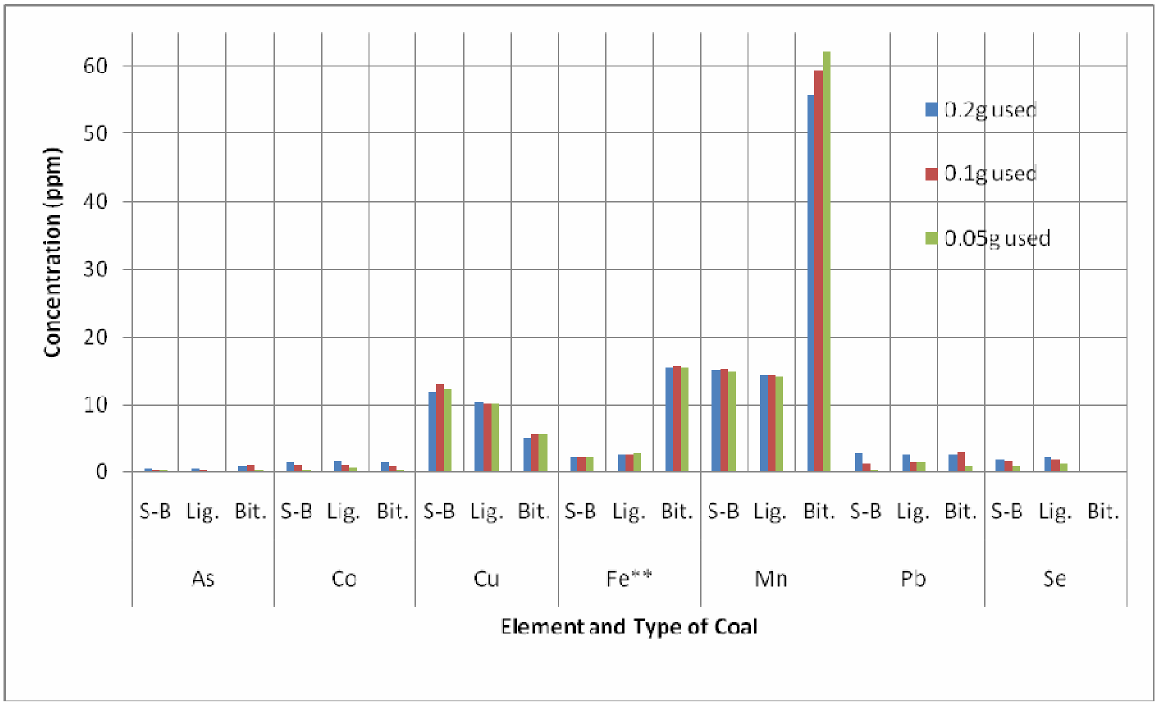

Figure 9. The effect of sample weight reduction for different types of coal.
(**Fe concentration is divided by thousand to fit the graph)

B-2. Microwave-Assisted Digestion: Optimization of Temperature

Second part of microwave-assisted acid digestion study was aimed at digestion temperature optimization. All other parameters (time, acid mixture, sample mass) were held constant. In the first run fly ash samples were digested for a total of 50 minutes at 230ºC. In next two runs temperature was decreased to 220ºC and 200ºC, respectively. In the original two-step method for digestion of coal samples temperature for each step was set to 180º and 220ºC, respectively. In following two runs the temperatures were raised to 200ºC/230ºC for the first run and to 230ºC/230ºC for the second run. The results for this part of study are presented in the next four figures and a table.

The effect of digestion temperature change on digestion of NIST 1633b is illustrated in Figure 10. and Table 7. For most of the elements observed temperature suggested by the original method (220ºC) was found to be optimal. The recoveries for As, Co, Cu, Cr, and Se were best when sample was digested at 220ºC. The recovery of Mn appears be optimal at lower temperature of 200ºC. The recovery of Pb was slightly enhanced by increased temperature of 230 ºC.

Figure 11. and Table 7. shows the effect of digestion temperature change on elemental recovery in NIST 1635 subbituminous coal standard. Once again we can observe two different patterns; recoveries of lower concentration elements (As, Co, Pb, Se) tend to decrease as the digestion tempeature is increased while recovery of higher concentration elements (Cu, Fe, Mn) slightly improves with the increase in temperature. The parameters (200ºC/230ºC) worked best for recovery of these three elements.

The results for different types of ash samples were somewhat similar to those obtained for NIST 1633b fly ash standard (Figure 12). The recovery of As, Cu, and Pb appears to be optimal when digestion temprature was set to 220ºC. The same result can be observed for recovery of Cr in subbituminous and lignite sample, but not for bituminous. The variations in digestion temperature did not influence the recovery of Co, Ni, or Se significantly. The recovery of Mn in all three types of ash seems to be optimized by lowering the temperature to 200ºC. The Figure 13. shows the effect of temperature increase on recovery of elements in three different types of coal. Similarily to the results for NIST 1635, here we can also observe two general patterns; the lower temperature setup was favored for the recovery of elements present in lower amounts (As, Co, Pb, Se), while Cu, Fe, and Mn recovery was increased with higher temperature.

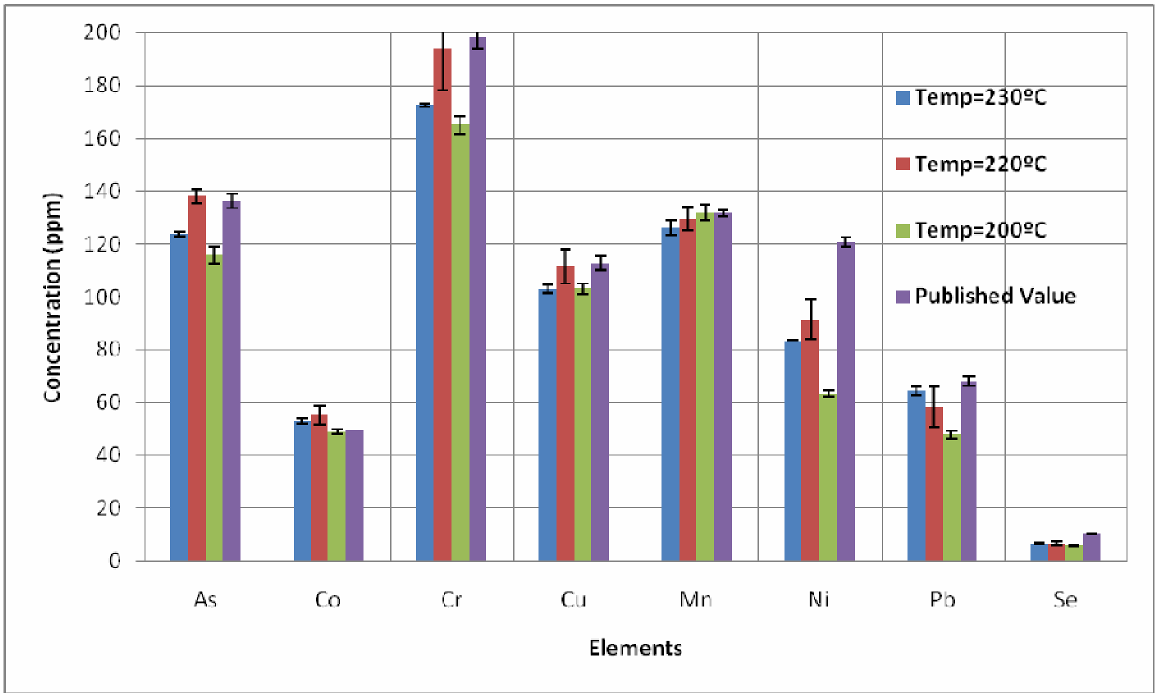

Figure 10. The effect of temperature change for NIST 1633b fly ash SRM.

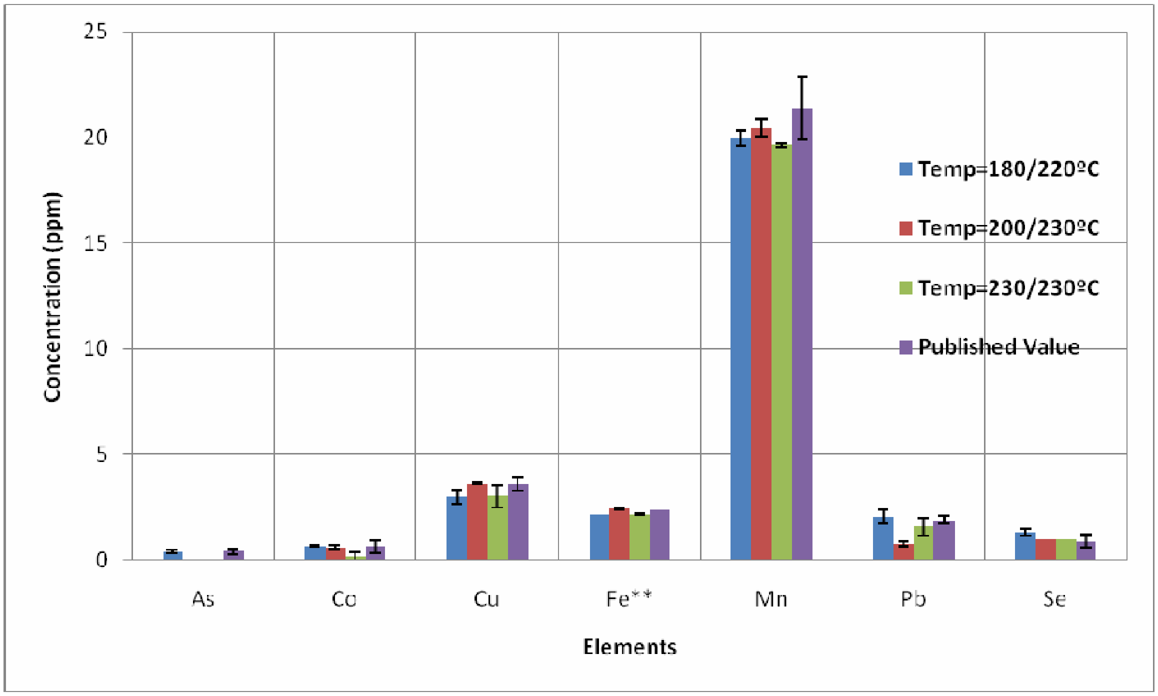

Figure 11. The effect of temperature change for NIST 1635 coal SRM.
(**Fe concentration is divided by thousand to fit the graph)

Table 7. The effect of temperature for NIST 1633b fly ash and NIST 1635 coal SRM

FLY ASH					
Element	Our Value (T(ºC)=230,220,200)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	123.87 ± 0.81	136.20 ± 2.60	90.95	26.260	yes
Co	52.91 ± 0.73	50.00	105.83	--	--
Cr	172.73 ± 0.76	198.32 ± 4.70	87.10	58.066	yes
Cu	102.98 ± 1.63	112.80 ± 2.60	91.29	10.448	yes
Mn	126.18 ± 2.98	131.80 ± 1.70	95.74	3.268	no
Ni	83.31 ± 0.22	120.60 ± 1.80	69.08	289.983	yes
Pb	64.37 ± 1.59	68.20 ± 1.10	94.39	4.157	no
Se	6.77 ± 0.22	10.26 ± 0.17	66.02	27.128	yes
As	138.06 ± 2.72	136.20 ± 2.60	101.37	1.182	no
Co	55.20 ± 3.56	50.00	110.40	--	--
Cr	193.61 ± 15.30	198.32 ± 4.70	97.62	0.533	no
Cu	111.59 ± 6.42	112.80 ± 2.60	98.92	0.328	no
Mn	129.56 ± 4.60	131.80 ± 1.70	98.30	0.844	no
Ni	91.48 ± 7.51	120.60 ± 1.80	75.85	6.720	yes
Pb	58.30 ± 7.61	68.20 ± 1.10	85.49	2.253	no
Se	6.88 ± 0.67	10.26 ± 0.17	67.02	8.707	yes
As	115.82 ± 3.16	136.20 ± 2.60	85.04	11.163	yes
Co	48.91 ± 0.76	50.00	97.81	--	--
Cr	165.16 ± 3.32	198.32 ± 4.70	83.28	17.276	yes
Cu	103.15 ± 1.99	112.80 ± 2.60	91.44	8.422	yes
Mn	131.92 ± 2.85	131.80 ± 1.70	100.09	0.075	no
Ni	63.38 ± 1.02	120.60 ± 1.80	52.56	97.005	yes
Pb	47.95 ± 1.63	68.20 ± 1.10	70.30	21.557	yes
Se	6.04 ± 0.16	10.26 ± 0.17	58.83	44.584	yes

COAL					
Element	Our Value (T(ºC)=180,200,230)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	0.39 ± 0.08	0.42 ± 0.15	92.90	0.628	no
Co	0.69 ± 0.01	0.65 ± 0.30	105.95	6.686	yes
Cu	2.99 ± 0.33	3.60 ± 0.30	83.12	3.227	no
**Fe	2.17 ± 0.01	2.39 ± 0.01	90.92	42.739	yes
Mn	19.97 ± 0.37	21.40 ± 1.50	93.33	6.651	yes
Pb	2.05 ± 0.32	1.90 ± 0.20	107.98	0.830	no
Se	1.33 ± 0.16	0.90 ± 0.30	147.74	4.602	yes
As	0.00 ± 0.00	0.42 ± 0.15	0.00	--	--
Co	0.61 ± 0.08	0.65 ± 0.30	93.33	0.935	no
Cu	3.61 ± 0.03	3.60 ± 0.30	100.41	0.821	no
**Fe	2.43 ± 0.03	2.39 ± 0.01	101.71	2.508	no
Mn	20.46 ± 0.40	21.40 ± 1.50	95.60	4.033	no
Pb	0.78 ± 0.10	1.90 ± 0.20	40.86	19.476	yes
Se	0.99 ± 0.01	0.90 ± 0.30	109.85	13.153	yes
As	0.00 ± 0.00	0.42 ± 0.15	0.00	--	--
Co	0.17 ± 0.22	0.65 ± 0.30	25.79	3.815	no
Cu	3.04 ± 0.54	3.60 ± 0.30	84.35	1.802	no
**Fe	2.18 ± 0.01	2.39 ± 0.01	91.30	26.227	yes
Mn	19.63 ± 0.06	21.40 ± 1.50	91.71	49.244	yes
Pb	1.59 ± 0.42	1.90 ± 0.20	83.54	1.285	no
Se	1.00 ± 0.01	0.90 ± 0.30	111.63	28.198	yes

(**Fe concentration is divided by thousand to match the graph)

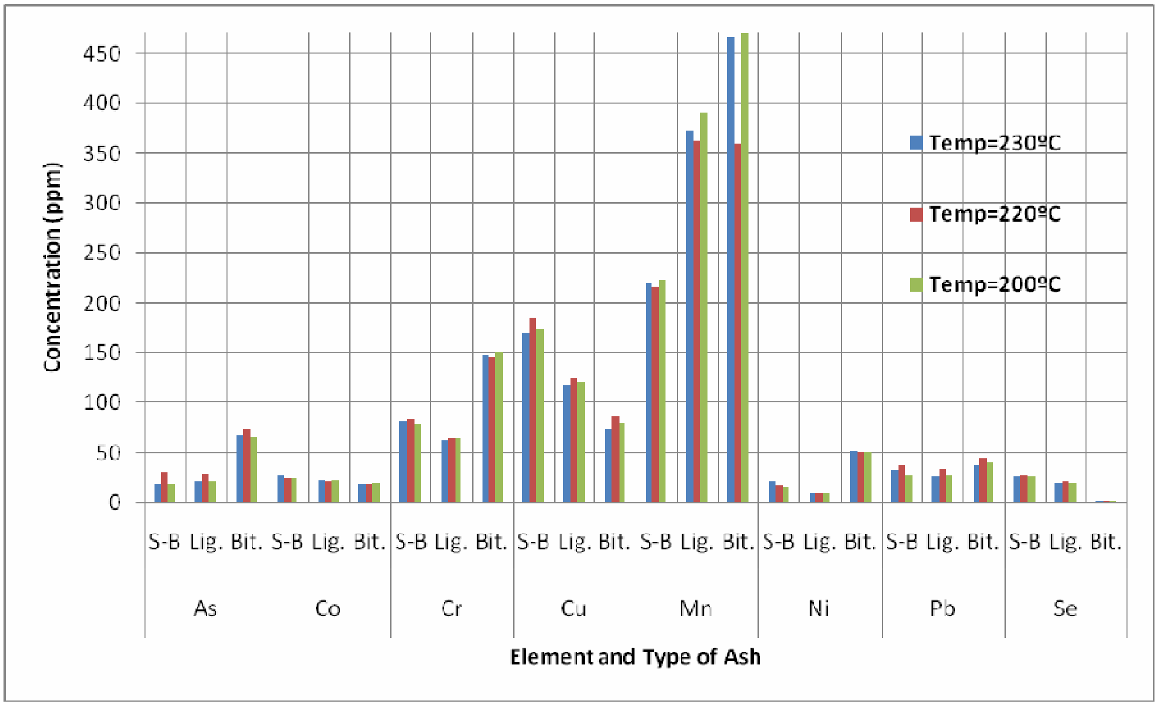

Figure 12. The effect of temperature change for different types of ash.

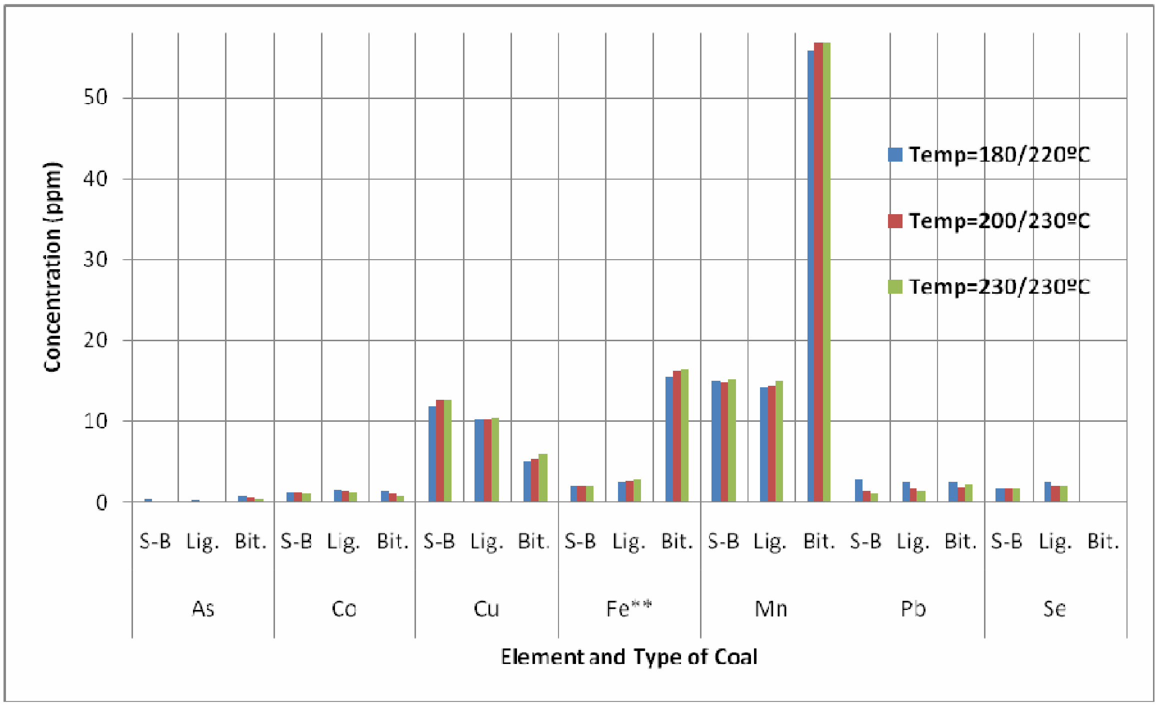

Figure 13. The effect of temperature change for different types of coal.
(**Fe concentration is divided by thousand to fit the graph)

B-3. Microwave-Assisted Digestion: Optimization of Time

In the third part of the study samples were subjected to varying digestion times while all other parameters were kept constant. The original digestion method for fly ash samples calls for a total of 50 minutes digestion. In two additional runs time was increased to 60 and 70 minutes, respectively. For the two-step digestion of coal samples, the original method that calls for a 15 minute digestion length for each step was modified by increasing both steps to 25 minutes in the first run and 35 minutes in the second run. The results are presented in four figures and a table below.

The effect of varying digestion time for NIST 1633b fly ash standard is presented in Figure 14. and Table 8. Only the recovery of Pb seems to be improved by the increasing the digestion times. The improvement in recovery was noted for Se, Mn, and Ni when time of digestion was increased to 60 minutes, but not to 70 minutes. The recovery of As, Co, Cr, and Cu appear to decrease by the prolonged digestion time.

The effect of varying digestion time for NIST 1635 coal standard is presented in Figure 15. and Table 8. The recovery of As, Co, Pb, and Se appear to be significantly influenced by the prolonged digestion time. Mn, and Fe, recovery, on the other hand, did improve by increasing the time of digestion. The recovery of Cu seem to be improved by increasing the digestion time to 25min/25min, but not to 35min/35min.

The similar pattern of change that occurred for NIST 1633b sample was observed with most of the fly ash samples analyzed as well (Figure 16). Recovery of all elements in all types of fly ash was increased by increasing the digestion time from 50 minutes to 60 minutes. The most significant change occurred in recovery of Cu and Mn.

The same pattern of recovery change for elements present in NIST 1635 coal was observed for all other coal samples (Figure 17). Increase in digeastion time negatively influenced the recovery of As, Co, and Pb, while recovery of other elements remained unaffected in most of the cases. Only exception was the recovery of Mn, which in this case, too, seem to be optimized by increasing the digestion time.

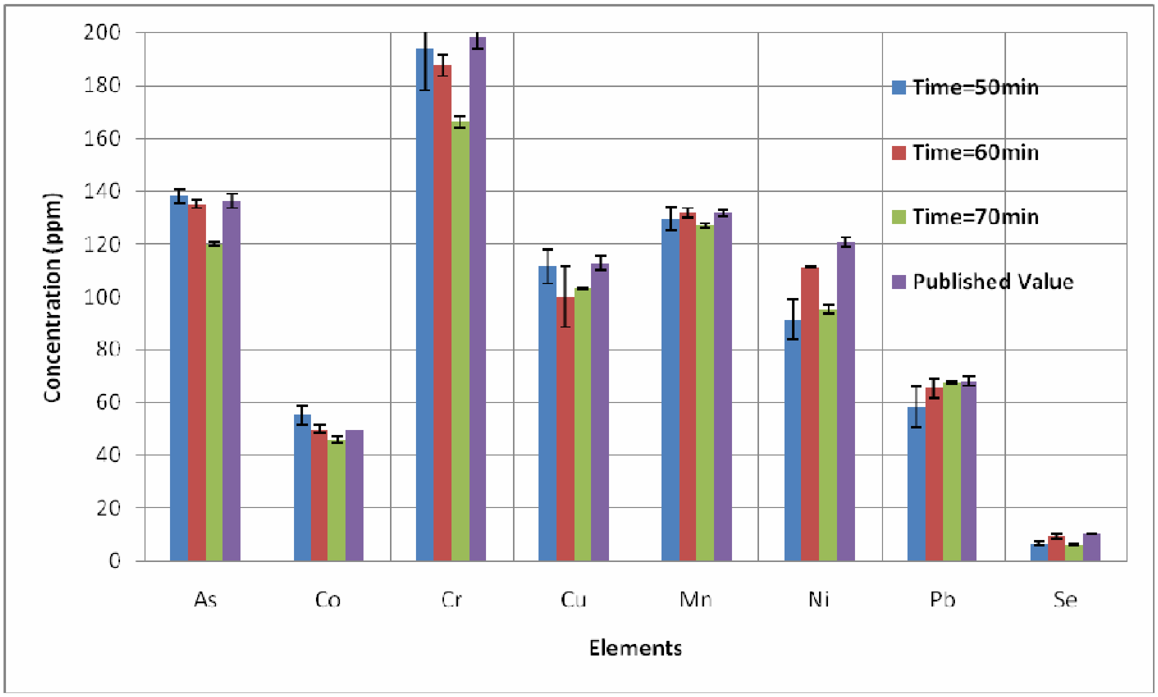

Figure 14. The effect of time change for NIST 1633b fly ash SRM.

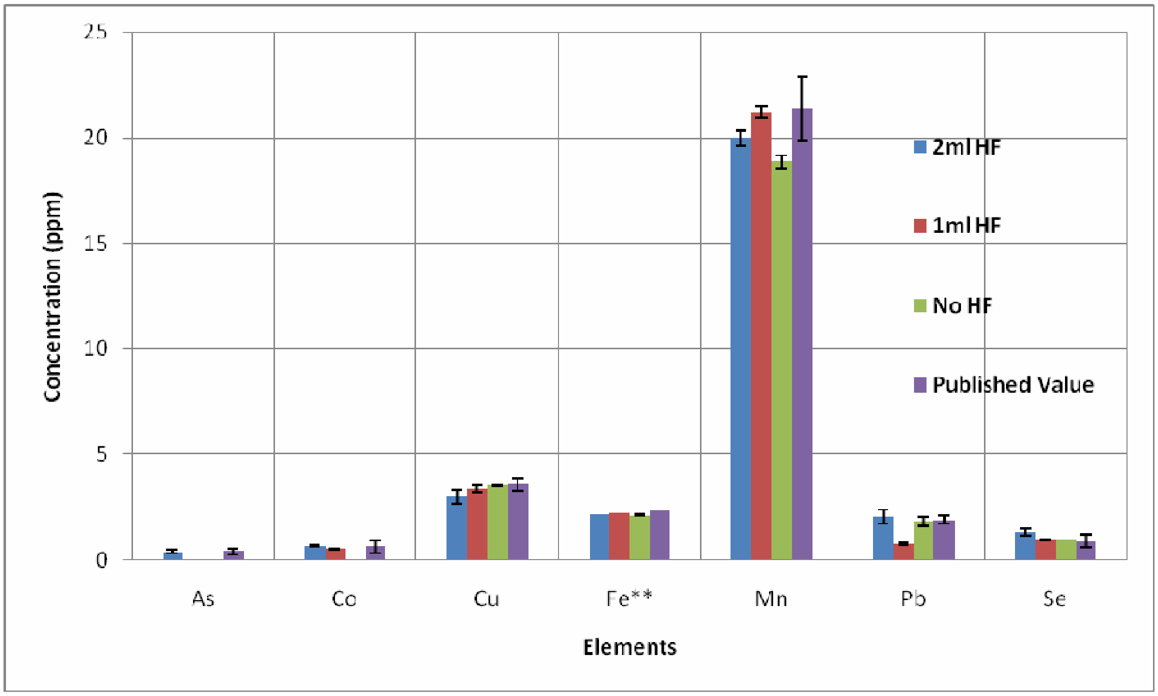

Figure 15. The effect of time change for NIST 1635 coal SRM.
(**Fe concentration is divided by thousand to fit the graph)

Table 8. The effect of time for NIST 1633b fly ash and NIST 1635 coal SRM

FLY ASH

Element	Our Value (T(min)=50,60,70)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	138.06 ± 2.72	136.20 ± 2.60	101.37	1.182	no
Co	55.20 ± 3.56	50.00	110.40	--	--
Cr	193.61 ± 15.30	198.32 ± 4.70	97.62	0.533	no
Cu	111.59 ± 6.42	112.80 ± 2.60	98.92	0.328	no
Mn	129.56 ± 4.60	131.80 ± 1.70	98.30	0.844	no
Ni	91.48 ± 7.51	120.60 ± 1.80	75.85	6.720	yes
Pb	58.30 ± 7.61	68.20 ± 1.10	85.49	2.253	no
Se	6.88 ± 0.67	10.26 ± 0.17	67.02	8.707	yes
As	135.01 ± 1.5645	136.20 ± 2.60	99.12	1.320	no
Co	50.002 ± 1.5531	50.00	100.00	--	--
Cr	187.48 ± 4.0561	198.32 ± 4.70	94.54	4.627	yes
Cu	100.15 ± 11.729	112.80 ± 2.60	88.78	1.869	no
Mn	131.7 ± 1.7665	131.80 ± 1.70	99.92	0.101	no
Ni	111.24 ± 0.4944	120.60 ± 1.80	92.24	32.797	yes
Pb	65.582 ± 3.5762	68.20 ± 1.10	96.16	1.268	no
Se	9.2707 ± 0.9498	10.26 ± 0.17	90.36	1.804	no
As	120 ± 0.514	136.20 ± 2.60	88.10	54.609	yes
Co	45.946 ± 1.0543	50.00	91.89	--	--
Cr	166.15 ± 2.2912	198.32 ± 4.70	83.78	24.318	yes
Cu	103.16 ± 0.3502	112.80 ± 2.60	91.45	47.675	yes
Mn	127 ± 0.9216	131.80 ± 1.70	96.36	9.016	yes
Ni	95.438 ± 1.7337	120.60 ± 1.80	79.14	25.137	yes
Pb	67.64 ± 0.6069	68.20 ± 1.10	99.18	1.597	no
Se	6.2727 ± 0.3165	10.26 ± 0.17	61.14	21.820	yes

COAL

Element	Our Value (t(min)=15,25,35)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	0.39 ± 0.08	0.42 ± 0.15	92.90	0.628	no
Co	0.69 ± 0.01	0.65 ± 0.30	105.95	6.686	yes
Cu	2.99 ± 0.33	3.60 ± 0.30	83.12	3.227	no
**Fe	2.17 ± 0.01	2.39 ± 0.01	90.92	42.739	yes
Mn	19.97 ± 0.37	21.40 ± 1.50	93.33	6.651	yes
Pb	2.05 ± 0.32	1.90 ± 0.20	107.98	0.830	no
Se	1.33 ± 0.16	0.90 ± 0.30	147.74	4.602	yes
As	0.00 ± 0.00	0.42 ± 0.15	0.00	--	--
Co	0.11 ± 0.00	0.65 ± 0.30	16.82	266.655	yes
Cu	3.56 ± 0.03	3.60 ± 0.30	98.95	2.272	no
**Fe	2.33 ± 0.02	2.39 ± 0.01	97.36	4.427	yes
Mn	20.02 ± 0.17	21.40 ± 1.50	93.55	13.851	yes
Pb	0.25 ± 0.03	1.90 ± 0.20	12.91	92.676	yes
Se	0.93 ± 0.05	0.90 ± 0.30	103.74	1.129	no
As	0.08 ± 0.09	0.42 ± 0.15	17.94	6.462	yes
Co	0.17 ± 0.05	0.65 ± 0.30	25.38	17.399	yes
Cu	2.77 ± 0.61	3.60 ± 0.30	76.92	2.348	no
**Fe	2.43 ± 0.03	2.39 ± 0.01	101.54	2.232	no
Mn	21.44 ± 0.10	21.40 ± 1.50	100.21	0.753	no
Pb	0.63 ± 0.04	1.90 ± 0.20	33.39	53.085	yes
Se	1.01 ± 0.01	0.90 ± 0.30	111.78	34.697	yes

(**Fe concentration is divided by thousand to match the graph)

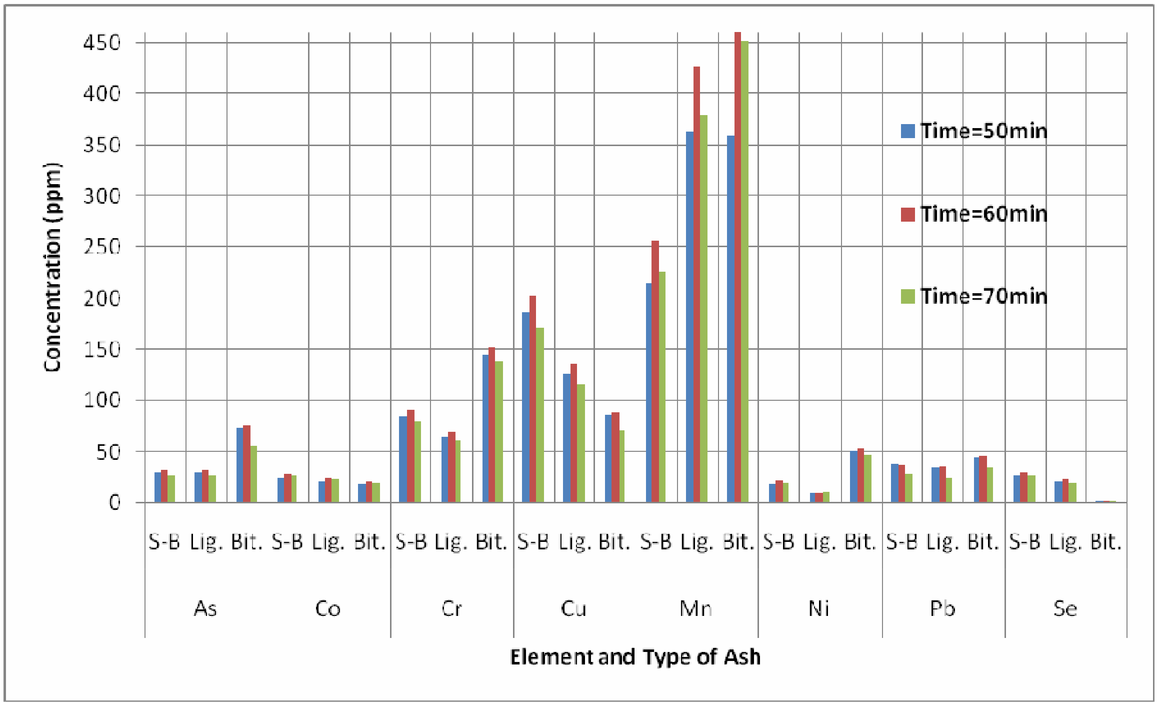

Figure 16. The effect of time change for different types of ash.

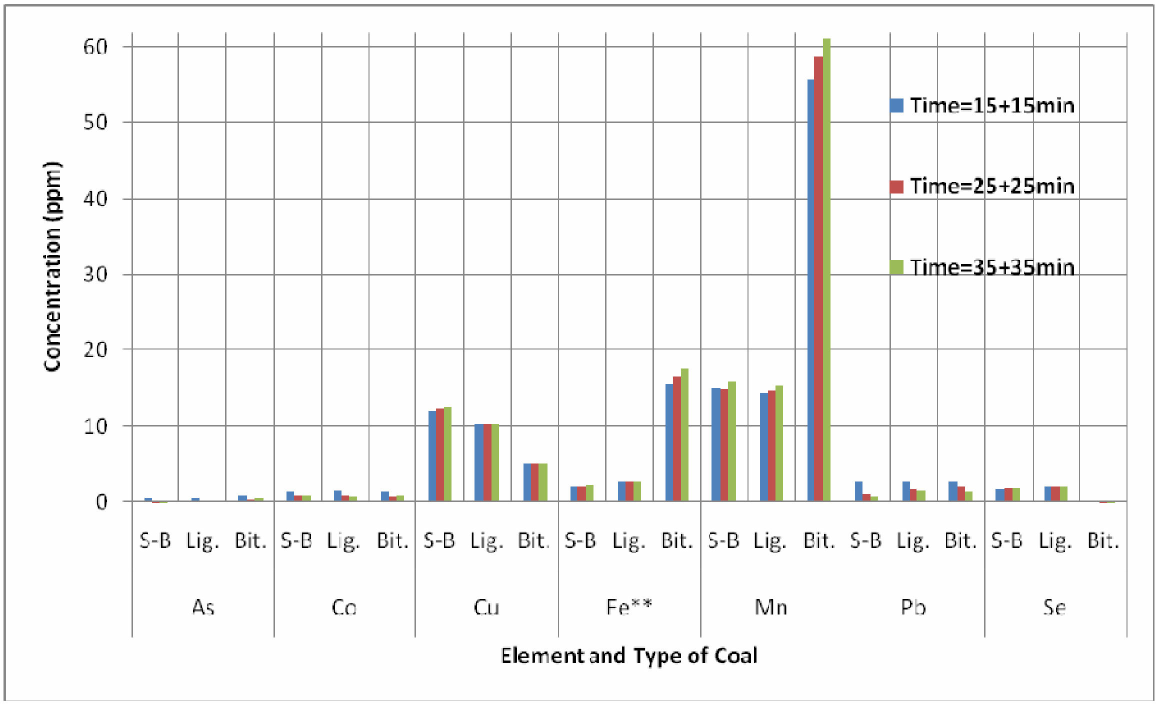

Figure 17. The effect of time change for different types of coal.
(**Fe concentration is divided by thousand to fit the graph)

B-4. Microwave-Assisted Digestion: The Amount of Hydrofluoric Acid Used

In the last part of the study the need for hydrofluoric acid was examined. The original method for fly ash digestion calls for addition of 2 mL of hydrofluoric acid. In the next run that amount was reduced to 1 mL and in the last run no hydrofluoric acid was used. The original two-step procedure for digestion of coal samples indicated that 2 mL of hydrofluoric acid should be added in the second step. In the following run the amount of hydrofluoric acid added was reduced to 1 mL and last run was performed with no hydrofluoric acid added. The results for this part of study are presented in four figures and a table below.

With the exception of Se, recovery of all other elements in NIST 1633b was decreased by changing the amount of hydrofluoric acid used to 1 mL or when samples were digested without hydrofluoric acid (Figure 18. and Table 9). It worth noting that for Se recovery slightly improved when volume of hydrofluoric acid was reduced to 1mL, but it decreased without hydrofluoric acid.

Most of the elements in NIST 1635 coal standard were managed to be extracted even without hydrofluoric acid used. The exception in this case was As an Co; with reduced volume of hydrofluoric acid as well as with no acid used, no As was recovered. Furthermore, Cu, Fe, Mn, and Se were recovered better less or no hydrofluoric acid was used.

The recovery trend set by NIST 1633b fly ash standard was closely followed by the other types of fly ash samples, too (Figure 20). Again, with the exception of Co, Mn, and Se other elements were poorly recovered with reduced volume or when no hydrofluoric acid was used. Similarily to the results obtained for NIST 1633b, decrease in recovery of Co, Mn, and Se was observed only when no hydrofluoric acid was used; no change was observed when volume was reduced to 1 mL.

Differently from fly ash, most of the elements in all types of coal samples were succesfuly extracted with reduced or no hydrofluoric acid used (Figure 21). Exception to this again is As that could not be extracted with reduced volume or completely without hydrofluoric acid.

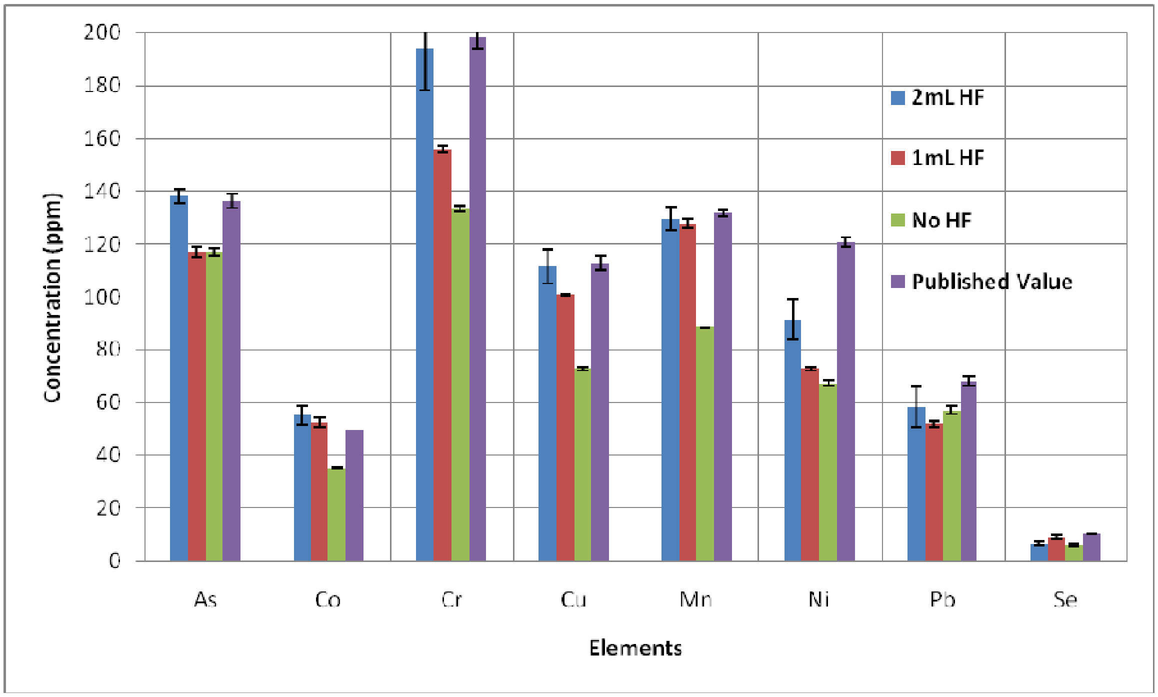

Figure 18. The effect of decreased amount of HF used for NIST 1633b fly ash SRM.

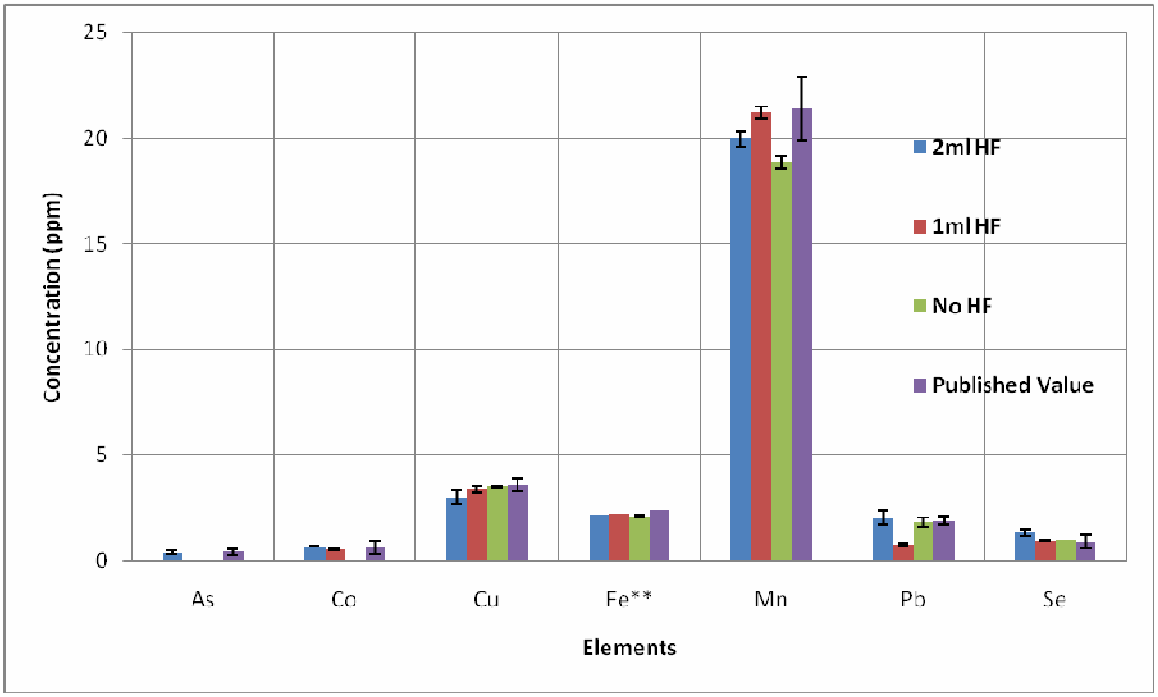

Figure 19. The effect of decreased amount of HF used for NIST 1635 coal SRM.
(**Fe concentration is divided by thousand to fit the graph)

Table 8. The effect of HF usage for NIST 1633b fly ash and NIST 1635 coal SRM

FLY ASH

Element	Our Value (HF=2ml,1ml,0ml)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	138.06 ± 2.72	136.20 ± 2.60	101.37	1.182	no
Co	55.20 ± 3.56	50.00	110.40	--	--
Cr	193.61 ± 15.30	198.32 ± 4.70	97.62	0.533	no
Cu	111.59 ± 6.42	112.80 ± 2.60	98.92	0.328	no
Mn	129.56 ± 4.60	131.80 ± 1.70	98.30	0.844	no
Ni	91.48 ± 7.51	120.60 ± 1.80	75.85	6.720	yes
Pb	58.30 ± 7.61	68.20 ± 1.10	85.49	2.253	no
Se	6.88 ± 0.67	10.26 ± 0.17	67.02	8.707	yes
As	116.95 ± 2.06	136.20 ± 2.60	85.87	16.193	yes
Co	52.67 ± 1.81	50.00	105.35	--	--
Cr	155.98 ± 1.31	198.32 ± 4.70	78.65	55.893	yes
Cu	100.93 ± 0.30	112.80 ± 2.60	89.48	68.914	yes
Mn	127.88 ± 1.79	131.80 ± 1.70	97.02	3.791	no
Ni	72.95 ± 0.74	120.60 ± 1.80	60.49	112.081	yes
Pb	51.99 ± 1.16	68.20 ± 1.10	76.24	24.190	yes
Se	9.08 ± 0.79	10.26 ± 0.17	88.51	2.585	no
As	116.97 ± 1.46	136.20 ± 2.60	85.88	22.879	yes
Co	35.21 ± 0.17	50.00	70.42	--	--
Cr	133.43 ± 1.30	198.32 ± 4.70	67.28	86.713	yes
Cu	72.86 ± 0.61	112.80 ± 2.60	64.59	113.503	yes
Mn	88.54 ± 0.23	131.80 ± 1.70	67.18	325.051	yes
Ni	67.46 ± 1.15	120.60 ± 1.80	55.94	80.254	yes
Pb	57.11 ± 1.43	68.20 ± 1.10	83.73	13.393	yes
Se	6.21 ± 0.31	10.26 ± 0.17	60.48	22.773	yes

COAL

Element	Our Value (HF=2ml,1ml,0ml)	NIST Value	% Recovery	t(calculated)	Significant (95% level)
As	0.39 ± 0.08	0.42 ± 0.15	92.90	0.628	no
Co	0.69 ± 0.01	0.65 ± 0.30	105.95	6.686	yes
Cu	2.99 ± 0.33	3.60 ± 0.30	83.12	3.227	no
**Fe	2.17 ± 0.01	2.39 ± 0.01	90.92	42.739	yes
Mn	19.97 ± 0.37	21.40 ± 1.50	93.33	6.651	yes
Pb	2.05 ± 0.32	1.90 ± 0.20	107.98	0.830	no
Se	1.33 ± 0.16	0.90 ± 0.30	147.74	4.602	yes
As	0.00 ± 0.00	0.42 ± 0.15	0.00	--	--
Co	0.53 ± 0.04	0.65 ± 0.30	81.85	5.153	yes
Cu	3.37 ± 0.18	3.60 ± 0.30	93.68	2.228	no
**Fe	2.24 ± 0.00	2.39 ± 0.01	93.77	61.574	yes
Mn	21.23 ± 0.27	21.40 ± 1.50	99.22	1.087	no
Pb	0.76 ± 0.04	1.90 ± 0.20	39.88	48.426	yes
Se	0.97 ± 0.04	0.90 ± 0.30	108.22	3.477	no
As	0.00 ± 0.00	0.42 ± 0.15	0.00	--	--
Co	0.00 ± 0.00	0.65 ± 0.30	0.00	--	--
Cu	3.54 ± 0.02	3.60 ± 0.30	98.29	4.957	yes
**Fe	2.14 ± 0.04	2.39 ± 0.01	89.66	11.722	yes
Mn	18.87 ± 0.31	21.40 ± 1.50	88.17	13.983	yes
Pb	1.82 ± 0.20	1.90 ± 0.20	96.02	0.659	no
Se	0.98 ± 0.01	0.90 ± 0.30	108.78	12.988	yes

(**Fe concentration is divided by thousand to match the graph)

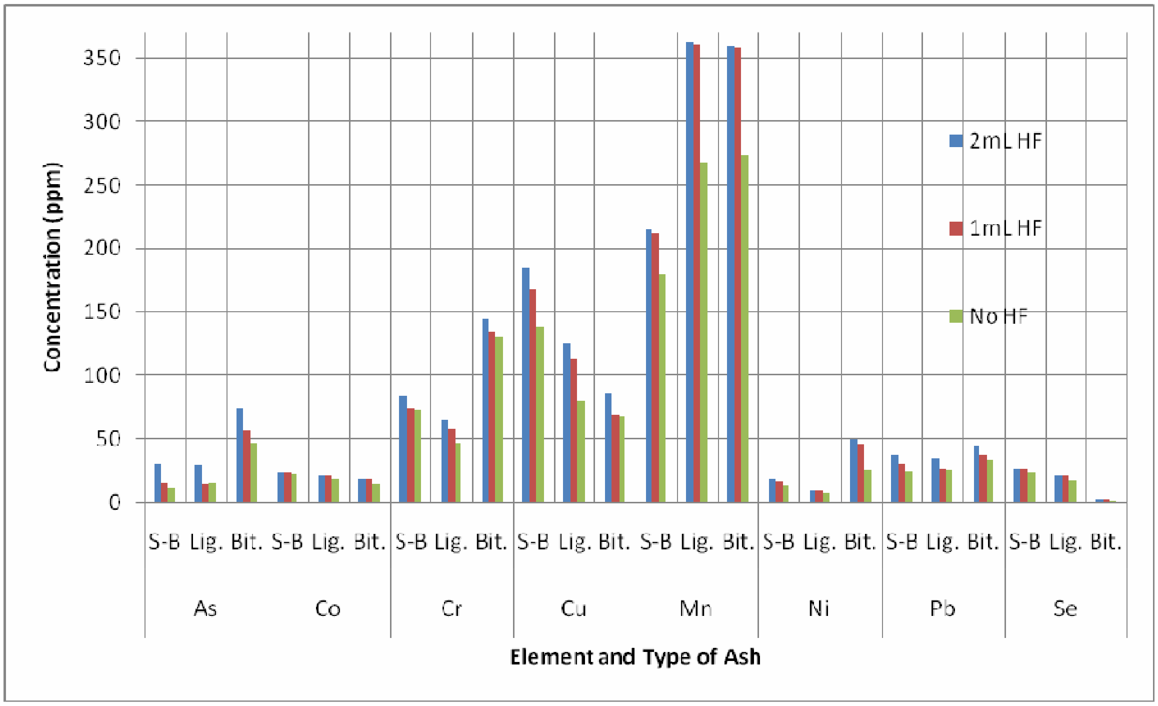

Figure 20. The effect of decreased amount of HF used for different types of ash.

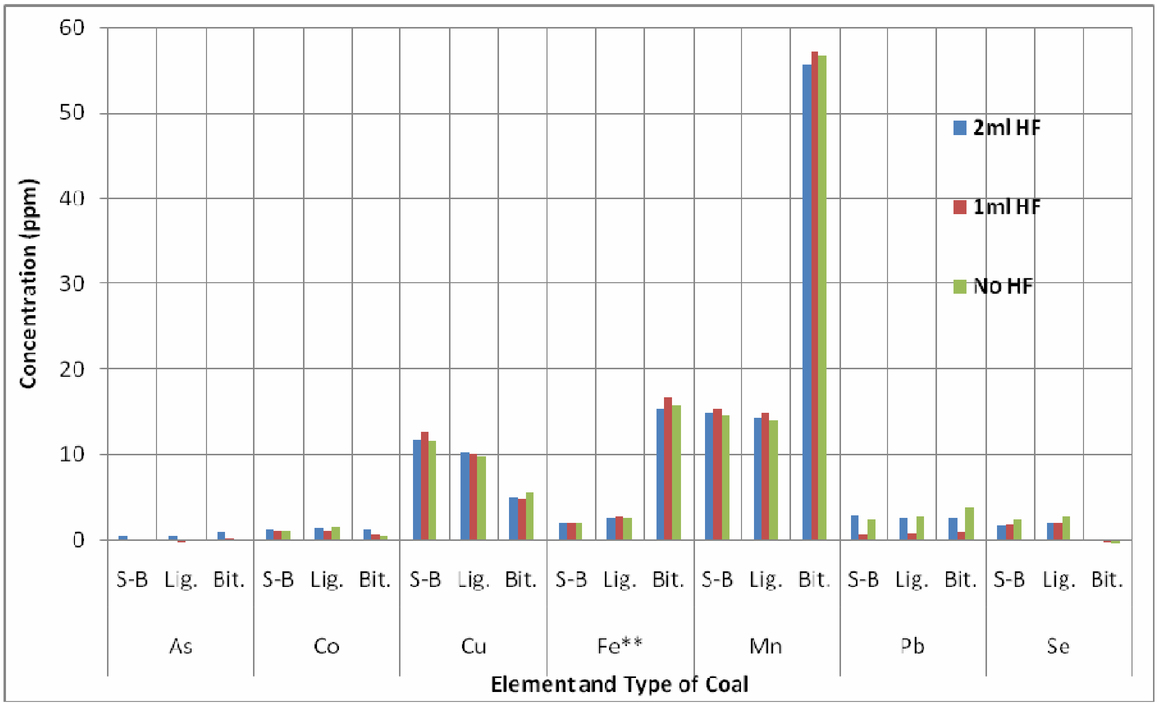

Figure 21. The effect of decreased amount of HF used for different types of coal.
(**Fe concentration is divided by thousand to fit the graph)

From the results presented we find that ASTM D6357-04 hot plate digestion method can be used for the digestion of fly ash samples with relative good recoveries for most of the elements. However, one must carefully follow the steps listed in this method in order to obtain repeatable results which can be somewhat difficult. Obtaining repeatable results will greatly depend on the ability to keep the several following parameters constant: temperatures used during ashing step and during digestion, completeness of the digestion, filtration, as well as the presence of analyzed trace metals in the environment where digestion was performed.

Microwave-assisted digestion method for fly ash samples also provided very good recoveries that are comparable to those obtained by ASTM D6357-04 method. Microwave-assisted method provides several advantages over traditional hot plate method, and most of them come from the fact that this method is performed under higher temperatures and pressures as well as under close vessel conditions. Ashing step prior to digestion is not necessary when microwave was used. Microwave system constantly monitors the temperature of reference vessel throughout the digestion procedure and automatically increases or decreases it when necessary. For example, if at some point during the digestion of sample an exothermic reaction occurs, spike in temperature will be observed. In that case instrument will cut the energy supply in order to lower the temperature to the set value. This ensures more constant and repeatable conditions compared to hot plate digestion. Another advantage is that digestion is performed in closed vessels. This condition provides the advantage of performing more complete digestion under higher temperatures and pressures without loss of more volatile elements.

Lastly, time needed for digestion is significantly reduced when microwave digestion system is used.

The results presented for the microwave-assisted digestion of fly ash samples showed that certain adjustments to the temperature, time, and sample weight/acid volume ratio can be made to improve the recovery of some elements. However, it should be noted that some adjustments can result in better recoveries for certain elements and at the same time give the poorer results for others. So parameters used in a digestion will depend on elements of interest. Investigations using reduced amount of hydrofluoric acid in fly ash digestion led to conclusion that for successful recovery of most of the metals hydrofluoric acid is, in fact, needed because fly ash primarily consists of silicates and oxides.

The recovery of elements present in coal samples using hot plate digestion was not as satisfying as recovery in fly ash samples. During pre-digestion ashing step, coal will lose approximately 85% to 90% of its initial mass. It is possible that during ashing at 500ºC some more volatile elements can be lost. In addition to that, if the digestion is not preformed until completeness, some elements may not be released into solution which will result in lower recoveries.

The conditions under which microwave-assisted digestion of coal was performed should eliminate the possibility of losing volatile elements. The results presented for the microwave-assisted digestion of coal showed in most of the cases improved recoveries some elements compared to the hot plate digestion results. However, an important problem with this particular method occurred throughout the whole study; while we were able to recover Se from the bituminous coal samples using hot plate digestion, no Se was recovered from bituminous coal using microwave-assisted method. Upon reviewing collected data for all variations of microwave-assisted digestion of coal, we can make a general conclusion that original method parameters will work best for most elements examined. It is, however, important to notice that successful recovery of most of the elements from coal (with the exception of As) can be obtained without using hydrofluoric acid. This is very important considering the health and safety issues involved with use of hydrofluoric acid. The same conclusion was reached by Ohki, et al. who performed two-step microwave-assisted coal digestion using nitric acid and hydrogen peroxide, and with and without hydrofluoric acid[5]. They suggested that complete recovery of both major and minor elements are possible without the use of hydrofluoric acid.

IV. CONCLUSIONS

The ASTM D6357-04 hot plate digestion method, in spite of being cumbersome and lengthy, was found to be a reliable method for digestion of many elements present in fly ash. That however was not the case with coal samples. With the exception of Cu and Ni, the recovery was not completely satisfactory.

The microwave-assisted digestion method for fly ash provided comparable or better results to that of hot plate digestion method. In addition, preparation and time needed for digestion was significantly reduced with this method. The variations in weight of sample, temperature, and time resulted in improved recoveries of several elements, but generally, the initial method parameters can be considered optimal.

The microwave-assisted method for coal did work better than hot plate digestion method. There is, however, room for more improvement in future research.

The use of hydrofluoric acid was absolutely necessary for digestion of fly ash because fly ash primarily consists of silicates and oxides. Most of the elements in coal were successfully extracted even without hydrofluoric acid.

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