South Dakota State University

1977

Preparation and Analysis of Coal for Metals

Jim Parker

PREPARATION AND ANALYSIS OF COAL FOR METALS

BY

JIM PARKER

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in Chemistry
South Dakota State University
1977

PREPARATION AND ANALYSIS OF COAL FOR METALS

By Jim Parker

Abstract

Under the Supervision of Dr. David C. Hilderbrand

The effect of sample preparation on the analysis of coal for metals is reported. Wet and dry ashing methods were investigated for the dissolution of coal samples. Nitric acid was the primary oxidizing acid. Sulfuric and perchloric acids were also used and their effect on the results is reported. Hydrofluoric acid was used to dissolve any siliceous material present in the coal. Different acid combinations were investigated for the dissolution of high temperature coal ash. The effect of particle size on oxidation was also investigated and the results are reported.

A National Bureau of Standards' coal sample was analyzed. The results were used to test the accuracy and precision of a method under investigation against an established method of analysis.

PREPARATION AND ANALYSIS OF COAL FOR METALS

This thesis is approved as a creditable and independent investigation by the candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

————————
                           Thesis Adviser   Date

————————
                           Head, Chemistry Department   Date

ACKNOWLEDGEMENTS

I would like to Thank Dr. David Hilderbrand for his advice, encouragement, and friendship throughout the course of my study at South Dakota State.

I would also like to Thank my wife, Faunie, for typing the manuscript and for being there for the last two years.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

STATEMENT OF THE PROBLEM

At the present time there is a growing national concern about the nature and quantity of trace elements that are entering the environment. In view of this concern there is a need for accurate and reliable analytical methods for the determination of essential and toxic elements in a variety of complex matrices. One of the pollution sources is combustion of fossil fuels, more specifically, combustion of coal. In 1973, 590×10^6 tons of coal were burned in the United States.[1] With increased emphasis on the use of coal as a primary energy source in the United States by the current administration that figure will probably increase in the coming years.

There are radiochemical methods of analysis available for determining concentrations of trace metals in raw coal samples, but wet chemical techniques are still the method of choice in many laboratories due to instrumental availability. Gorsuch presented a detailed discussion of the problems encountered in the destruction of organic material by acid digestion and dry ashing techniques,[2] but the majority of his sample material was cocoa leaves. Coal being an entirely different matrix should in addition present different ashing problems. Von Lehmden, Jungers, and Lee demonstrated the need for study in this area by reporting the results of analysis of twenty-eight elements by nine different laboratories of coal, fly ash, fuel oil, and

gasoline samples.[3] Differences of less than an order of magnitude were reported for some elements in the coal analysis, but differences of one and two orders of magnitude were more frequent.

The purpose of this work is to examine the relationship between sample preparation and the analysis of coal samples for trace metals. Copper, zinc, sodium, and arsenic were selected as representative elements. It is not the intent of this study to develop a new analytical method for the oxidation of raw coal samples. Rather it is to determine if the wide variation in reported values of the analysis of coal for trace metals in some studies is due to the sample preparation step.

LITERATURE SEARCH

Over 60 different elements have been identified in coal samples.[4] Included are such environmental toxins as mercury, lead, cadmium, arsenic, beryllium, selenium, and nickel. Many of these are present in coal only in trace quantities. However, when the total amount of coal burned in one location is taken into consideration then the potential for environmental damage becomes significant. Using the figure of 590×10^6 tons of coal burned a year, at 1 part per million a trace element such as mercury will produce 590 tons of a potentially dangerous toxin. The percentage of mineral matter in coal samples has been reported to be from 9.04% to 32.26% in coal samples selected from various locations across the United States.[1] Using 15% as an average value, this would amount to approximately 89×10^6 tons of mineral matter a year.

As our dependence on coal as an energy source increases so does the importance of research on the conversion of coal to liquid and gaseous fuels. One important aspect of this type of research is catalysis considerations. Since minerals and trace elements in coal can play an important part in catalysis it is important that characterization of the trace metals in coal samples be precise and accurate.

Neutron activation analysis[3,5] and photon activation analysis[5] have been used in the analysis of coal for trace

metals. These methods are accurate and require no sample pre-
treatment unless they are necessary for removal of interferents[6,7]
or for a possible enrichment step,[7] but they are time consuming
and usually require the use of a nuclear reactor. Spark source
mass spectroscopy,[3,8,9] anodic stripping voltammetry,[3] atomic
absorption spectroscopy,[3,9,14,15] optical emission,[3,10] and ion
selective electrodes[11] have been used for the analysis of trace
metals in coal samples. X-ray fluorescence[3,12] and isotope di-
lution mass spectrometry[13] have been used to analyze both whole
coal and coal subjected to a pretreatment step. Atomic absorption
is often the method of choice in the analysis of trace metals.
Atomic absorption has the advantage of low cost, high speed,
small sample size, simplicity, precision, accuracy, and sensi-
tivity.

In general, analysis by atomic absorption spectroscopy
requires digestion of the sample matrix and analysis of the re-
sultant solution. The objective of the ashing step is to oxidize
any organic matter present in the coal, and to leave the elements
of interest in solution. It is essential that the true concen-
trations of the elements of interest are not altered by volatili-
zation or reagent contamination. Precipitation of insoluble
species, inclusion by species not of interest and absorption to
any glassware or container must be avoided. Numerous ashing
procedures have been used for solubilization of the mineral con-
tent of coal. Some of these procedures will be reviewed.

Combustion bombs are often used to destroy complex sample matrices. Combustion bombs are closed systems and operate at elevated pressures and temperatures. They are quite often used when the specie of interest is extremely volatile.

Bernas used a specially designed Teflon (DuPont) vessel for the decomposition and analysis of silicate rocks.[16] The decomposition vessel has a metal body lined with a teflon crucible. A teflon sealing disk fits between the crucible body and a metal screw cap. The teflon sealing disk provides an effective means of sealing the vessel when the metal cap fit with the sealing disk is manually screwed onto the crucible body. The vessel measures approximately 51 mm by 58 mm. Bailey used Bernas's method to digest high temperature coal ash for trace analysis by solvent extraction and atomic absorption.[17] That method was modified by Hartstein, Freedman, and Platter to include an additional oxidation step.[15] The revised procedure used fuming nitric acid for destruction of the organic matter and hydrofluoric acid for the destruction of the siliceous material. Boric acid was used to complex any fluorine remaining in solution. The teflon bomb has the advantage of small sample size (50 mg), freedom from contamination, volatilization, and rapid destruction. A similar procedure was used by Ruch et al to destroy high and low temperature coal ash for atomic absorption analysis.[18]

Parr bomb combustion techniques have also been used for the destruction of coal samples. Thomas and Gluskoter used benzoic

acid and sodium hydroxide in a combustion bomb in the determination of fluorine in coal.[11] Pollock used a combustion bomb containing a dilute nitric acid solution under 24 atmospheres of oxygen to analyze coal samples for mercury, fluorine, boron, and selenium.[14]

Fusion techniques using carbonates, hydroxides, and borates of sodium, potassium, and lithium are often used in the dissolution of raw coal, coal ash, and inorganic siliceous materials.[19-23] They require no elaborate equipment and are relatively quick and simple. This method of sample dissolution is most often used after a preconcentration step such as dry ashing. However, fusion techniques may suffer from incomplete attack of the sample as well as limited solubility of some metal ions in the particular flux environment. Fusion techniques are most often used in the analysis of non-volatile elements, due in part to the high temperatures involved in forming the melt. Temperatures required for the fusion technique are generally $900^{\circ}C$ or greater. The fusion step is followed by acid dissolution of the melt.

Electronic low-temperature ashing in an oxygen atmosphere has been used to ash coal samples. Samples prepared by low-temperature ashing have several advantages over other methods. Few elements are volatilized at the temperatures required for ashing, and no reagents other than oxygen are used. In this technique oxygen is passed through a high energy electromagnetic

field produced by a radio-frequency oscillator (13.56 Mhz). A
discharge takes place, which produces an activated gas plasma
consisting of a mixture of atomic and ionic species as well as
electronically and vibrationally excited states.[24] Oxidation
occurs as the activated oxygen passes over the coal sample. The
temperature is usually less than $150^{o}C$. A study of the effect
of low-temperature ashing on potentially volatile trace elements
by Ruch, Gluskoter, and Shimp showed only mercury (up to 90%),
bromine (100%), and antimony (up to 50%) to be lost during low-
temperature ashing of coal.[18] Fluorine was not tested and was
assumed to be 100% volatilized. Pollock used atomic absorption
to analyze coal samples for arsenic and antimony after low-
temperature ashing.[14]

Destruction of an organic matrix can also be accomplished
by wet chemical means. Temperatures are generally lower in wet
ashing techniques, so volatilization is not a major problem.
Mercury, osmium, and ruthenium can be lost under oxidizing con-
ditions, selenium under reducing conditions, and arsenic and
germanium may be lost if chloride ion is present in a wet ash
procedure.[25] There is a greater possibility of sample contami-
nation from reagents and handling. Losses from spattering and
bumping when using a wet ash digestion may also occur.

Nitric acid is often used alone or in combination with
sulfuric, hydrochloric, perchloric, or hydrofluoric acids.

When used in any combination nitric acid is the primary oxidizing agent. When perchloric acid is used in combination with nitric acid care must be taken to ensure that the majority of the oxidation is completed before the nitric acid is depleted and the temperature approaches the boiling point of perchloric acid. Oxidation by perchloric acid is rapid and is accompanied by the liberation of chlorine and oxygen gas. Fires and/or explosions are probable under these conditions. Nitric acid must be used with sulfuric or perchloric acid if a temperature greater than 120° is necessary. Smith discussed the use of different acid combinations for the wet oxidation of organic compositions.[26,27] Spielhotz and Diehl studied the wet oxidation of coal with perchloric and periodic acids.[28] They have reported that coal is smoothly oxidized if the starting acid is 68-69% perchloric. When the concentration of perchloric exceeds 70% then an explosion is probable. Hydrofluoric acid is used in combination with other acids to dissolve any siliceous material present in coal. Hydrofluoric acid can be removed from solution by boiling off as an azeotrope with water,[29] or it can be reacted with boric acid (H_3BO_3) to form fluoroboric acid (HBF_4).[16,30]

Fenton's reagent, which is 50% hydrogen peroxide and either Co^{+2} or Fe^{+2}, is also used in the oxidation of organic matter.[31] Fenton's reagent acts through an induced chain mechanism involving hydroxyl radicals, and produces oxygen and water as by-products.

Murphy used hydrogen peroxide and sulfuric acid to oxidize coal samples for mercury analysis by atomic absorption.[32] Murphy also attempted to use chromium trioxide and potassium permanganate as oxidizing agents in his study.

High temperature dry ashing is mentioned many times in the literature as an ashing method prior to coal analysis.[4,9,10,14,18] Temperatures from $400^{\circ}C$ to $800^{\circ}C$ are used depending on the specie of interest. Dry ashing is recommended for its simplicity and freedom from blank contamination. However, dry ashing is troubled by the loss of element by volatilization and retention of the element of interest on the ashing crucible. Dry ashing is often used as a preconcentration step.[4] A ten fold concentration change can be effected for some elements. A large sample is ashed and the ash weight calculated. The coal ash is stored and subsamples are taken when needed for analysis.

In general one of two approaches are taken with the ash resulting from a high temperature ashing procedure. It can be directly analyzed by one of the techniques mentioned earlier in this section, such as X-ray fluorescence or neutron activation analysis. The ash could be subjected to further dissolution and solublization by a fusion technique, a bomb technique, or a wet chemical treatment.

A comparison of sample preparation methods has not been recorded in the literature. Several ashing methods have

been discussed in this section. Representative techniques were
studied to determine which technique would effect the greatest
precision and reliability.

EXPERIMENTAL

The experimental section will be discussed in three parts, Reagents, Optimization of Analysis, and Proof of Analysis.

REAGENTS

The reagents used for this study are described in this section.

Coal Sample

The coal sample was obtained from the South Dakota State University power plant. The coal was mined in Colorado at the Valley Camp Coal Mine. Approximately 2000 g of sample was ground to 20 mesh and oven dried at 110°C to constant weight. The sample was weighed after 24 and 40 hours of drying. The sample was reground and any portion not passing through a standard 60 mesh sieve was discarded. Later analyses were performed on a portion of the 60 mesh coal that was reground so that all particles passed through a standard 80 mesh sieve and at least 90% passed through a standard 100 mesh sieve. The coal sample was stored in a glass bottle with an air tight screw cap. Each individual sample portion was redried for 1-2 hours at 110°C prior to analysis.

Zinc Calibration Standard

Zinc metal (30 mesh), Baker Analyzed Reagent, was used to

prepare standard solutions for atomic absorption analysis. The
zinc was used as provided. A stock solution of 1000 ppm was
prepared by dissolving 1.0000 g of reagent in 25 ml of 6N
hydrochloric acid. The solution was diluted to 1.00 l with
deionized water and transferred to a polypropylene container.
Working standards were prepared by dilution from the stock solu-
tion.

Sodium Calibration Standard

Sodium nitrate $(NaNO_3)$, Baker Analyzed Reagent, was used to
prepare the standard solutions for atomic absorption analysis.
The sodium nitrate was oven dried at $110^{\circ}C$ for 2 hours prior to
weighing. A stock solution of 1000 ppm was prepared by dissolving
3.6971 g of the reagent and diluting to 1.00 l with deionized
water. The solution was transferred to a polypropylene con-
tainer. Working standards were prepared by dilution from the
stock solution.

Arsenic Calibration Standard

Arsenous Oxide (As_2O_3), Thorn Smith Chemist (99.98%), was
used to prepare the standard solutions for arsenic analysis. A
stock solution of 1000 ppm arsenic was prepared by the following
procedure. To 7.4 g of potassium hydroxide dissolved in 90 ml
of water was added 1.3202 g of arsenous oxide. After dissolution
of the arsenous oxide in the hydroxide solution, 260 ml of water,

28 ml of 6N hydrochloric acid, and 21.96 g of potassium bicarbonate were added to the solution. The solution was then made to 1.00 l with deionized water.

Copper Calibration Standard

Copper metal, A.D. Mackay, Inc. (99.9%), was used to prepare the standard solutions for atomic absorption analysis. A stock solution of 1000 ppm was prepared by dissolving 1.0000 g of the reagent in 25 ml of a 1:1 nitric acid/water solution. The solution was diluted to 1.00 l with deionized water and transferred to a polypropylene container. Working standards were prepared by dilution from the stock standard.

Nitric Acid

Nitric acid (HNO_3), DuPont Reagent, was glass distilled for initial investigations and doubly distilled for the latter work.

Hydrochloric Acid

Hydrochloric acid (HCl), DuPont Reagent, was singly distilled for all uses.

Perchloric Acid

Perchloric acid ($HClO_4$-70%), Allied Chemical ACS Reagent grade, was used as provided.

Sulfuric Acid

Sulfuric acid (H_2SO_4-fuming 15-18% free SO_3), Baker Analyzed Reagent, was used as provided.

Hydrofluoric Acid

Hydrofluoric acid (HF-49%), Fisher Scientific Company ACS Reagent grade, was used as provided.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2-50%), Fisher Scientific Company ACS Reagent grade, was used as provided.

Silver Diethyldithiocarbamate-Pyridine Solution

Silver Diethyldithiocarbamate (AgDDC), Fisher Scientific Company ACS Reagent grade, was used as provided. The solution was prepared by dissolving 1.1600 g of AgDDC in 250 ml of pyridine. The pyridine was J.T. Baker Chemical Company purified grade, and was dried over anhydrous barium oxide and used without further purification.

Water

Initial investigations and arsenic analysis by AgDDC used water treated by a Bantam mixed bed demineralizer. Later experiments used tap distilled water that had been redistilled in glass vessels. After distillation the water was stored in a 5 gallon polyethylene container.

Methods Used to Clean Glassware

Volumetric flasks, caps, and pipettes were rinsed thoroughly at least one time with 3N hydrochloric acid and then three times with glass distilled water. The 100 ml Kjeldahl flasks, 100 ml teflon beakers, and 150 ml pyrex beakers were subjected to boiling hydrochloric acid for at least 5 minutes and then rinsed three times with glass distilled water prior to use. If more vigorous cleaning with chromic acid was necessary then it was always followed with at least one rinse with 3N hydrochloric acid and three rinses with distilled water. In addition to the acid treatment the ashing crucibles were heated to 900°C for at least 1 hour prior to use.

OPTIMIZATION OF ANALYSIS

A series of ashing procedures were investigated to determine the method of sample preparation which would yield the best accuracy and precision.

Ashing of Samples

Sulfuric, nitric, hydrochloric, perchloric, and phosphoric acids were tested as oxidizing agents. The efficiency of nitric acid and sulfuric acid as oxidizers was tested alone and in selected combinations with the other acids, and the results compared. The wet ashing was performed in either 150 ml beakers or 100 ml Kjeldahl flasks. Nitric acid was the primary oxidizing agent in all wet acid digestions. The digestions were carried out at minimum practical heating rates through the nitric acid phase. The heating rate was increased after the digestion reached the boiling point of perchloric acid and the majority of the oxidation was completed. If perchloric acid was the highest boiling acid in the digestion then the digestion was taken to within 0.5 ml of dryness. If sulfuric acid was present then the heating rate was taken to the highest setting for at least 10 minutes after the appearance of white fumes. Hydrofluoric acid was used for the dissolution of any siliceous material. The hydrofluoric acid work was carried out in either 250 ml Nalgene flasks or 100 ml Teflon beakers.

Dry ashing was performed in muffle furnaces capable of temperature control. Ashing temperatures were varied between 300°C and 700°C. The samples were ashed for at least 16 hours, in uncovered porcelain crucibles from Coors Industries. Hydrochloric, nitric, perchloric, and hydrofluoric acids were used for further dissolution of the sample. The ash was transferred to either 150 ml beakers or to the teflon beakers if hydrofluoric acid was used in the acid dissolution step. The crucibles were rinsed with distilled water and the appropriate acid with mild heat. The rinse solutions were transferred to the beakers containing the coal ash. The beakers were heated and the contents taken to incipient dryness. The residue was put back into solution with distilled water and 1 ml of 6N hydrochloric acid and then transferred to volumetric flasks. Acid volumes were adjusted to provide the minimum practical volume.

Ash Weights

Ash weights were determined to test the effect of grinding and particle size on oxidation. Sixty and one hundred mesh samples were dry ashed at temperatures from 450°C to 700°C. The percentage of ash remaining was computed. Sixty mesh samples ashed at 525°C were transferred to 150 ml beakers. The crucibles were rinsed three times (5 ml each time) with 6N hydrochloric acid and distilled water. The rinsings were transferred to the beakers containing the coal ash. The beakers were heated and

the contents taken to incipient dryness. Distilled water and 1 ml 6N hydrochloric acid were added to each beaker to put any soluble material back into solution. The residue was filtered, weighed, and additional weight loss was calculated. Selected samples were reashed overnight at 550°C and additional weight loss was calculated. A similar analysis was performed on a set of wet ashed samples.

Sample Blanks

Sample blanks were used to measure the contamination from reagents and glassware. The sample blanks were treated exactly the same as the samples. To find the source of blank contamination, reagents were diluted and analyzed. The reagents were analyzed at all steps of the oxidation process. The efficiency of the washing step was investigated. Volumetric glassware was washed with either 3N hydrochloric acid, Alconox, or cleaning solution and rinsed three times with distilled water. The volumetric flasks were diluted to the mark with distilled water and shaken. The contents were analyzed for contamination and the results compared.

Temperature Gradient

The possibility that a temperature gradient in the muffle furnace was great enough to cause significant error was investigated. Samples were ashed at extreme ends of the furnace and

the percentage of ash remaining was calculated. The samples were then treated with hydrochloric, nitric, and hydrofluoric acids. The samples were analyzed for zinc and arsenic, and the results compared.

Hydrogen Peroxide Digestions

Digestion of coal samples with 50% hydrogen peroxide and Fenton's reagent was investigated under varying conditions. First, 5 ml of 50% hydrogen peroxide was added to 1.00 g samples in 150 ml beakers. The beakers were placed in a water bath and the temperature was taken to $35^{\circ}C$. Since hydrogen peroxide is more efficient as an oxidant in alkaline solution, additional 1.00 g samples were added to 5 ml of hydrogen peroxide and 15 ml of pH 8 phosphate buffer. The buffered samples were also temper-ature controlled. The use of Fenton's reagent (Co^{+2}) was studied at pH 8-13. One g of sample was added to 150 ml beakers with 10 ml of 50% hydrogen peroxide, 10 ml of the appropriate buffer, and 5 ml of $0.2M$ Co^{+2}. The effect of the concentration of Co^{+2} on the digestion procedure was studied. The effect of variation of the amount of $0.2M$ Co^{+2} added to 1.00 g samples buffered at pH 9 was determined. Fenton's reagent using Fe^{+2} was compared to the reagent using Co^{+2}. Samples buffered at pH 8 and 9 were tested with 5 ml and 10 ml of $0.2M$ Co^{+2} and Fe^{+2}. A single sample buffered at pH 12 was also studied. Fenton's reagent was also used to treat coal ash from a dry ash procedure. One gram

samples were dry ashed overnight at $500^{\circ}C$. The ash was trans-
ferred to 150 ml beakers and 15 ml pH 9 buffer, 5 ml hydrogen
peroxide, and 3 ml $0.2M$ Fe^{+2} were added to the coal ash. The
samples treated with Fenton's reagent were analyzed by atomic
absorption.

Arsenic Analysis by AgDDC

Arsenic can be determined colorimetrically by complexation
with AgDDC in pyridine.[33] Arsenic is reduced to the 3+ oxidation
state by potassium iodide in an acidic solution. Stannous
chloride is added to the reaction mixture to reduce iodine back
to the iodide ion. Arsine (AsH_3) is formed by reaction with
hydrogen generated due to addition of zinc to the acidic solution.
The heat of reaction causes the arsine gas to be volatilized
from solution. Sulfides and other contaminants are removed from
the arsine when the gas passes through a plug of glass wool im-
pregnated with lead acetate. The arsine then passes through a
fritted glass disc and is complexed by the AgDDC in the pyridine
about the frit. The apparatus used for collection of the vola-
tilized arsine shown in Figure 1 is a Gutzeit generator. The
arsenic complex absorbance can be measured at 535 nm in the
visible spectrum.

Initial experiments were performed to establish the standard
curve. Standards were prepared by adding 0, 1, 2, 5, and 10 ml
of a 1 ppm arsenic solution to 10 ml of 6N hydrochloric acid in

Figure 1

GUTZEIT GENERATOR

← Pyridine-AgDDC Solution

← Fritted Glass Disc

← Lead Acetate Scrubber

← Generator
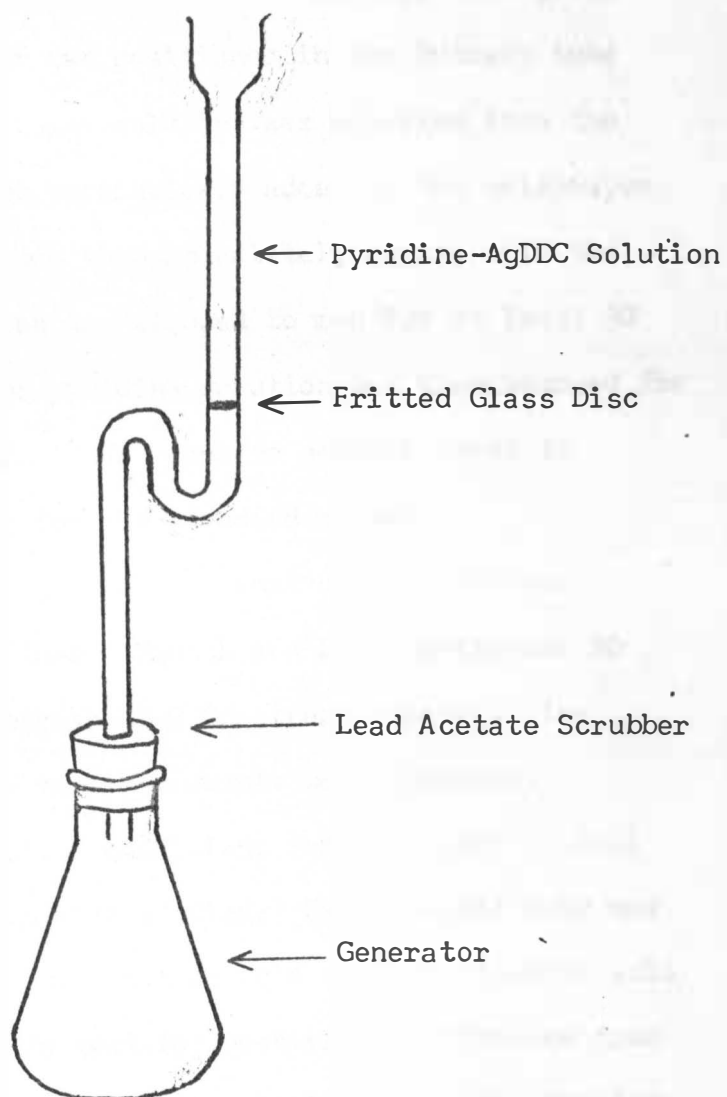
250 ml erlenmeyer flasks. Added to this solution was 2 ml of 15% potassium iodide solution. The contents of the flask were mixed and allowed to stand for 15 minutes to allow reduction of any As(V) to As(III). After standing 9 drops of 34% stannous chloride were added to the solution with stirring. The glass wool-lead acetate scrubber was positioned in the Gutzeit tube and 4 ml of the AgDDC-pyridine solution was pipetted into the tube. Three grams of zinc were quickly added to the erlenmeyer flask, and the generator was then immediately capped with the Gutzeit tube. The reaction was allowed to run for at least 30 minutes. A portion of the pyridine solution was then removed for measurement. This procedure was repeated several times to establish constant values for the standard curve.

The absorbance readings used to construct the standard curves were taken from either a Bausch and Lomb Spectronic 20 Spectrophotometer or a Beckman DB-G Spectrophotometer. The results obtained from the two instruments were compared.

The appropriate chemical conditions for treatment of coal ash from a dry ashing step were studied. Hydrochloric acid was used alone in combination with nitric acid and hydrofluoric acid in this treatment step. To test for possible interference from the presence of nitric acid, a sample was treated with ammonium oxalate and analyzed for arsenic. To test the effect of solution volume on precision, standards were developed with varying solution

volume in the generator. The standards were analyzed and the results compared. A comparison was also made of the results from standards developed using mossy zinc and 20 mesh zinc. The amount of 15% potassium iodide solution added to the generator was varied from 5 to 15 ml and its effect on standard curves evaluated.

Analysis of Samples

After ashing, the samples were transferred to appropriate size volumetric flasks and made to volume. Samples were diluted when necessary and standards were prepared to cover the appropriate sample concentration range. The standards were made acidic with 6N hydrochloric acid. Excess potassium was added to samples and standards for sodium analysis. The potassium was added as an ionization suppressant. Potassium is ionized more easily than sodium in the flame. Ionization of potassium provides an excess of electrons which inhibit the ionization of sodium present in the flame.[34] Nickel ion was used to modify the sample matrix for selected arsenic analyses. Arsenic is known to form stable compounds with nickel.[35] Addition of nickel to the matrix allows a significantly higher charring temperature to be used without loss of arsenic prior to the atomization step. The higher charring temperature aids in further ashing of the sample and reduces possible interference effects by volatilization. The flame analyses described in this section were performed on a

Jarrell-Ash model 82-516 Atomic Absorption/Flame Emission Spectrophotometer using a total consumption burner and an air-H_2 flame. The readout was recorded on a Sargent-Welch model XKR strip chart recorder. The flameless analyses were performed on a Perkin-Elmer model 503 Atomic Absorption Spectrophotometer with a Perkin-Elmer HGA 2100 graphite furnace and deuterium arc background corrector.

The light source for sodium analysis was a Jarrell-Ash Sodium-Potassium Hollow Cathode Tube operated at a current of 25mA. The line at 589.0 was selected as the analytical line. Standards run with the sodium analyses were made to 0, 0.2, 0.4, 1, 2, and 4 ppm from the stock standard. The air-H_2 flame was a lean, blue, oxidizing flame. The temperature produced by this type of flame is approximately 2000°C. The light source for zinc analysis was a Jarrell-Ash Zinc Hollow Cathode Tube operated at 18mA. The line at 213.9nm was selected as the analytical line. The standard run with zinc analyses were made to 0, 0.1, 0.5, and 1 ppm. The flame was also made slightly lean and oxidizing. Copper analysis used a Perkin-Elmer Intensitron Copper Hollow Cathode Lamp. The current was limited to approximately 8mA. A higher current would exceed the capacity of the deuterium arc background corrector. The line at 324.7 nm was selected as the analytical line. The drying, charring, and atomizing temperatures were 100°C, 900°C, and 2700°C respectively. The drying cycle

was set at 15 seconds per 10 ul of injection. The sample was
charred for 20 seconds and atomized for 7.5 seconds. Standard
values of 0, 0.3, 0.6, and 1 ng were obtained by injection of 50
ul of 0 ppm solution, 10 ul of 0.03 ppm solution, 20 ul of 0.03
ppm solution, and 10 ul of 0.1 ppm solution. The light source
for arsenic analysis was a Perkin-Elmer Electrodeless Discharge
Lamp operated at 8 watts. The line at 193.7 nm was selected as the
analytical line. The instrumental conditions for arsenic were
the same as those for copper with the exception of the charring
temperature which was 1000°C. Standard values for arsenic analysis
were the same as those used in the copper analysis.

Sample concentrations were determined from standard curves
made from the standards run with each analysis. Absorbance values
were plotted against ppm for flame analysis and against ng for
flameless analysis. Typical curves are shown in Figures 2 and 3.
These calculations were used to find final sample concentration
in ppm:

for flame:

$$\text{ppm (sample)} = \text{ppm (from graph)}^* \times \text{dilution factor} \times \frac{\text{original volume}}{\text{sample weight}}$$

for flameless:

$$\text{ppm (sample)} = \left(\frac{\text{ng}}{\text{volume injected}}\right)^* \times \text{dilution factor} \times \frac{\text{original volume}}{\text{sample weight}}$$

* corrected for blank contamination by subtraction.

Figure 2

ZINC CALIBRATION CURVE
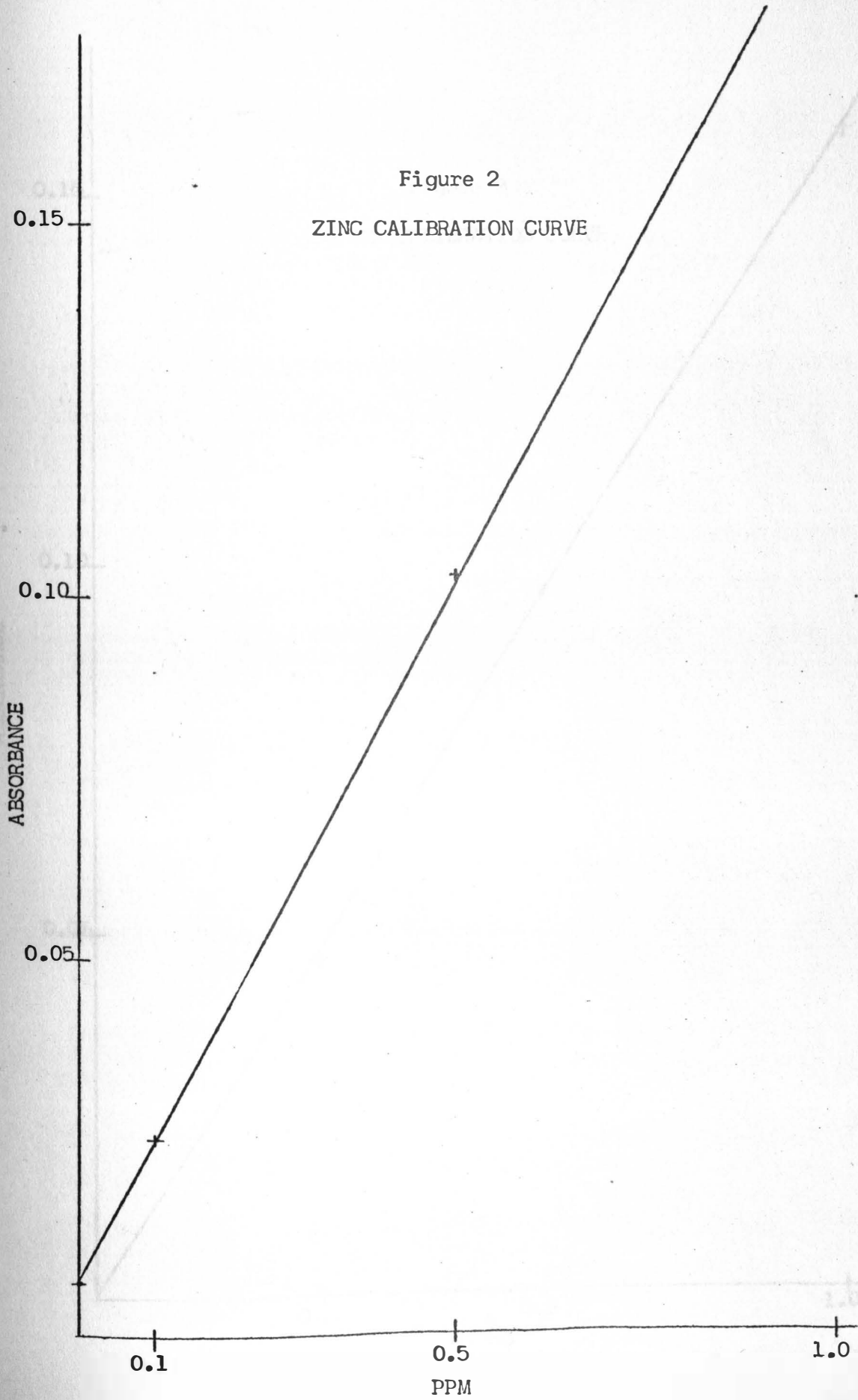
Figure 3

COPPER CALIBRATION CURVE
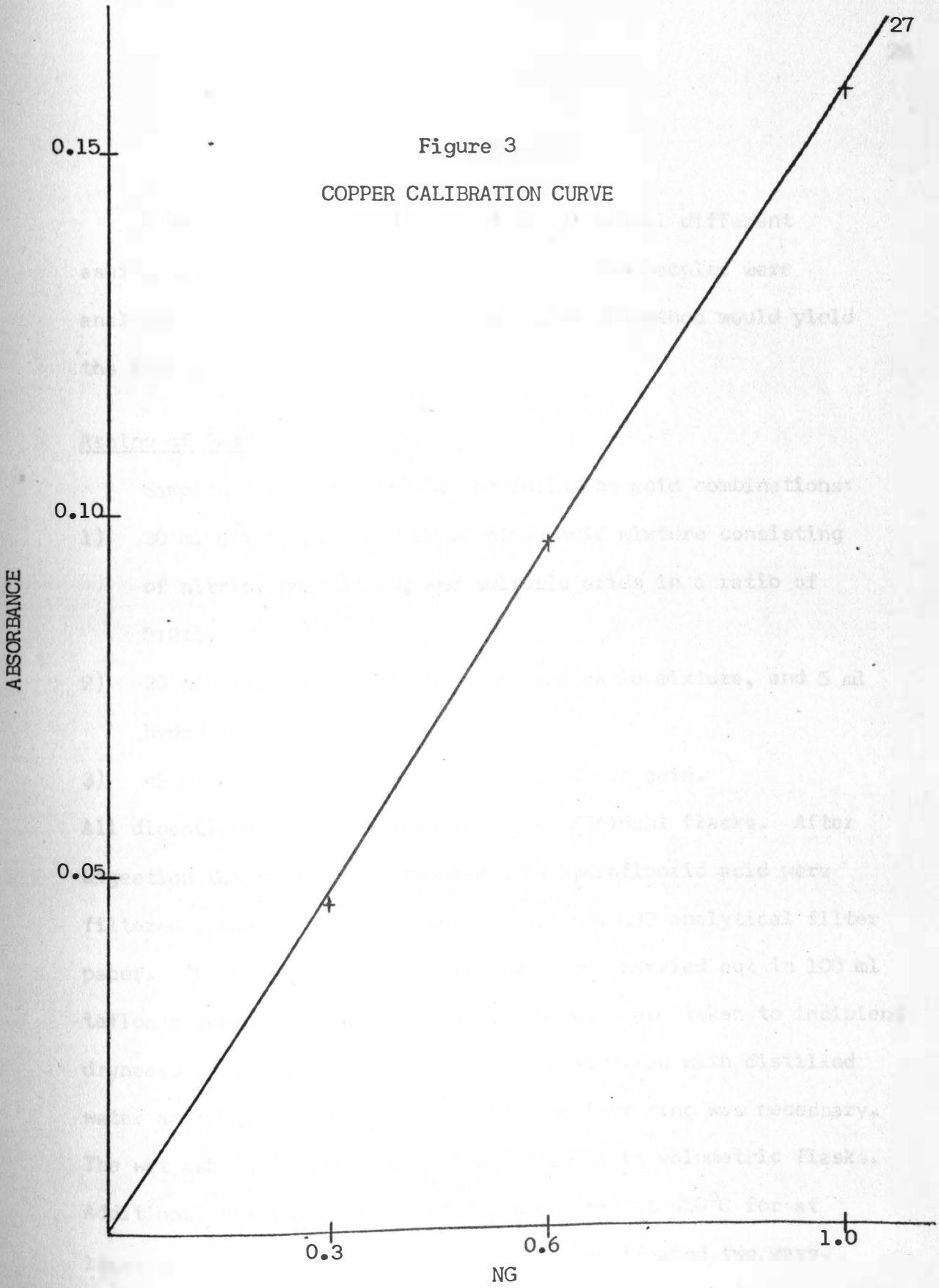
PROOF OF ANALYSIS

A series of samples were treated by several different
ashing methods under optimum conditions. The samples were
analyzed and the results used to prove which method would yield
the best accuracy and precision.

Ashing of Samples

Samples were wet ashed by the following acid combinations:

1) 30 ml nitric acid and 15 ml of an acid mixture consisting
    of nitric, perchloric, and sulfuric acids in a ratio of
    5:2:1.

2) 30 ml nitric acid, 15 ml of the same acid mixture, and 5 ml
    hydrofluoric acid.

3) 45 ml nitric acid and 3 ml of perchloric acid.

All digestions were performed in 100 ml Kjeldahl flasks. After
digestion the samples not treated with hydrofluoric acid were
filtered through Schleicher and Schuell no. 589 analytical filter
paper. The hydrofluoric acid treatment was carried out in 100 ml
teflon beakers. The contents of the beaker were taken to incipient
dryness. The residue was put back into solution with distilled
water and 1 ml 6N hydrochloric acid. No filtering was necessary.
The wet ashed samples were diluted to 50 ml in volumetric flasks.
Additional samples were dry ashed, uncovered at 450°C for at
least 16 hours. The resulting coal ash was treated two ways.

In the first case, the coal ash was transferred to 150 ml beakers.
The crucibles were rinsed three times (5 ml each rinse) with 6N
hydrochloric acid and with mild heating between each rinse. The
coal ash and rinsings were heated in the 150 ml beakers and then
filtered through Schleicher and Schuell no. 589 analytical
filtered paper. In the second case, the coal ash was added to
100 ml teflon beakers. The crucibles were rinsed in a similar
manner with 5 ml hydrochloric acid and 5 ml nitric acid. The
teflon beakers were heated until approximately 0.5 ml of solution
remained. The residue was diluted with distilled water and
transferred without filtering to 50 ml volumetric flasks. Sample
blanks were carried through each analysis.

Analysis of Samples

The samples were analyzed for zinc, copper, and sodium by
flame atomic absorption, and for copper by the furnace technique.
The zinc and copper analyses in the flame used undiluted samples.
Sodium analyzed using flame atomization and copper analyzed by
the flameless technique used samples diluted appropriately. The
diluted samples were made to approximately 2000 ppm potassium
for sodium analyses. The flame analyses in this section were
performed on a Perkin-Elmer model 303 with a single slot premix
burner and an air-acetylene flame. The air-acetylene flame
operates at a temperature of approximately 2300°C. The flame
was made slightly oxidizing for all three elements. The sodium

analyses used standards made at 0, 0.3, 1, 2, and 3 ppm diluted from a stock solution. The sodium standards were made to 2000 ppm potassium. The zinc and copper analyses used standards made to 0, 0.1, 0.5, and 1 ppm from a stock solution. A Perkin-Elmer signal averaging unit was used to readout the absorbance. The details for flameless analyses, standard solutions, blanks, and calculations were discussed in the previous section on analysis of samples.

The results from these analyses were subjected to statistical analysis. Mean and standard deviations were computed for each ashing procedure. The t-test as described by Laitinen and Harris was used to test any difference between mean values for copper and zinc analyses from varying sample preparations.[36] The t-test was also used to test for any difference between the analysis of copper using flame and furnace techniques. The F-test as described by Barnett was used to show probable source of deviation in the sodium analysis.[37]

Seventy-five grams of National Bureau of Standards' Standard Reference Material no. 1632 was obtained for analysis. Portions of the sample were dried for at least 1 hour, dry ashed at $450^{o}C$ for at least 16 hours, and treated with hydrochloric, nitric, and hydrofluoric acids. Sample size and dilutions were adjusted to allow analysis in the optimum concentration range. The samples were analyzed and compared with the values certified by NBS.

RESULTS AND DISCUSSION

The results of experiments presented in the previous sections are discussed here. The ashing procedures investigated in this study are also discussed. The experiments used to optimize conditions, and the resultant analyses of samples are presented. A statistical analysis of the experiment discussed in the previous section, Proof of Analysis, is presented here. Also discussed is the analysis of a National Bureau of Standards' Standard Reference Material.

Observations on the Ashing of Samples

Sulfuric, nitric, hydrochloric, perchloric, and phosphoric acids were tested alone and in selected combinations for oxidizing ability. The following acid combinations and ashing conditions were found to be of little practical value for a wet oxidation and were not used again. Diluted acids exhibited little oxidizing ability and bumped excessively. Hydrochloric acid showed no particular advantage when used in combination with nitric acid. Sulfuric acid used alone produced some charring and bumping and left a tar-like residue. Phosphoric acid reduced the amount of tar-like residue when used with sulfuric acid, but did not eliminate the charring and bumping problems. Temperatures below the boiling point of nitric acid were found to be impractical.

Nitric acid heated to it's boiling point was found to be

the most effective oxidizing agent. Perchloric acid and sulfuric acid were found to be the most effective in oxidation of particles not affected by nitric acid. Approximately 45 ml of nitric acid was found to be adequate for the preliminary oxidation of one gram of coal. If the sample was heated too rapidly, then some of the nitric acid was distilled off and was not reduced. Additional nitric acid would have to be added prior to the perchloric acid phase. It was found that 3 ml of perchloric acid was sufficient for completing the oxidation step. When perchloric acid was used in a mixture without sulfuric acid then the procedure was taken through the boiling point of the perchloric acid. After the frothing and bubbling typical of a perchloric acid digestion subsided the boiling rate was increased and the contents of the ashing vessel were taken to 0.5 ml of dryness. If the temperature was raised too quickly and the contents taken to dryness then a fire would usually result. The resultant residue was difficult to put into solution and was discarded if a fire occurred. Gorsuch cautioned against the use of sulfuric acid with samples containing a high level of calcium.[2] Low recoveries due to adsorption on or co-precipitation with a precipitate of calcium sulfate may occur. However, the presence of sulfuric acid in the acid mixture simplifies the wet ashing procedure. With the higher boiling sulfuric acid present the perchloric acid can be completely distilled away at low heat. This greatly

reduces the probability of a fire. After the appearance of
white fumes the solution can be boiled at high heat for at least
10 minutes to effect some reduction in volume. After cooling,
approximately 25 ml of distilled water should be added to the
residue and the mixture reheated. This helps to solublize any
included or adsorbed species.

Vessels used for wet oxidation were 150 ml beakers and 100 ml
Kjeldahl flasks. Initial investigations used the beakers, which
were found to be unacceptable for quantitative work and were
replaced by the Kjeldahl flasks. The beakers were subject to
loss of sample by bumping and spattering. Foaming of the sample
was harder to control in a beaker. Consequently, if watch glass
covers were used there was a possibility of sample loss when the
foaming reached the watch glass cover. Foaming during the first
20-25 minutes of ashing required some control. When the foaming
began to rise up the neck of the flask then the flask was removed
from the Kjeldahl rack and cooled in a beaker of water. This
was repeated until the foaming subsided and the sample could be
held at the boiling point of nitric acid.

Bumping was a problem when the majority of the coal particles
were reduced in size by oxidation. Bumping occurred more fre-
quently when the ashing process was interrupted and restarted
after cooling to room temperature. Bumping was minimized with
the addition of 3-4 boiling chips.

Hydrofluoric acid was used to dissolve any siliceous material present in the coal samples. Neutralization of remaining hydrofluoric acid with base was attempted and found to be inefficient. In subsequent experiments excessive hydrofluoric acid was removed from solution by volatilization at $113^\circ C$ as an azeotrope with water (38.26% HF). The volume of hydrofluoric acid added was varied from 0.5 ml to 7 ml. Studies on the weight of residue remaining from hydrofluoric acid digestions showed 2 ml to be the minimum volume needed for the hydrofluoric acid treatment. However, some isolated digestions left a fine white precipitate when 2 ml of hydrofluoric acid was used. Some workers report the use of boric acid to dissolve any insoluble metal fluorides resulting from a hydrofluoric acid digestion.[29,30] The precipitate was not identified, but was not a problem when 5 ml of hydrofluoric acid was added indicating that the precipitate was not a fluoride salt.

Hydrochloric, nitric, hydrofluoric, and perchloric acids were used to treat the residue from a dry ash procedure. Hydrochloric acid was compared to perchloric acid for treatment of coal ash. Duplicate samples treated with each acid were analyzed for zinc, copper, sodium, and arsenic. The results are shown in Table 1. The concentration values are reported in ppm. The results did not show one acid to have an advantage over the other. There were no blank problems with either acid. In subsequent ashings

Table 1

ACID TREATMENT OF HIGH-TEMPERATURE COAL ASH

15 ml 6N HCl (PPM)		1 ml $HClO_4$ (PPM)
Sodium	1140	1230
	1120	1160
Copper	15	19
	14	15
Zinc	14	14
	12	11
Arsenic	14	6
	12	6

hydrochloric acid was used due to safety considerations and the lower temperature needed for the effective use of hydrochloric acid.

A combination of nitric, hydrochloric, and hydrofluoric acids was found to be an effective combination for complete dissolution of high temperature coal ash. Nitric acid was present to provide a specie with a higher boiling point than the water-hydrofluoric acid azeotrope. Hydrochloric acid contributed less blank contamination than nitric acid, so 5 ml of each acid was used rather than 10 ml of nitric acid.

Temperatures in the muffle furnace were varied from $300^{o}C$ to $700^{o}C$. Samples were ashed for at least 16 hours. Calculations were made on the percentage of ash remaining after overnight ashing of samples at temperatures of $300^{o}C$ and $400^{o}C$. The values from dry ashings at temperatures less than $450^{o}C$ were inconsistent and showed only partial oxidation of the coal sample. It was reported in the literature that a temperature of $450^{o}C$ was used for high temperature dry ashing of coal with minimum problems of volatilization.[18] On the basis of this information dry ashings were carried out at $450^{o}C$ throughout the remainder of this study.

Ash Weights

Ash weights were determined to test the effect of grinding and particle size on ashing. Samples ground to 60 mesh were dry ashed at $525^{o}C$ and $700^{o}C$ in the muffle furnace. The weight loss

was computed and the percentage of sample as ash was calculated. The samples ashed at 525°C had an average ash weight of 7.24% with a range in values of 6.30% to 9.25%. The samples ashed at 700°C had an average ash weight of 7.98% with a range in values of 7.58% to 8.34%. The samples ashed at 525°C were treated with hydrochloric acid. The residue was filtered, dried, and weighed. The residue had an average value of 4.16% with a range in values of 3.42% to 5.12%. The residue from a wet ash procedure was also filtered, dried, and weighed. The wet ash residue had an average value of 4.58% with a range in values of 4.06% to 5.32%. Selected samples from the wet and dry ashings were reashed overnight at 550°C. No additional weight loss was found. The large variation in ash weights suggested that the sample was not ground to a small enough mesh. If the residue consisted in part of one or more of the species of interest then inconsistant particle size would lead to a significant source of error. A portion of the 60 mesh coal sample was reground in an attempt to improve the homogeneity of particle size. The sample was ground so that all pieces would pass through a standard 80 mesh sieve and at least 90% through a standard 100 mesh sieve. A determination of the percentage of ash in the 100 mesh coal was made. Samples were ashed overnight at 450°C. The ash had an average value of 10.19% with a range of values from 10.15% to 10.24%. This data indicated that the additional grinding had been sufficient.

Sample Blanks

Sample blanks were run with each analysis to determine the amount of contamination from reagents, glassware, and handling. To find the source of blank contamination reagents were analyzed at all stages of the ashing process. Particular attention was paid to the way in which glassware was handled. Initial blank investigations showed nitric acid to be contaminated with zinc and copper. The hydrochloric acid was contaminated with significant levels of zinc and sodium. Sulfuric acid was found to contain high levels of sodium and zinc. The hydrofluoric acid was contaminated with arsenic and copper. Significant levels of sodium were found in the deionized water. Nitric acid, hydrochloric acid, and tap distilled water were distilled in a glass apparatus. This reduced contamination in these reagents to a constant level. The nitric acid was later redistilled for use in some experiments. The sulfuric acid was replaced with reagent grade sulfuric acid. Nothing was done to purify the perchloric and hydrofluoric acids. Their contribution to the blank contamination was constant and not excessive. Additional experiments were performed to test for the possibility of contamination from the ashing crucibles and beakers. The reagents were isolated and analyzed for zinc at all points of a dry ashing procedure. The results showed no significant contamination from the ashing crucibles or Teflon beakers. There was a consistent level of zinc in the nitric acid.

There was no detectable zinc contamination in the hydrochloric
acid. The most probable source of random error was attributed
to handling of the ashing crucibles.

An experiment was carried out to test the possibility that
a particular washing might be contributing to random blank con-
tamination. Volumetric flasks were washed with either 6N hydro-
chloric acid, Alconox, or cleaning solution. After washing, each
volumetric flask was rinsed three times with distilled water,
diluted to the mark, and shaken. The contents were analyzed for
copper, zinc, and sodium. The results showed efficiency of the
two acid washes to be comparable. The Alconox wash showed con-
sistently higher levels for all three metals. The analyses were
also less consistent than for the acid washes. The hydrochloric
acid wash was picked over the chromic acid wash for subsequent
experiments. Hydrochloric acid is less subject to contamination
and does not require the caution necessary for handling chromic
acid.

The possibility of contamination from boiling chips was also
studied. Boiling chips were subjected to boiling 6N hydrochloric
acid for 5 minutes and then washed three times with distilled
water. The contents of volumetric flasks exposed to varying
numbers of boiling chips were analyzed for copper, zinc, and
sodium. The results showed no contamination from the use of
boiling chips.

Temperature Gradient

An experiment was carried out to determine whether or not a temperature gradient existed in the muffle furnace great enough to cause significant error. Two sets of samples were dry ashed on different days at 450°C for 16 hours. Samples in each set were ashed at extreme ends of the furnace. Ash weights were determined for one set of samples and the percentage of sample as ash was calculated. The four samples ashed at the rear of the furnace had an average ash content of 10.17% with a range in values of 10.11% to 10.24%. The four samples ashed at the front of the furnace had an average content of 10.21% with a range in values of 10.10% to 10.26%. The ash from both sets of samples were treated with nitric, hydrochloric and hydrofluoric acids. The samples were analyzed for zinc and arsenic. Sodium and copper analyses were not included due to their low volatility. The results of the analyses are shown in Table 2. Concentration values are given in ppm. Based on the analyses of these samples the precision of a dry ashing procedure is not affected by any temperature gradient present in the muffle furnace.

Observations on the Use of Hydrogen Peroxide and Fenton's Reagent

Hydrogen peroxide and Fenton's reagent were investigated for use as oxidizing agents. Coal samples were treated with 50% hydrogen peroxide in buffered and unbuffered solutions. Attempts at raising the solution temperature above 35°C caused the solution

Table 2

TEMPERATURE GRADIENT

		Zinc (PPM)	Arsenic (PPM)
Set no. 1			
	front	15, 16, 17, 16	12, 10, 11, 9
	rear	16, 16, 17	11, 11, 11
Set no. 2			
	front	16, 15, 15, 16	8, 8, 12
	rear	17, 16, 17, 16	11, 9, 9, 9
Average			
	front	16	10
	rear	16	10

to bubble excessively. The low temperature required to keep the solution in the beaker prevented the use of this oxidation method for raw coal samples.

The use of Fenton's reagent using Co^{+2} as an oxidizing agent was investigated at pH 8-13. None of the procedures using Co^{+2} were successful in oxidizing raw coal samples. The temperature of the reaction solution would gradually rise until a certain point and then it would rise quickly and suddenly. The reaction solution could not be contained in the reaction flask at this point. The time required for this sudden rise in temperature decreased with decreasing pH. The buffers were not able to keep the solutions buffered at the correct pH.

The use of Fenton's reagent using Fe^{+2} was investigated. Solutions utilizing $Fe^{+}2$ were found to be controllable at pH 9. Although solutions using Fe^{+2} appeared to be actively oxidizing the sample very little reduction in sample weight (10%) was found after 1 hour of digestion. Ash from a high temperature dry ashing procedure was treated with Fenton's reagent using Fe^{+2}. The resultant solutions were analyzed for zinc, copper, and arsenic. The results were compared to those from a conventional wet and dry ash procedure. The peroxide values were low by a factor of two. The use of Fenton's reagent and 50% hydrogen peroxide were found to have no advantage over a conventional acid digestion. Further studies on these two oxidizing agents were not pursued.

Observations on the Analysis of Arsenic by AgDDC

Arsenic can be determined colormetrically by complexation
with AgDDC in pyridine. The quantity of arsenic in the unknown
solution is compared to a standard curve constructed from known
amounts of arsenic. A typical standard curve is shown in Figure 4.
It was necessary to obtain a reproducible standard curve. Different
combinations of 30 mesh, granular, and mossy zinc were used in the
generator. It was necessary for the zinc to react rapidly for
at least 40 minutes, but not so rapidly that some of the pyridine
solution was bubbled out of the Gutzeit tube. The 30 mesh zinc
reacted too quickly causing loss of solution. The granular zinc
did not produce enough pressure to keep the pyridine solution
above the frit for 40 minutes. Combinations of the two types of
zinc were unpredictable due to varying particle size found in each
type of zinc. Combinations were also tried with mossy zinc. How-
ever, it was found that six grams of mossy zinc met the necessary
requirements and was used in subsequent experiments. The quanti-
ties of reagents used to develop the standards were increased
from those suggested in the literature.[33] The increase was made
in an attempt to improve the reproducibility of the standard curve.
Straighter lines were obtained, but their slopes varied from one
trial to the next. Reproducible curves were obtained when the
volume of solution in the reaction generator was held constant.

Absorbance readings for a standard curve were taken on a

Figure 4

ARSENIC-AGDDC CALIBRATION CURVE
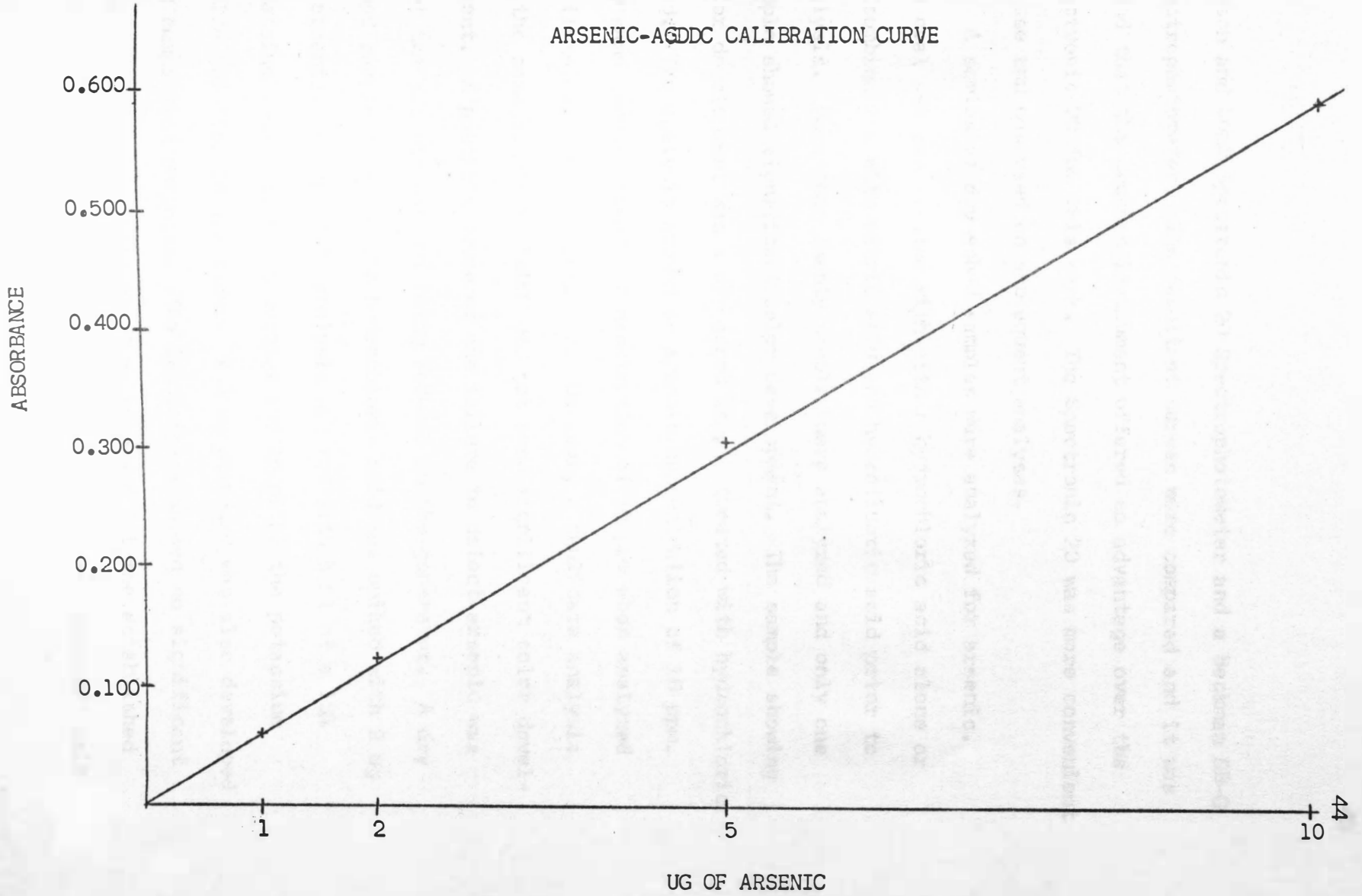
Bausch and Lomb Spectronic 20 Spectrophotometer and a Beckman DB-G Spectrophotometer. The resultant curves were compared and it was found that the Beckman instrument offered no advantage over the Spectronic 20 for this work. The Spectronic 20 was more convenient to use and was used on subsequent analyses.

A series of dry ashed samples were analyzed for arsenic. The coal ash was treated with either hydrochloric acid alone or in combination with nitric acid and hydrofluoric acid prior to analysis. More than twenty samples were analyzed and only one sample showed significant color development. The sample showing color development was a dry ashed sample treated with hydrochloric acid. The analysis showed an arsenic concentration of 10 ppm. The same sample showed a concentration of 15 ppm when analyzed by flameless atomic absorption. However, a duplicate analysis of the same sample by AgDDC did not show significant color development. A possible cause of the failure to detect arsenic was that the arsenic was not being reduced in the generator. A dry ashed sample treated with hydrochloric acid was spiked with 2 ug of arsenic. A duplicate analysis was run with 5 ml of a 15% potassium iodide in one generator and 15 ml of the potassium iodide solution in the other. A 2 ug standard was also developed for comparison purposes. The two samples showed no significant color development, while the 2 ug standard fit the established calibration curve. A comparison was also made on standards using

different types of zinc. Mossy zinc and 20 mesh zinc were used to develop 10 ug standards. The results were significantly different, which showed that the type of zinc used would affect the standard curve. No further work was done to solve these questions.

Analysis of Samples

Studies were carried out to test the reported effect of Ni^{+2} on arsenic analysis by flameless atomic absorption.[35] In an attempt to achieve greater precision a 20 fold excess of nickel sulfate was added to a series of dry ashed samples. The coal ash was treated with either hydrochloric acid alone or in combination with nitric acid and hydrofluoric acid. The nickel was added to the volumetric flask prior to dilution to the mark. Nickel ion was also added to the standard solutions. The absorbance of the standard solutions changed considerably from prior analysis. This caused the results of the analysis to differ by a factor of 6 to 7 from prior analyses. The cause was not pursued and no additional analyses of arsenic were performed.

A series of samples were treated by different ashing methods using optimized conditions. The samples were analyzed for copper, zinc, and sodium. Included in the different ashing methods were wet acid digestions using three different acid combinations, and a dry ash followed by two different acid treatments. The results of the analyses are shown in Tables 3-12. The levels of significance are defined as 95% being significant and 99% being very signifcant.

Table 3

ZINC ANALYSIS

Method of Digestion	no. of Samples	Average (PPM)	Standard Deviation
Wet Ash $HNO_3/HClO_4/H_2SO_4$	13	17	2.50
Wet Ash $HNO_3/HClO_4/H_2SO_4/HF$	11	16	1.05
Wet Ash $HNO_3/HClO_4$	15	17	1.36
Dry Ash HCl	12	16	1.21
Dry Ash $HCl/HNO_3/HF$	12	17	1.04

Table 4

ZINC ANALYSIS – COMPARISON OF MEANS BY T-TEST

	t-Value	Level of Significance
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4/H_2SO_4/HF$	1.23	not significant
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4$	0	not significant
$HNO_3/HClO_4/H_2SO_4$ vs Dry Ash/HCl	1.26	not significant
$HNO_3/HClO_4/H_2SO_4/HF$ vs Dry Ash/HCl/HNO_3/HF	2.28	significant
Dry Ash/HCl vs Dry Ash/HCl/HNO_3/HF	2.17	significant

Table 5

COPPER ANALYSIS BY FLAME ATOMIZATION

Method of Digestion	no. of Samples	Average (PPM)	Standard Deviation
Wet Ash $HNO_3/HClO_4/H_2SO_4$	12	18	2.24
Wet Ash $HNO_3/HClO_4/H_2SO_4/HF$	11	18	1.14
Wet Ash $HNO_3/HClO_4$	9	18	1.50
Dry Ash HCl	12	13	1.68
Dry Ash $HCl/HNO_3/HF$	12	17	1.86

Table 6

COPPER ANALYSIS - FLAME - COMPARISON OF MEANS BY T-TEST

	t-Value	Level of Significance
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4/H_2SO_4/HF$	0	not significant
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4$	0	not significant
$HNO_3/HClO_4/H_2SO_4$ vs Dry Ash/HCl	6.05	very significant
$HNO_3/HClO_4/H_2SO_4/HF$ vs Dry Ash/HCl/HNO_3/HF	1.54	not significant
Dry Ash/HCl vs Dry Ash/HCl/HNO_3/HF	3.12	very significant

Table 7

COPPER ANALYSIS BY FLAMELESS ATOMIZATION

Method of Digestion	no. of Samples	Average (PPM)	Standard Deviation
Wet Ash $HNO_3/HClO_4/H_2SO_4$	12	22	1.13
Wet Ash $HNO_3/HClO_4/H_2SO_4/HF$	11	22	2.00
Wet Ash $HNO_3/HClO_4$	9	18	1.62
Dry Ash HCl	12	15	1.04
Dry Ash $HCl/HNO_3/HF$	12	21	1.65

Table 8

COPPER ANALYSIS - FLAMELESS - COMPARISON OF MEANS BY T-TEST

	t-Value	Level of Significance
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4/H_2SO_4/HF$	0	not significant
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4$	6.68	very significant
$HNO_3/HClO_4/H_2SO_4$ vs Dry Ash/HCl	15.45	very significant
$HNO_3/HClO_4/H_2SO_4/HF$ vs Dry Ash/HCl/HNO_3/HF	1.32	not significant
Dry Ash/HCl vs Dry Ash/HCl/HNO_3/HF	10.50	very significant

Table 9

COPPER ANALYSIS - COMPARISON OF ATOMIZATION TECHNIQUES
BY T-TEST

Method of Digestion	t-Value Flame vs Flameless	Significance at 95% Level
Wet Ash $HNO_3/HClO_4/H_2SO_4$	5.78	very significant
Wet Ash $HNO_3/HClO_4/H_2SO_4/HF$	5.69	very significant
Wet Ash $HNO_3/HClO_4$	0	not significant
Dry Ash HCl	3.50	very significant
Dry Ash $HCl/HNO_3/HF$	5.57	very significant

Table 10

SODIUM ANALYSIS

Method of Digestion	no. of Samples	Average (PPM)	Standard Deviation
Wet Ash $HNO_3/HClO_4/H_2SO_4$	11	1370	159
Wet Ash $HNO_3/HClO_4/H_2SO_4/HF$	12	1860	141
Wet Ash $HNO_3/HClO_4$	9	1390	102
Dry Ash HCl	12	1330	45
Dry Ash $HCl/HNO_3/HF$	12	1890	77

Table 11

SODIUM ANALYSIS - COMPARISON OF MEANS BY T-TEST

	t-Value	Level of Significance
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4/H_2SO_4/HF$	8.03	very significant
$HNO_3/HClO_4/H_2SO_4$ vs $HNO_3/HClO_4$	0.33	not significant
$HNO_3/HClO_4/H_2SO_4$ vs Dry Ash/HCl	0.87	not significant
$HNO_3/HClO_4/H_2SO_4/HF$ vs Dry Ash/$HCl/HNO_3/HF$	0.65	not significant
Dry Ash/HCl vs Dry Ash/$HCl/HNO_3/HF$	21.76	very significant

Table 12

SODIUM ANALYSIS - SOURCE OF DEVIATION BY F-TEST

Category	Degrees of Freedom	Difference in Sum Of Squares	Variance (diff/df)	F-Test
Total	11	945,625	85,966	
Day	2	79,850	39,925	5.18
Method of Ash	3	819,492	273,164	35.41
Remainder	6	46,283	7,714	

In the zinc analysis, a comparison of means from digestion with the triple acid mixture with and without hydrofluoric acid shows no significant difference when hydrofluoric acid is used in the acid mixture. Zinc is not significantly volatilized at $450^{\circ}C$ in the muffle furnace. This is proven by a comparison of the means for a conventional wet and dry ashing. The analysis does not indicate physical trapping to be a problem when sulfuric acid is used in the acid combination. Comparisons of wet and dry ashings using hydrofluoric acid and dry ashings using different acid treatments show no definite trends. There is more than one variable in each case, so no conclusion can be offered to explain the level of significance.

Analysis of the copper data (flameless) shows the need for either sulfuric acid or hydrofluoric acid in the ashing procedure. A comparison of the means from a wet and dry ashing prove that copper is not significantly volatilized in the furnace. The data shows that it is not necessary for hydrofluoric acid to be in the acid mixture if sulfuric acid is present. These observations are supported by the data from the analysis using flame atomization. The only anomaly is the comparison of means from wet digestions using the triple and double acid mixtures. This comparison shows no significant difference. There is no evidence of physical trapping when sulfuric acid is used in either set of data. The mean values from the analysis using flame atomization are

significantly lower in all cases, with the exception of the wet
digestion with the double acid mixture, than those using flameless
atomization. In both analyses the mean values from the dry ash-
ing followed by acid treatment with hydrochloric acid are much
lower than the other means. These two observations have not been
explained at this time.

The analysis of sodium shows higher values when hydrofluoric
acid is used. This was expected since sodium is often a minor
constituent of the silica matrix.[1] There is no significant dif-
ference between wet and dry ashings with no hydrofluoric acid
included in the treatment and no significant difference between
wet and dry ashings with hydrofluoric acid included in the proce-
dure. There is no evidence of physical trapping due to sulfuric
acid and no evidence of volitilization of sodium in the furnace.
The analysis of variance showed the major source of deviation to
be the method of ashing. The analysis of variance also showed
the day of ashing to be significant. An F-value of 5.14 would
show the day of ashing to be not significant.

A Standard Reference Material coal sample was obtained from
the National Bureau of Standards for analysis. The sample was
analyzed for zinc, copper, and sodium. Dry ashing followed by
acid treatment with hydrochloric nitric, and hydrofluoric acids
was chosen as the ashing method that would effect the greatest
accuracy and precision on the analysis. The levels of copper and

zinc in the sample are certified by the NBS. The results of the
analysis for copper and zinc are shown in Table 13. The values
are within the limits certified by NBS. The standard deviations
are lower than those reported by NBS. The concentration of
sodium in the sample is not certified by NBS. A value of 412±20
ppm was reported in the literature in an inter-laboratory com-
parison of the NBS standard.[5] This value was used for comparison
purposes. The samples were ashed in four different sets. The
values from the first three sets were high and erratic. This type
of problem had not been a problem with previous sodium analyses,
so the reason for this deviation was not pursued. The fourth set
contained five samples and had an average of 401 ppm. The
standard deviation was 15 ppm.

Table 13

ANALYSIS OF NBS SRM 1632

Element	No. of Samples	Average (PPM)	Standard Deviation	NBS Value (PPM)
Zinc	14	37	1.3	37±4
Copper	13	19	1.4	18±2

CONCLUSION

In the preceding sections several different ashing methods have been examined and their effect on the analysis of coal for metals has been shown. The dry ashing methods most generally yielded the lowest standard deviations. They were also less subject to blank contamination problems. The use of hydrofluoric acid eliminated the presence of any precipitates and hence the need for a filtering step, but hydrofluoric acid was shown to be unnecessary for the analysis of copper and zinc. It was shown that sulfuric acid can be used in a wet acid digestion without the problems of physical trapping by calcium sulfate if the proper procedure is followed. The effect of particle size on oxidation was studied. Samples ground to 100 mesh were found to contain a consistent ash weight.

A National Bureau of Standards' coal sample was analyzed. The sample was dry ashed and then treated with hydrofluoric acid. The results of the analyses performed on the sample were in close agreement with the values certified by NBS.

The purpose of this study was to determine whether or not the sample preparation step was responsible for some of the variation in the analysis of coal samples. Significant differences were found for some of the methods. Therefore, if the proper digestion method is not used for the element being analyzed then significant error may result.

BIBLIOGRAPHY

1. H.J. Gluskoter in "Trace Elements in Fuel," Advances in Chemistry Series 141, S.P. Babu, Ed., American Chemical Society, Washington, D.C., 1975, Chapter 1.

2. T.T. Gorsuch, Analyst, 84, 135(1959).

3. D.J. vonLehmden, R.J. Jungers, and R.E. Lee, Jr., Anal. Chem., 46, 239(1974).

4. V.E. Swanson and C. Huffman, Jr., "Guidelines for Sample Collecting and Analytical Methods Used in the U.S. Geological Survey for Determining Chemical Composition of Coal," Geological Survey Circular 735, U.S. Dept. of Interior, 1976, pp. 4-8.

5. J.M. Ondov, W.H. Zoller, I. Olmez, N.K. Aras, G.E. Gordon, L.A. Rancitelli, K.H. Abel, R.H. Filby, K.R. Shah, and R.C. Ragaini, Anal. Chem., 47, 1102(1975).

6. E. Orvini, T.E. Gills, and P.D. LaFleur, Anal. Chem., 46, 1294(1974).

7. F.W. Wilshire, J.P. Lambert, and F.E. Butler, Anal. Chem., 47, 2399(1975).

8. A.G. Sharkey, Jr., T. Kessler, and R.A. Friedel in "Trace Elements in Fuel," Advances in Chemistry Series 141, S.P. Babu, Ed., American Chemical Society, Washington, D.C., 1975, Chapter 4.

9. R.J. Guidoboni, Anal. Chem., 45, 1275(1973).

10. G.B. Dreher and J.A. Schleicher in "Trace Elements in Fuel," Advances in Chemistry Series 141, S.P. Babu, Ed., American Chemical Society, Washington, D.C., 1975, Chapter 3.

11. J. Thomas, Jr. and H.J. Gluskoter, Anal. Chem., 46, 1321(1974).

12. J.K. Kuhn, W.F. Harfst, and N.F. Shimp in "Trace Elements in Fuel," Advances in Chemistry Series 141, S.P. Babu, Ed., American Chemical Society, Washington, D.C., 1975, Chapter 6.

13. J.A. Carter, R.L. Walker, and J.R. Sites in "Trace Elements in Fuel," Advances in Chemistry Series 141, S.P. Babu, Ed., American Chemical Society, Washington, D.C., 1975, Chapter 7.

14. E.N. Pollock in "Trace Elements in Fuel," Advances in Chemistry Series 141, S.P. Babu, Ed., American Chemical Society, Washington, D.C., 1975, Chapter 2.

15. A.M. Hartstein, R.W. Freedman, and D.W. Platter, Anal. Chem., 45, 611(1973).

16. B. Bernas, Anal. Chem., 40, 1682(1968).

17. A. Bailey, Proc. W. Va. Acad. Sci., 47, 46(1975).

18. R.R. Ruch, H.J. Gluskoter, and N.F. Shimp, "Occurance and Distribution of Potentially Volatile Trace Elements in Coal," Illinois State Geological Survey Environmental Geology Notes, no. 72, 1974, pp. 59-85.

19. P.L. Boar and L.K. Ingram, Analyst, 95, 124(1970).

20. D.N. Bowden and H.S. Roberts, N. Zeal. J. Sci., 18, 119(1975).

21. C.O. Ingamells, Anal. Chim. Acta, 52, 323(1970).

22. J.W. Owens and E.S. Gladney, Atomic Absorption Newsletter, 15, 95(1976).

23. R.B. Muter and C.F. Cockrell, Appl. Spectro., 23, 493(1969).

24. C.E. Gleit and W.D. Holland, Anal. Chem., 34, 1454(1962).

25. H.A. Laitinen and W.E. Harris, "Chemical Analysis," 2nd ed., McGraw-Hill Book Company, New York, N.Y. 1975, p. 317.

26. G.F. Smith, Talanta, 11, 633(1964).

27. G.F. Smith, Anal. Chim. Acta, 8, 397(1953).

28. G.I. Spielholtz and H. Diehl, Talanta, 13, 991(1966).

29. F.J. Langmyhr and P.E. Paus, Anal. Chim. Acta, 43, 397(1968).

30. N.K. Pradhan, "Coal and Petroleum Analysis by Atomic Absorption Spectroscopy," Varian Techtron, 1976, pp. 5-8.

31. H.A. Laitinen and W.E. Harris, "Chemical Analysis," 2nd ed., McGraw-Hill Book Company, New York, N.Y. 1975, p. 318.

32. J. Murphy, Atomic Absorption Newsletter, 14, 151(1975).

33. American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," 12th ed., American Public Health Association, Inc., New York, N.Y., 1966, pp. 56-58.

34. E.D. Olsen, "Modern Optical Methods of Analysis," McGraw-Hill Book Company, New York, N.Y., 1975, pp. 283-284.

35. R.D. Ediger, Atomic Absorption Newsletter, 14, 127(1975).

36. H.A Laitinen and W.E. Harris, "Chemical Analysis," 2nd ed., McGraw-Hill Book Company, New York, N.Y. 1975, p. 543.

37. R.N. Barnett, "Clinical Laboratory Statistics," Little, Brown and Company, Boston, 1971, pp. 32-39.

APPENDIX

Definition of Standard Deviation

$$s = \left(\frac{\sum (x-\bar{x})^2}{n-1} \right)^{\frac{1}{2}}$$

$$s = \left(\frac{d_1^2 + d_2^2}{n_1 + n_2 - 2} \right)^{\frac{1}{2}}$$

Definition of t

$$t = \left(\frac{\bar{x}_1 - \bar{x}_2}{s} \quad \frac{n_1 n_2}{n_1 + n_2} \right)^{\frac{1}{2}}$$

Definition of F

$$F = \frac{\text{Variance of Category of Interest}}{\text{Variance of Remainder}}$$