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A method for the determination of trace metals in carbon by atomic absorption spectroscopy

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A METHOD FOR THE DETERMINATION

OF TRACE METALS IN CARBON

BY ATOMIC ABSORPTION SPECTROSCOPY

BY

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A THESIS
SUBMITTED TO THE GRADUATE FACULTY
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FOR THE DEGREE OF
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APPROVED:

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DEDICATION

Dedicated to my wife and children whose patience, understanding, and encouragement have afforded me the opportunity of completing this work.

ACKNOWLEDGMENT

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INTRODUCTION

The object of this research was to develop an accurate, rapid and economical method for determining trace amounts of metals in carbons, especially in activated carbons designed as gas adsorbents. More specifically, the investigation was directed primarily to the determination of K, Ca, and Fe in carbons.

The only rapid method currently known for the analysis of metals in carbon is emission spectroscopy, which requires considerable capital investment. Other methods currently used involve lengthy procedures such as ashing and/or extractions followed by either colorimetric, gravimetric or spectrographic techniques.

The recent introduction of atomic absorption spectroscopy has shown excellent promise as a tool for determining trace amounts of elements. It was the intent of the author to develop a method for determining trace metals in carbon

using atomic absorption spectroscopy.

The use of the term <u>active carbon</u> in this report will apply to any form of carbon possessing adsorptive power, principally as related to gas adsorption. Likewise, the use of the words <u>carbon</u> and <u>charcoal</u> will be considered synonymous.

HISTORICAL

I.   Carbon

The primary process for preparing carbon involves carbonization of a raw material, usually in the absence of air, at temperatures ranging from 400 to 1100°C (18).

There are many substances suggested in the literature as suitable raw materials for preparing active carbon (17); however, in this work only carbons derived from coconut shells, petroleum and wood were investigated.

The use of carbon or charcoal as an adsorbent was first recorded by Scheele in 1773 (5) during experiments conducted on various gases exposed to charcoal. Similar gas adsorptive properties of charcoal were reported by Fontana in 1777 (14). From 1785 through 1850 the major efforts on carbons were directed toward their use as liquid decolorants for the sugar industry. In 1854 Stenhouse (35) suggested the use of charcoal to ventilate sewers and described the forerunner of the modern gas mask. In 1865 Hunter (19) reported on the

gas adsorbing power of coconut charcoal. Work by Ostrejko
(30) at the turn of the century essentially paved the way
for the development of modern commercial active carbons.
He described basic processes for the preparation of car-
bons including incorporation of metallic chlorides with
carbonaceous materials before carbonization. The first
commercial carbons were produced around 1910 for use pri-
marily in the cane sugar field.

The use of active carbons for gas adsorption received
its greatest impetus from gas attacks in World War I. The
early and successful accomplishment of producing granular
active carbons for use in gas masks (23) not only influenced
the course of the war but contributed innumerable industrial
benefits in the pursuing years. Among the many and varied
applications for active gas adsorbent carbons are the fol-
lowing:

        a. Organic vapor recovery
        b. Gas purification
        c. Odor removal
        d. Smoke filtration

Aside from metallic impurities already present in the
base raw material, other metals or metallic salts are often
times added to enhance the adsorptive properties of the car-
bon, the earliest reported being $CaCl_2$, $MgCl_2$ and $ZnCl_2$ (2).
The most extensively used process for preparing activated

carbon is the so-called zinc chloride process, which involves addition of the salt to the base raw material prior to carbonization. Among the other metals frequently employed as adsorption enhancers are K (29), Fe (8), Al (3), Cu (27), and Mn (24). The most recent trend in the active carbon industry is the impregnation of a carbon with specific metals to provide selective absorption of a given compound, i.e., the so-called "Whetlerite" carbons are impregnated with a copper salt for selective adsorption of AsH_3.

II. Analysis of Carbon

The analysis of carbon for the various constituents present has been of interest since its first commercial use in the sugar industry in the early 1900's. At that time determination of the percentage ash was the principal and essentially the only analysis carried out on carbons and remained so until the early 1920's. Various investigators had reported from time to time on the presence of a specific metal such as Ra (34), Ni (33) and Mn (6). Some of the earliest reported methods for analyzing carbons for metals were a wet chemical and microscopic method for P in wood charcoal by Eckermann in 1924 (9), and a microscopic analysis of Norit (a wood charcoal) by Tanner in 1925 (36). The analysis of a carbon ash for Si and Al by wet chemical

methods was reported by Garino and Afferni in 1939 (15).

A method for determining sulphur was reported in 1948 (4),

and several carbon ash extraction procedures were reported

in 1955 as a means to separate the metal impurities into

groups of metals (13) (1). The first reported overall

analysis of the metals in carbon was reported in 1959 (26)

by Micka in which he attempted to analyze suspensions of

charcoal by a polarographic technique. It was also in 1959

that the first quantitative spectrographic analysis of the

metals in carbon was reported by Demidov and Gorbunova (7).

They reported a possible 25 to 30% error. In 1960 Hegemann

and Russman reported on the quantitative spectral analysis

of traces of impurities in carbons using a direct current

arc (20).

III. Atomic Absorption

Since the end of World War II there has been an increas-

ing interest in impurities present in materials in the parts

per million range. This is evidenced by the rapid develop-

ment of new and improved colorimetric procedures and superior

spectrophotometers for determining optical densities of

colored solutions at narrowly defined wavelengths. It was

in 1955 that Walsh (38), the father of atomic absorption,

in attempting to devise an improved spectrochemical procedure,

first reported on what is today known as atomic absorption spectrophotometry.

Walsh's primary objective was to devise a spectrochemical procedure free from the interelement effects present and frequently troublesome in emission spectroscopy (10). Walsh centered his efforts on one source of interference, the variation of discharge temperature, and examined the effects of changes in temperature on atomic vapor in thermal equilibrium. In emission spectroscopy the determination of the amount of an element present is based upon determination of light emitted from excited atoms according to the equation:

$$N_i = \left(N_o \frac{P_i}{P_o}\right) e^{-\left(\frac{E_i}{kT}\right)}$$

P_i = statistical weight for excited state

P_o = statistical weight for ground state

E_i = excitation energy

N_i = number of atoms in excited state

N_o = number of atoms in ground state

k = Boltzman constant

T = ° Kelvin

From the equation it is apparent that the number of excited atoms varies exponentially with temperature. What is even more significant is the fact that at the normal operating temperatures, usually below 3000°K, the fraction $\frac{N_i}{N_o}$ is very small (10^{-3} or less) (11) and N_i negligible compared to N_o. Thus, while N_i varies exponentially with temperature, N_o, or

the number of atoms in the ground state, will remain virtually constant.

If we now consider a parallel beam of radiation of intensity I_o, at a frequency v, incident on an atomic vapor of thickness 1 cm, then if I_v is the intensity of transmitted radiation, the absorption coefficient K_v of the vapor at frequency v is defined as follows:

$$I_v = I_o \ e^{-Kl}$$

The value of K_v will vary with v since the absorption line has a finite width, but according to classical dispersion theory, the integrated absorption $(\int K_v \ dv)$ is given by the relation:

$$\int K_v \ dv = \frac{\pi e^2}{mc} \ N_v f$$

e = electronic charge
m = electronic mass
c = velocity light
N_v = number atoms capable of absorbing radiation at frequency v
f = oscillator strength (the average number of electrons per atom capable of being excited by the incident radiation)

Thus, for a transition initiated from the ground state, where N_v is essentially equal to N_o, the integrated absorption is proportional to the concentration of free atoms in the absorbing medium and is independent of the temperature of the vapor.

The problem is how to measure the integrated absorption.
Factors that establish the line width are:

1. Natural width of the line
2. Doppler broadening due to movements of the atoms relative to the observer
3. Pressure broadening due to the presence of neighboring atoms
4. Stark broadening due to external electric fields or charged particles

The natural width of the line ($\sim 10^{-4}$ Å) can be neglected in relation to the other factors. Both Doppler and pressure broadening occur in flame sources, and all three, Doppler, pressure and Stark broadening occur with conventional spectrographic arc and spark excitation sources. In order to measure the profile of an absorption line accurately, and thus obtain the integrated absorption, it would require an optical instrument with a resolution well beyond the capabilities of most spectrographs. Walsh's suggested method eliminated the need for a high resolution instrument by using a sharp line source which emits lines with a much smaller half width than the absorption line. Then the absorption coefficient at the center of the line can be measured. Mitchell and Zemansky (28) showed that if the shape of the absorption line is completely determined by Doppler broadening then:

$$K_{max} = \frac{2\lambda^2}{D_\lambda} \sqrt{\frac{\log_e 2}{\pi}} \frac{\pi e^2}{mc^2} Nf$$

K_{max} = absorption coefficient at center of the line

D_λ = Doppler line width

Since D_λ is proportional to $\sqrt{T}$, K_{max} does not vary significantly with temperature and there remains a linear relationship between absorption and concentration of free atoms in the absorbing medium. Thus with a sharp line source high resolution is not required, only the ability to separate lines, and this can be accomplished with simple spectrographic equipment.

The method Walsh chose for obtaining an atomic vapor was to atomize a solution containing the element into a flame. The presence of gases other than the vaporized sample will cause pressure broadening; however, this will be a constant factor causing constant proportional lowering of K_{max}, reducing only the sensitivity of the method and not the linear relationship between concentration and absorption. Increasing the concentration of the sample vapor will result in resonance broadening and a reduction in absorption. The reduction will not be linear with concentration, and for this reason, calibration curves of concentration versus absorption will be required as well as operation within concentration limits below the plateau of the calibration curves.

Essential requirements for atomic absorption spectro-photometry include:

a. Sharp line source
b. Means for vaporizing samples
c. Wavelength selector
d. Intensity measurement and recording equipment

Sharp line sources for atomic absorption spectroscopy should emit resonance radiation of the metal with a line half width smaller than the Doppler width of the absorbing line. The radiation must be sufficiently intense to permit measurements to be made accurately. For these reasons normal spectrographic arcs, sparks or flame sources are not sufficient. The two most commonly used emission sources for atomic absorption are vapor discharge lamps and hollow cathode lamps (12). Vapor discharge lamps are the best source of radiation for the alkali metals (Na, K, Rb, Cs) and such metals as Hg and Tl. For the remainder of the metals, hollow cathode lamps are the most convenient and useful source of radiation and are commercially available (21). The lamp consists of a hollow cylinder, made from material containing the metal to be determined enclosed in a low pressure rare-gas atmosphere, usually helium or argon. The lamp is energized by a potential of about 400 volts with a current up to about 100 milliamps. The spectrum of the glow discharge is characteristic of the cathode material and

the carrier gas. If helium is the carrier gas, the spectrum is largely due to ions (spark spectrum). With argon, arc lines, or lines due to the atom, are predominant because argon has a lower ionization potential. Argon is preferred because the resonance lines of the cathode material are enhanced. The best source of information regarding the principles and methods of operation of sharp line sources is Tolansky's book "High Radiation Spectroscopy" (37).

Schematic diagrams of an atomic absorption spectrophotometer and the optical scheme are shown in Figures I and II.

Since Walsh's report in 1955, several companies have developed commercially available atomic absorption spectrophotometers. Foremost among these is the Perkin-Elmer Corporation. The Perkin-Elmer Corporation also publishes a regular series of reports on atomic absorption developments and techniques (32) which has served as a reference library for the author.

To date all published research on atomic absorption has been carried out on solutions (32).

No references concerning the direct analysis of slurries could be found for atomic absorption analyses; however, an article by Gilbert (16) in 1962 first suggested the feasibility of analyzing powdered materials in a viscous

Figure I

Block Diagram of Atomic Absorption Spectrophotometer
Perkin-Elmer Model 303
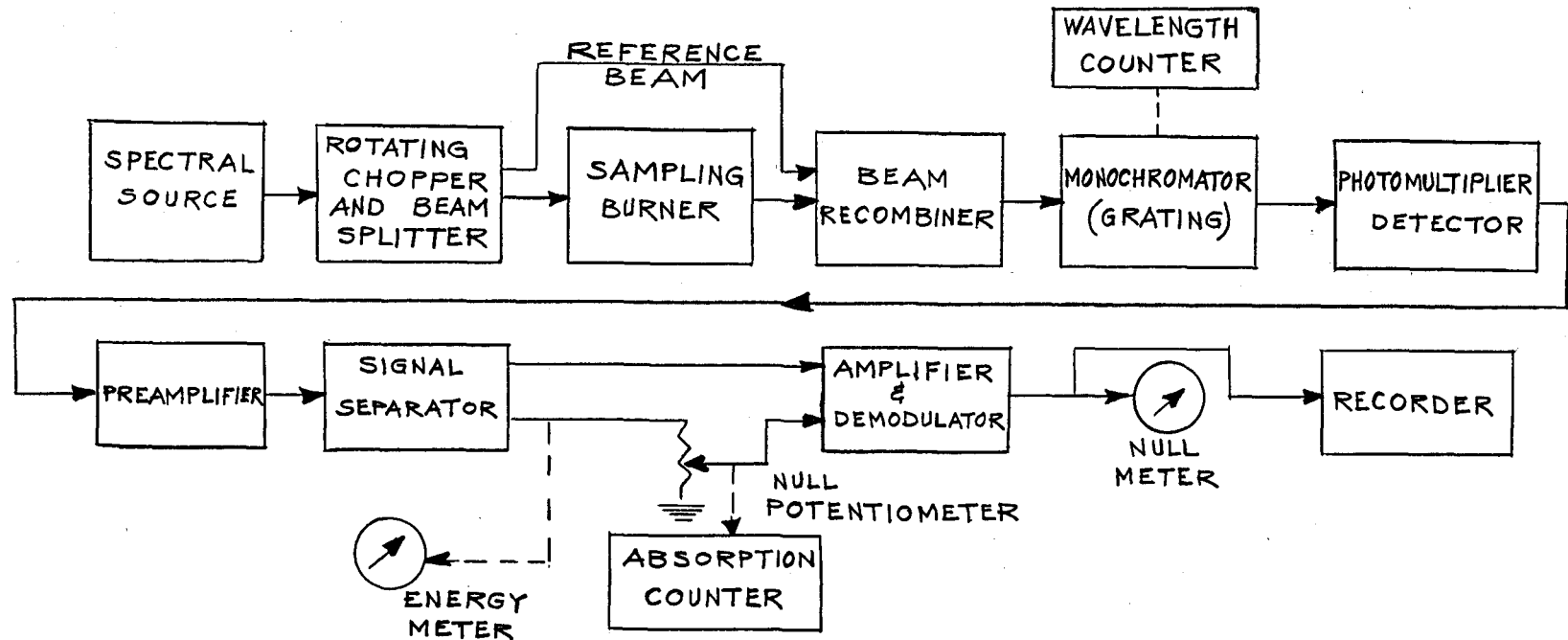
The emission from the source is split into two beams. One beam is directed through the flame at the sampling burner, while the other by-passes it. After being recombined the beams pass through a grating monochromator to a detector and preamplifier after which the signal is separated into sample and reference channels. The reference voltage is then attenuated by a slidewire (the null potentiometer) and recombined with the sample voltage in such a way that only the difference between them remains. This difference voltage is then amplified, rectified and fed to a microammeter and automatically recorded on the readout recorder. Manual adjustment of the null meter can also provide a visual readout.

Figure II

Optical Schematic of Atomic Absorption Spectrophotometer
Perkin-Elmer Model 303
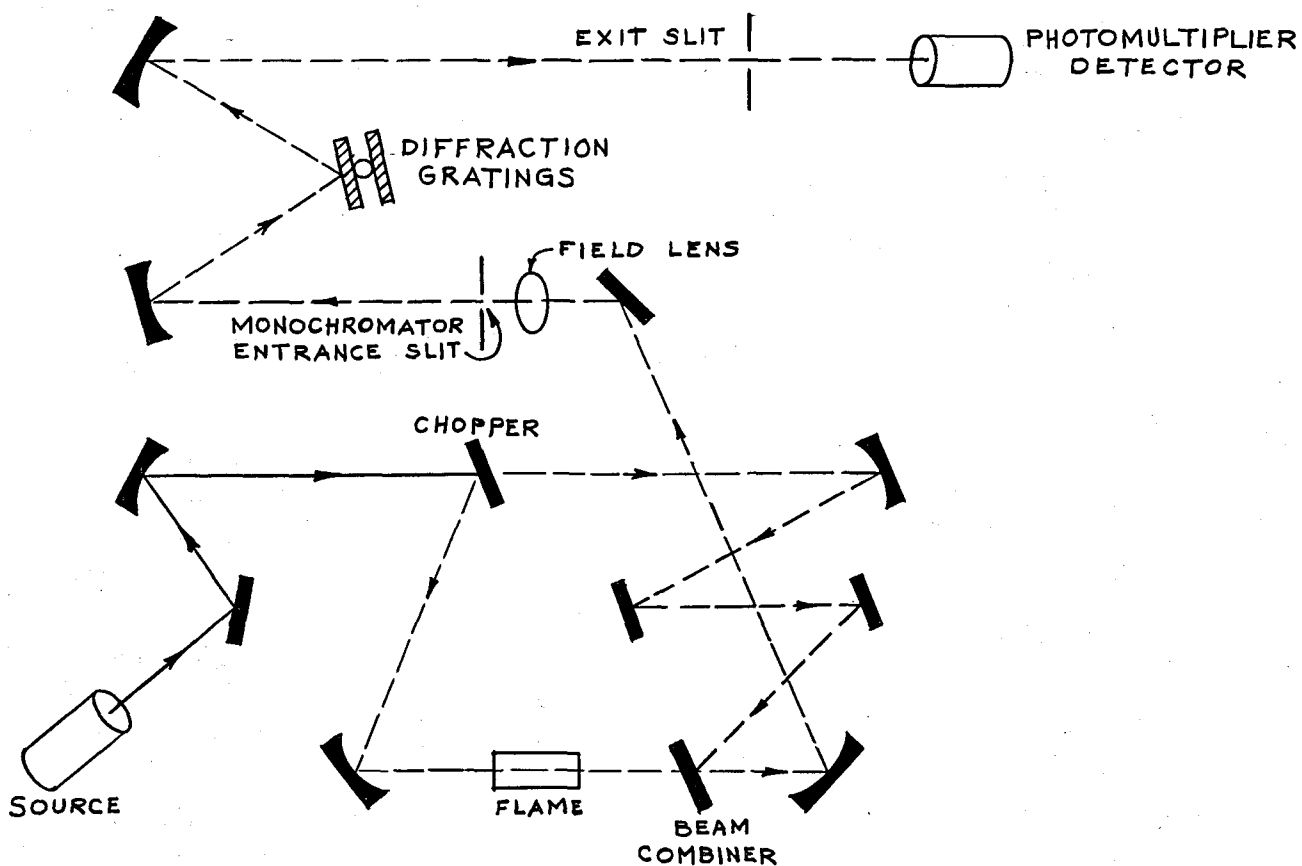
Light from the source is directed via mirrors to the chopper,
from whence two beams result. One beam is focused in the
sample area (flame), the second is used as a reference beam.
The beams are recombined after the sample beam has passed
through the sample and focused on a monochromator entrance
slit via mirrors. From the slit the light is collimated by
a spherical mirror and directed to one of two diffraction
gratings. Diffracted light is then reflected via a mirror
to the exit slit and photomultiplier detector.

medium using flame photometry. Although Gilbert's efforts were directed primarily to work on flame photometry, he did suggest the possibility of applying the method to atomic absorption spectroscopy. In 1963, Mason (25) demonstrated the practicality of Gilbert's idea by directly analyzing ground plant leaves in a glycerol solution for K by flame photometry. This thesis will show the practicality of extending Gilbert's idea to atomic absorption spectrophotometry.

EXPERIMENTAL

I. Reagents

Acetylene, Air Reduction Company

Magnesium ribbon, purified, J. T. Baker Chemical Company

Iron powder, carbonyl purified, General Aniline & Film Corp.

Spectroscopic grade carbon powder, Union Carbide Corp.

Coconut carbon, PCB grade, Pittsburgh Carbon Company

Petroleum base carbon, Columbia LC grade, Union Carbide Corp.

Wood base carbon, Darco KB grade, Atlas Chemical Industries, Inc.

Distilled water, deionized by passing through a Crystalab
  Deeminizer Water demineralizer

All other reagents used for this project were common labora-
  tory reagents of C.P. or equivalent grade.

II. Apparatus

Atomic Absorption Spectrophotometer Model 303 with fuel

    and burner regulator, source power supply, and read-

    out control unit.

E. H. Sargent Recorder, Model SR

Sodium discharge lamp

Potassium discharge lamp

                          Osram, made in Germany by

                          Gesellschaft mit beschränkter

                          Haftung

Calcium hollow cathode lamp

Magnesium hollow cathode lamp

Iron hollow cathode lamp

Nickel hollow cathode lamp

Copper hollow cathode lamp

                          Atomic Spectral Lamps Pty, Ltd.

                              Melbourne, Australia

The remainder of the equipment was common laboratory equip-

    ment.

III. Development of Method

A. Atomic Absorption

1. Preparation of Standard Solutions

In order to run an atomic absorption analysis and obtain meaningful and useful results it is mandatory that particular care be employed in preparing standard reference solutions. The normal procedure, as recommended by the Perkin-Elmer Corporation (31), is to prepare solutions containing 1000 ppm of a given metal, then dilute this concentrated solution down to the operation range of the various metals being studied. The operating range is that concentration range of any given metal expressed in ppm (mg per liter) throughout which the absorption calibration curve is linear. The absorption calibration curve is a plot of absorbance versus concentration. The absorbance is obtained by converting the % absorption recorded on the automatic readout recorder according to the following equation:

$$\text{Absorbance} = \log \frac{100}{100 - \%\ \text{absorption}}$$

At higher concentrations the calibration curve tends to reach a plateau (due to resonance broadening) and cannot be interpreted with any degree of accuracy. Normal operating ranges vary from 0.5 ppm to as high as 25 ppm, e.g., K range

is 1 to 10 ppm, Mg range is 0.5 to 5.0 ppm, Ca and Fe range

is 1 to 20 ppm, Ni range is 2 to 25 ppm. The reason for

starting with higher concentration standards and then diluting

is basically twofold:

1. The larger the sample, the smaller the percentage
   error.

2. A 1000 ppm solution can be kept for a period of
   approximately six months to one year, while lower
   concentration levels should not be used for more
   than two to three months.

Although K, Ca and Fe were the major metals of interest in

this program, four other metals were also given a cursory

examination - Na, Mg, Ni and Cu. Standard solutions for

each of the above mentioned metals were obtained by first pre-

paring a 1000 ppm solution, then diluting the 1000 ppm solu-

tion down to the operating range for each metal. The 1000

ppm solutions were prepared as follows:

K - KCl was oven dried to constant weight, and 1.9066
     grams was dissolved in 1 liter of distilled deionized
     H_2O.

Ca - $CaCO_3$ was oven dried to constant weight, and 2.4972
     grams was dissolved in 1 liter of a 60:40 by volume
     concentrated $HCl:H_2O$ (distilled and deionized) solution.

Fe - Purified iron powder was oven dried to constant weight,
     and 1.000 gram was dissolved in 1 liter of the 60:40
     $HCl:H_2O$ solution previously described.

Na - NaCl was oven dried to constant weight, and 2.5423 grams
     was dissolved in 1 liter of distilled deionized H_2O.

Mg - Mg ribbon was oven dried to constant weight, and 1.000
gram was dissolved in 1 liter of the 60:40 $HCl:H_2O$
solution previously described.

Cu - CuO was oven dried to constant weight, and 1.2518
grams was dissolved in 1 liter of the 60:40 $HCl:H_2O$
solution previously described.

Ni - NiO was oven dried to constant weight, and 1.2722 grams
was dissolved in 1 liter of the 60:40 $HCl:H_2O$ solution
previously described.

Each of the 1000 ppm solutions was then diluted down
to the recommended operating range of that particular metal.

Later in the program, when it became necessary to use
solvents other than HCl and H_2O, standard solutions contain-
ing other solvents were prepared in exactly the same manner
using the same solvent concentrations as that being utilized
for the carbon samples.

2. Instrument Operation

Procedures for operation of the atomic absorption spec-
trophotometer were supplied by the Perkin-Elmer Corporation
in the form of a brochure (31) supplied with the instrument
at the time of purchase. The brochure contains not only
recommended operating procedures, but also a complete list
of settings and ranges for all the elements currently able
to be analyzed.

The normal procedure is to first insert the sharp line

source lamp - a discharge lamp for Na and K, a hollow cathode lamp for alkaline earth and transition metals - and permit the source lamp to warm up for a period of at least 30 minutes under the recommended amperage for the particular lamp. During warm-up, the slit opening, desired wave length, spectrum setting (UV or visible range) and energy level are adjusted for the particular metal under observation. The flame is then lit by turning on the air source first, then gradually increasing the acetylene flow while holding a flame to the burner. In the case of this research, all work was carried out using an air-acetylene flame with an air flow of approximately 9 liters/minute and an acetylene flow of 8 liters/minute. Once the lamp has warmed up, and the energy level balanced out to a steady reading, the automatic absorption recorder is turned on. Standard solutions are then aspirated from 2 ml polyethylene sample beakers, through a fine capillary teflon tube, into the flame, and the recorder adjusted for readout of the operating range of the metal under observation. Normal aspiration is at the rate of 2 ml per minute. With the recorder adjusted, the operator is now ready for analysis of a sample.

3. Sample Analysis

At the start of an analysis a distilled deionized H_2O blank is run to clean out the aspirator lines and burner.

A solvent blank is then run to establish the level of the metal in the solvent, followed by a distilled deionized H_2O blank to remove the solvent from the lines. The procedure then is to run one standard solution level after another, with an H_2O blank between each, to establish an absorption curve. After the standards are run, the sample solutions are run, with an H_2O blank between each run. After the samples are run, the standard solutions are again run to insure that the absorption level has not changed. Should the sample analysis show absorption higher than the recommended operating range for a given metal, it becomes necessary to dilute the sample to yield a reading within the recommended operating range. The concentration of metal in the sample solution is then determined from the absorption calibration curve, and the percent metal determined by calculating back to the original sample weight. A typical calibration curve for K is shown in Figure III. For elucidation purposes only, assume that a 10 gram carbon sample was extracted with 100 ml of H_2O. On analyzing a 2 ml aliquot of the 100 ml solution it was found necessary to dilute the sample tenfold to obtain an absorbance reading of 0.17, indicating a concentration of 5 ppm. Since the sample had to be diluted tenfold, this means the 100 ml solution contains 10 x 5, or 50 ppm of K. The weight of K

FIGURE III.

K CALIBRATION CURVE

Absorbance vs Concentration

- 23 -
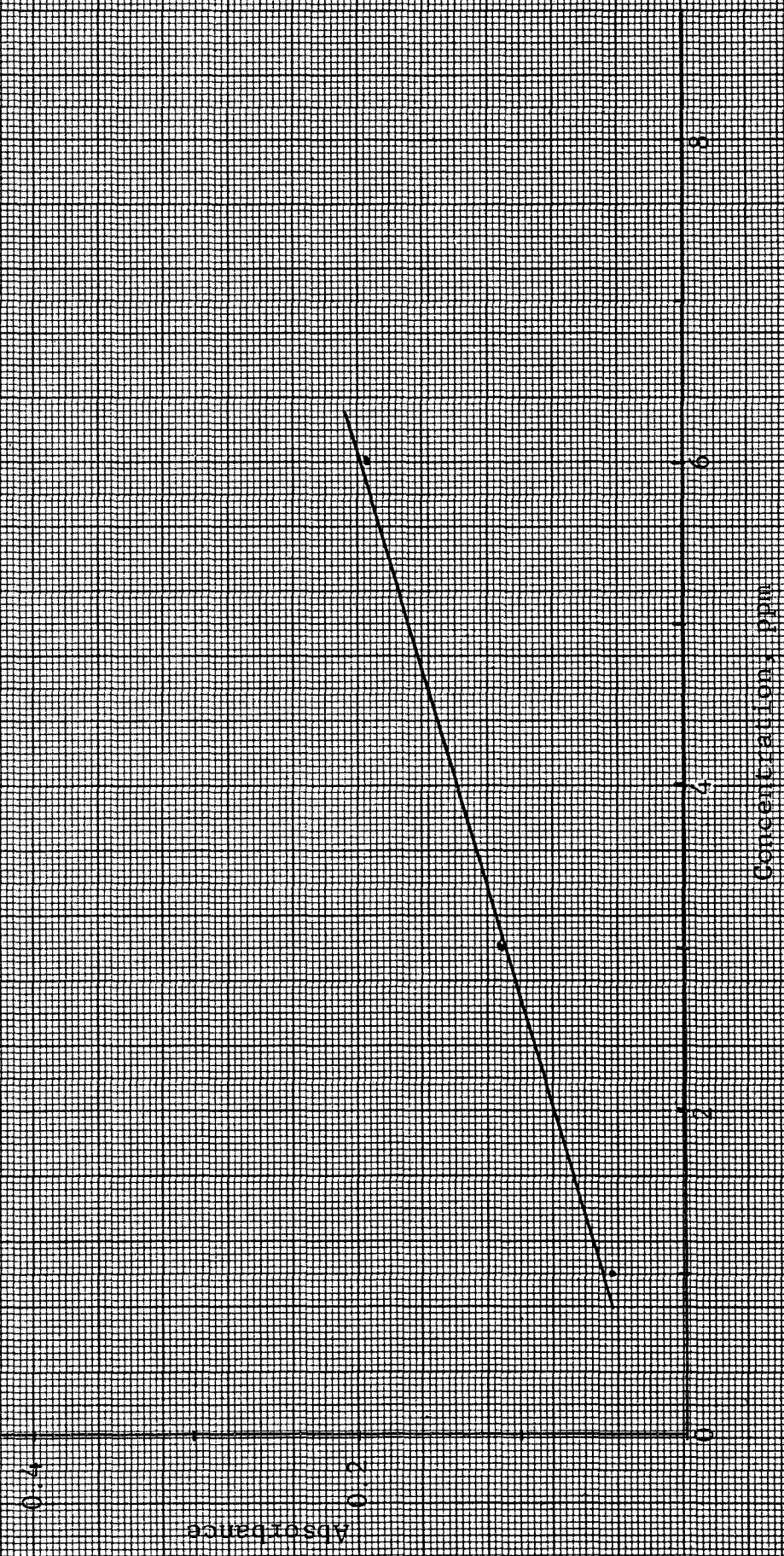
is then calculated by multiplying the ppm found by the volume

of the sample solution and dividing by 1,000,000 as follows:

$$\text{weight K} = \frac{50 \text{ ppm x } 100 \text{ ml}}{1,000,000} = \frac{5,000}{1,000,000} = .005 \text{ gram K}$$

The percent K in the carbon is then determined as follows:

$$\% \text{ K} = \frac{.005 \text{ gram K}}{10 \text{ grams carbon}} \times 100 = \frac{.5}{10} = .05\%$$

All calculations for percentage metals in carbon were carried

out in the manner just shown.

For the analysis of carbon slurries (which will be dis-

cussed in more detail in a later section of this thesis) it

was found necessary to modify the analytical technique. To

prevent carbon from settling out of the solution and thus

insure a more homogeneous sample, it was decided to magnetic-

ally stir the carbon slurry during sample aspiration. It

was further decided to aspirate on a constant time rather

than a constant volume basis. This was found to work

exceptionally well using polyethylene bottles and teflon

coated magnetic bars in the bottles. Also, in order to

eliminate any background interference due to the presence

of the carbon particles in the samples, spectro grade carbon

from Union Carbide Corporation was added to the standard

reference solutions. The standards were also analyzed in

the same manner as the carbon slurry samples using the mag-
netic stirring technique described. It was also found
necessary to use capillary teflon tubing with a larger I.D.
opening - .025 to .032 inches - for aspirating the material
into the flame so as to prevent clogging due to agglomera-
tion of the particles present in the slurry. No change
was required in the burner itself.

B. Extraction of Metals from Carbon

The initial efforts of this phase of the research was
centered on devising a method for extracting the metals from
the carbons. Since some success had been reported in the
literature regarding an aqueous extraction for alkali metals
followed by acid extraction for alkaline earth and trans-
ition metals (13, 1), this approach was attempted. As men-
tioned in the introduction, three basic carbon types were
chosen for this study: coconut shell, petroleum and wood
base carbons. Each of the three carbons was treated iden-
tically as follows: The carbons were sieved to obtain fine
mesh carbon (-325 mesh and finer) to enhance the possibility
of extracting the major portion of the metals. After sieving,
the carbon was heated in an oven at 110°C, until a constant
weight was obtained, to insure complete removal of H_2O and
volatiles and thus obtain a true carbon base weight. Thirty
to forty grams of carbon, weighed to the nearest tenth of

a milligram, was placed in a 250 ml round bottom flask and
100 ml of distilled deionized water added. A reflux con-
denser was attached and the flask and contents were heated
with a glas-col heater at reflux temperature for a period
of six hours. The resulting slurry was then filtered hot
using a 5 cm Buchner funnel and Whatman #1 filter paper.
The carbon residue was then twice reslurried with 25 ml of
distilled deionized H_2O, heated to boiling, and filtered
as before. The filtrate was saved and stored in polyethy-
lene bottles which had previously been rinsed several
times with distilled deionized H_2O and oven dried at 100°C.
The carbon residue was then reslurried with 100 ml of a
60:40 by volume concentrated $HCl:H_2O$ solution and again
heated at reflux temperature for a period of six hours. The
slurry was then filtered hot using a 5 cm Buchner funnel and
two sheets of Whatman #1 filter paper. Two sheets of filter
paper were required to prevent breakdown of the paper by
the HCl solution. As before, the carbon residue was twice
reslurried with 25 ml of the 60:40 $HCl:H_2O$ solution, heated
to boiling and filtered as described. The filtrate was saved
in polyethylene bottles, rinsed and dried as described above.

Both the water and HCl extracts of the carbons produced
varied colored solutions indicating that either metals were
being extracted or the carbons contained organic impurities.

The water extract of the coconut shell carbon was amber colored while the extracts of the petroleum and wood base carbons were essentially colorless. The HCl extracts of the carbons were yellow-green, green and amber for the coconut shell, petroleum and wood base carbons, respectively.

Because the atomic absorption analyses of the solutions resulting from this first extraction did not correspond well with semi-quantitative spectrographic data on the carbons received from an outside source (22) (see Table 1), it was decided to ash each of the carbons and extract the ash in the same manner as the carbon extractions. It was anticipated that this would give a direct comparison on the completeness of the carbon extraction. It was further decided to repeat the carbon extractions using a larger Buchner funnel, thus providing a larger surface area for the filtration and thereby reducing the possibility of readsorption of the metals extracted.

The carbon extractions were repeated in exactly the same manner as previously described with the exception that a 12 cm Buchner funnel was used in place of the 5 cm funnel. Somewhat smaller carbon samples were used and the amount of extracting solvent was doubled. For the ash extraction, sieved samples of the carbons were oven dried at 110°C to constant weight and ashed in platinum crucibles at 900°C for a period of 8 to 10 hours. Approximately 3.5 to 5.0 grams of carbon, weighed

to the nearest tenth of a milligram, was used for the ashing.
The ash of each of the carbons was of a different color
indicating a difference in the metallic content of each. The
coconut carbon had an ash content of 4.1%, which was a brown
color. The petroleum base carbon showed an ash content of
2.2%, which was a reddish brown color, while the wood base
carbon had an ash content of 4.9%, which was a white color. The
ash was placed in polyethylene bottles, rinsed and dried as
previously described, and 50 ml of distilled deionized water
was added. The solution was permitted to stand 48 hours
with intermittent shaking, then filtered through a 12 cm
Buchner funnel using Whatman #1 filter paper. The ash resi-
due was twice reslurried with 25 ml of distilled deionized
H_2O and filtered as before. The filtrate was saved in rinsed
and dried polyethylene bottles and the ash residue was re-
slurried with 50 ml of a 60:40 by volume concentrated $HCl:H_2O$
(distilled and deionized) solution. The acid solution was
allowed to stand 48 hours with intermittent shaking, then
filtered through a 12 cm Buchner funnel using 2 sheets of
Whatman #1 paper. The ash residue was twice reslurried with
25 ml of the $HCl:H_2O$ solution and filtered as described. The
filtrate was saved in rinsed and dried polyethylene bottles.

Atomic absorption analyses on the second carbon extrac-
tions yielded somewhat higher results than the initial extrac-
tions; however, in general, the extracted ash samples yielded

higher results and were closer to the semi-quantitative spec-
trographic results previously mentioned (see Table 1).

As a result of these extractions it was concluded that
the metals were not being thoroughly enough extracted from
the carbons. It was felt that more intimate contact of the
carbon with the solvent was required over and above the mere
boiling and bubbling produced by refluxing. It was decided
to use the high speed stirring of a Waring Blendor for the
water extraction to obtain better contact of the water with
the carbon. For the HCl extraction the Waring Blendor could
not be used since the stirring blade was stainless steel and
the HCl would dissolve the blade. It was therefore decided
to utilize a magnetic stirrer with a teflon coated magnetic
bar.

Sieved, dried and weighed carbon samples of approximately
10 to 15 grams, weighed to the nearest tenth of a milligram,
were placed in a Waring Blendor and 100 ml of boiling distilled
deionized water was added. The slurry was stirred at high
speed for approximately 30 minutes, then filtered through a
12 cm Buckner funnel using Whatman #1 filter paper. The car-
bon residue was twice reslurried with 25 ml of boiling dis-
tilled deionized water, stirred at high speed in the Waring
Blendor for approximately 5 minutes, then filtered as described
above. The filtrate was saved and stored in polyethylene

bottles, rinsed and dried as described in the initial extrac-
tion procedure. The carbon residue was then slurried with
100 ml of a 60:40 by volume concentrated $HCl:H_2O$ solution
previously heated to boiling and placed in a thick walled
250 ml Erlenmeyer flask along with a teflon coated magnetic
stirring bar. The solution was stirred at as high a speed
as possible for a period of approximately 30 minutes, and
filtered through a 12 cm Buckner funnel using 2 sheets of
Whatman #1 filter paper. The carbon residue was reslurried
twice using 25 ml of the 60:40 $HCl:H_2O$ solution previously
heated to boiling, stirred with the magnetic stirrer for
approximately 5 minutes, and filtered as described. The
filtrate was saved and stored in rinsed and dried polyethy-
lene bottles.

For comparative purposes a second carbon ash extraction
on each of the samples was likewise carried out under identi-
cal conditions. The procedures followed are identical to the
initial ashing and the extractions were essentially parallel
to the above described extractions of the carbons.

Atomic absorption analyses on these extracts yielded for
the most part even lower values than the previous extractions
(see Table 1) and it appeared that an extraction of carbon
was not a particularly desirable route to follow.

Table 1

ATOMIC ABSORPTION ANALYSES ON CARBON AND CARBON ASH EXTRACTIONS

	Coconut Shell Carbon						Petroleum Base Carbon						Wood Base Carbon					
	Carbon Extractions			Ash Extractions			Carbon Extractions			Ash Extractions			Carbon Extractions			Ash Extractions		
Metal	1st	2nd	3rd	1st	2nd	Reported[1]	1st	2nd	3rd	1st	2nd	Reported[1]	1st	2nd	3rd	1st	2nd	Reported[1]
Na	.024	.038	.026	.104	.102	.01-1.0	.347	.385	.312	.467	.323	.01-1.0	.279	.431	.304	.035	.018	.1-1.0
K	.175	.234	.213	.430	.326	.1-1.0	.014	.012	.009	.009	.009	.01-.1	.004	.006	.003	.004	.001	.001-.1
Ca	.092	[2]	.059	.150	.042	.1-1.0	.003	.019	.005	.052	<.001	.01-1.0	.005	.035	.005	.044	.009	.01-1.0
Mg	.088	.150	.039	.065	.023	.001-.1	.007	.005	.003	.007	.002	.001-.01	.009	.006	.003	.011	.013	.001-.1
Fe	.037	.021	.007	.351	.214	.1-10.0	.111	.108	.027	.292	.154	.01-1.0	.001	.010	.009	.022	.053	.01-.1
Ni	.001	.003	.002	.005	.005	.001-.01	.016	.017	.016	.014	.009	<.001	.001	.043	.030	.006	.004	<.001
Cu	<.001	.001	.001	.002	<.001	.001-.01	<.001	.003	.003	.002	.001	.001-.01	<.001	.001	.009	.004	.003	.001-.01

[1] % Reported based on semi-quantitative spectrographic analysis by outside source (22)

[2] Ca determination could not be run due to faulty lamp which was thereafter replaced

Note: All percentages based on dry carbon weight

C. Carbon Slurry Method

In searching through the literature for more information regarding extraction procedures, an article by Gilbert (16) was uncovered that suggested the direct use of a slurry for flame photometric analysis. A second article by Mason (25) showed the practicality of the suggestion for the determination of K by flame photometry using a slurry of plant leaves. It was from these articles that the idea of using a carbon slurry was first conceived. If a carbon slurry could be used, this would completely eliminate the extraction procedures and result in a very rapid, simple and economical analytical technique.

Since no literature references could be found describing the use of a slurry on an atomic absorption spectrophotometer, initial attempts to develop a method were based on the slurry work conducted by Mason (25) on a flame photometer.

The first attempt was conducted on a glycerine-water-carbon slurry using various ratios of glycerine to water. No absorption for any of the metals was found. From observation it appeared that the solution tended to quench the flame, indicating the metals were not being vaporized in the flame. Because of the perceptible quenching effect it was decided to try low boiling organic solvents to enhance the burning. For this purpose acetone and ethanol were investigated and various

ratios of acetone and ethanol-water-carbon slurries were pre-
pared. The acetone-water-carbon slurries showed no absorption
for any of the metals, and they burned very rapidly with a
loud ringing whistle. The ethanol-water-carbon slurries showed
absorption for each of the metals tested and was the first
indication that the method would work. This particular com-
bination also burned rather rapidly and gave a low whistling
sound. It was decided to try isopropanol in place of the
ethanol, and this particular combination worked very well,
giving good absorption for each of the metals tested. A low
whistling sound was emitted only now and then. After trying
various ratios of isopropanol to water it was found that a
50:50 by volume ratio seemed to burn best and still yield good
absorption.

Carbon slurries with varying amounts of carbon had to be
prepared to have samples available for all operating ranges
of the metals under investigation, as well as to account for
the variation in concentration from metal to metal present in
the carbons. This was easily accomplished by merely weighing
out different amounts of the sieved and dried carbons on a
Mettler gramatic balance to the nearest tenth of a milligram,
and then preparing isopropanol-H_2O slurries with the different
weights of carbon.

Slurries were prepared containing .050, .100, .250 and

1.000 grams of each of the three carbons in a 100 ml 50:50 mixture of isopropanol and H_2O (distilled and deionized). Atomic absorption analyses were run on these slurries using the slurry concentration required to remain in the operating range of the metal under analysis. Results are shown in Table 2. To each of the standard reference solutions used in this analysis was added spectro grade carbon, sieved and dried to constant weight, corresponding to the concentration of carbon in the slurry sample being analyzed. These initial results were very encouraging, yielding values in the same neighborhood as that obtained from the carbon and carbon ash extractions, with the exception of the iron analysis. This particular isopropanol-water-carbon slurry was thus adopted as the best system for analyzing the carbons for trace metals by atomic absorption spectroscopy. The system was easy to prepare and eliminated the lengthy and cumbersome task of extracting the carbons or carbon ash residues with a solvent.

Effect of Carbon Particles

Since no previous atomic absorption analyses have been reported utilizing slurries, it was decided to investigate whether or not the particles in the solution were causing absorption interferences - either increases or decreases. To this end standard reference solutions of the three metals, K, Ca and Fe, with and without spectro grade carbon, were prepared in concentration ranges from 50 mg per 100 ml of solution to

Table 2

ATOMIC ABSORPTION ANALYSES ON CARBON SLURRIES

	Coconut Shell Carbon				Petroleum Base Carbon				Wood Base Carbon			
	% Found				% Found				% Found			
Metal	Carbon Slurry	Average Carbon Extr.	Average Ash Extr.	% Reported[1]	Carbon Slurry	Average Carbon Extr.	Average Ash Extr.	% Reported[1]	Carbon Slurry	Average Carbon Extr.	Average Ash Extr.	% Reported[1]
Na	.038	.029	.103	.01-1.0	.282	.348	.395	.01-1.0	.322	.371	.026	.1-1.0
K	.223	.207	.378	.1-1.0	.010	.012	.009	.01-.1	.002	.004	.002	.001-.1
Ca	.048	.071	.096	.1-1.0	.015	.009	.027	.01-1.0	.026	.015	.026	.01-1.0
Mg	.002	.092	.044	.001-.1	.002	.005	.004	.001-.01	.001	.006	.012	.001-.1
Fe	.005	.022	.283	.1-10.0	.007	.082	.223	.01-1.0	.004	.007	.038	.01-.1
Ni	.005	.002	.005	.001-.01	.004	.016	.012	<.001	.002	.025	.005	<.001
Cu	.001	.001	.001	.001-.01	.001	.002	.002	.001-.01	.001	.004	.004	.001-.01

All percentages based on dry carbon weight

[1] % Reported based on semi-quantitative spectrographic analysis by outside source (22)
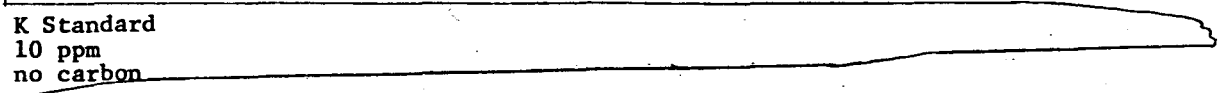
1.000 grams per 100 ml of solution. Atomic absorption analysis of the standards with and without carbon showed essentially no change in absorption for the slurry concentrations studied, as shown in Figures IV, V and VI. This, in effect, meant it was not necessary to add spectro grade carbon to the standard reference solutions. However, all analyses were conducted with the spectro grade carbon in the reference standards to eliminate the possibility of interferences.
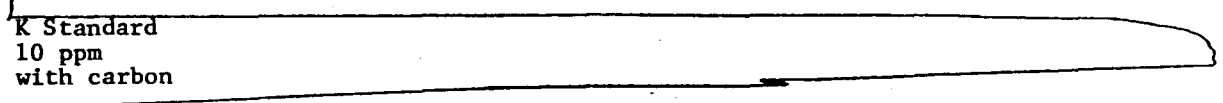
Ca Interference Studies

Atomic absorption analysis for Ca is subject to many interferences (40), the principal interference being P. It has been reported that most of these interferences can be eliminated by the addition of lanthanum to the sample solution (40). A study was therefore conducted on the effect of La concentration on absorption for both the standard solutions and the carbon slurry samples. In investigating the effect of adding La to the standard solutions, it was found that no increase or decrease in absorption occurred, up to a concentration of 5% La (the maximum tried). The use of La in the carbon slurries, however, produced a pronounced effect on readout and subsequently on the % Ca in the carbons, as shown in Table 3.

K Standard
10 ppm
no carbon

K Standard
10 ppm
with carbon

K Standard
6 ppm
no carbon

K Standard
6 ppm
with carbon
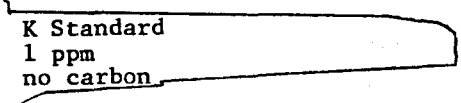
K Standard
3 ppm
no carbon

K Standard
3 ppm
with carbon

K Standard
1 ppm
no carbon

K Standard
1 ppm
with carbon

Figure IV

Atomic Absorption Spectrum of K Standards With and Without Spectro Grade Carbon

Figure V

Atomic Absorption Spectrum of Ca Standards With and Without Spectro Grade Carbon

Note: All standards contain 3.3% La

Figure VI

Atomic Absorption Spectrum of Fe Standards With and Without Spectro Grade Carbon

Note: All standards contain 10% by volume HCl

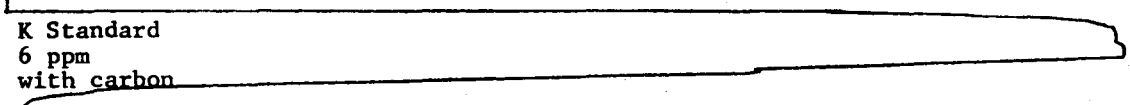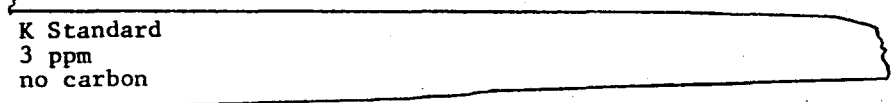Fe Standard
10 ppm
no carbon

Fe Standard
10 ppm
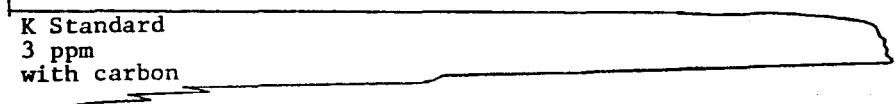with carbon

Fe Standard
5 ppm
no carbon

Fe Standard
5 ppm
with carbon

Fe Standard
2 ppm
no carbon

Fe Standard
2 ppm
with carbon

Fe Standard
1 ppm
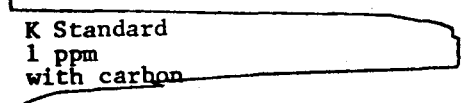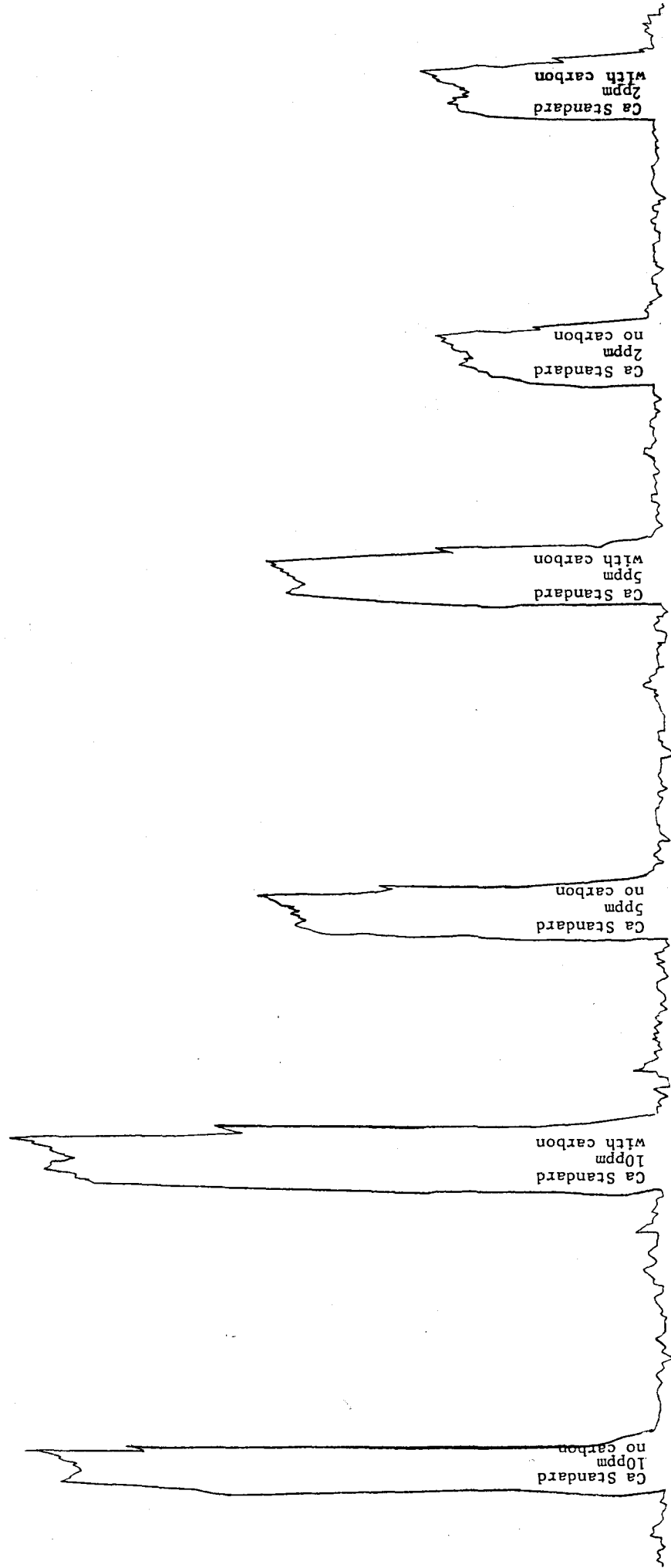no carbon

Fe Standard
1 ppm
no carbon
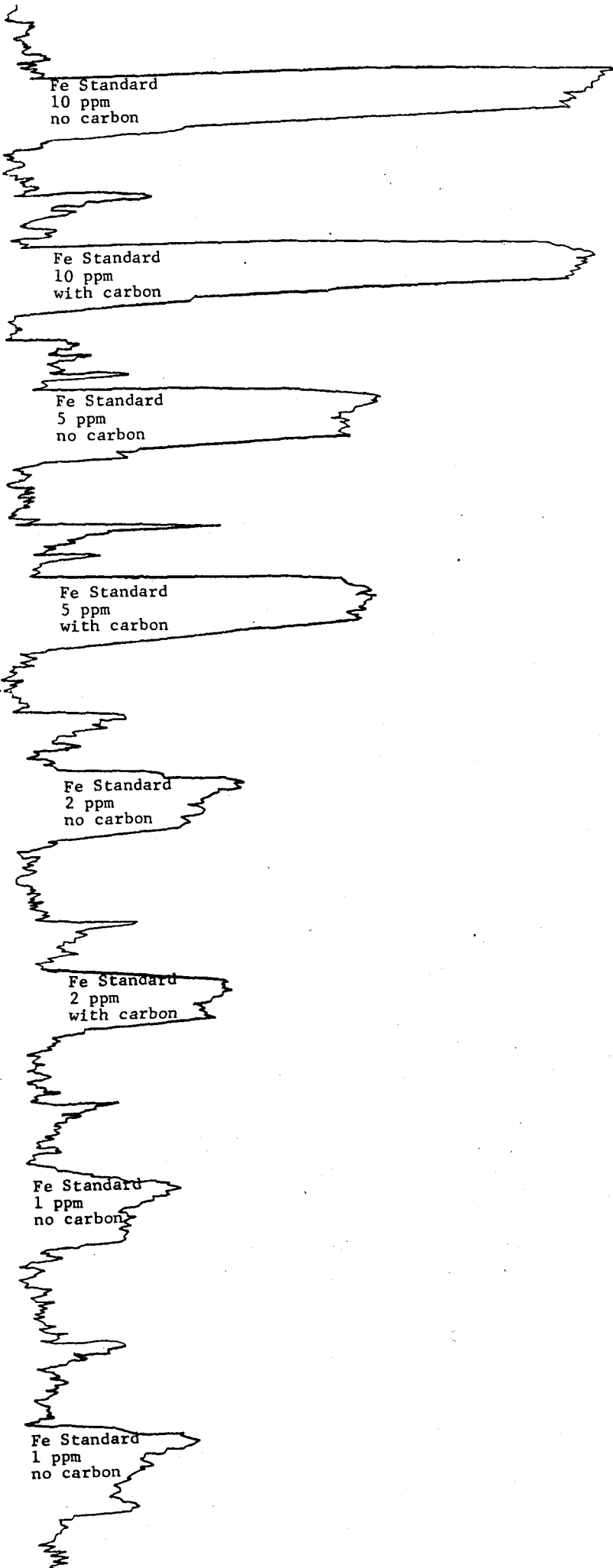
Table 3

EFFECT OF LANTHANUM ADDITION ON

ATOMIC ABSORPTION ANALYSIS OF CARBON SLURRIES FOR Ca

% La Added	Coconut Shell Carbon		Petroleum Base Carbon		Wood Base Carbon	
	% Ca Found	% Ca Reported	% Ca Found	% Ca Reported	% Ca Found	% Ca Reported
0.0	.010	0.1-1.0	.007	.01-1.0	.001	.01-1.0
0.7	.018	0.1-1.0	.011	.01-1.0	.015	.01-1.0
1.3	.052	0.1-1.0	.011	.01-1.0	.017	.01-1.0
2.0	.065	0.1-1.0	.011	.01-1.0	.021	.01-1.0
2.6	.095	0.1-1.0	.011	.01-1.0	.022	.01-1.0
3.3	.095	0.1-1.0	.011	.01-1.0	.022	.01-1.0

As a result of this series of analyses it was concluded that approximately 3.0 to 3.3% La must be added to the carbon slurry in order to determine the Ca content.

Fe Interference Studies

The initial atomic absorption analysis of the carbon slurries for Fe content yielded exceptionally low values, especially when compared to the carbon and carbon ash extraction results. In comparing the extraction and slurry techniques, HCl was the one variable missing in the carbon slurry. It was further noted that in order to prepare Fe standards it was necessary to use some HCl in order to solubilize the iron powder, and

even though the concentrated solution was diluted to prepare the lower concentration reference solutions, some HCl was still present in the standard solutions. It has been reported that oxide formation during burning is a possible absorption interference for various metals (39). It was postulated that HCl could help to prevent this potential interference either by prohibiting the formation of an iron oxide or solubilizing same if it did form. For this reason it was decided to investigate the addition of HCl to the carbon slurries as well as the reference standards. A series of runs using various concentrations of HCl in the standard solutions showed essentially no change in the absorption readings. The addition of HCl to the carbon slurries, however, resulted in a tremendous increase in the absorption readings and consequently the % Fe in the carbons. These results are shown in Table 4.

Table 4

EFFECT OF HCl ADDITION ON ATOMIC
ABSORPTION ANALYSIS OF CARBON SLURRIES FOR Fe

% by Vol. Conc. HCl	Coconut Shell Carbon		Petroleum Base Carbon		Wood Base Carbon	
	% Fe Found	% Fe Reported	% Fe Found	% Fe Reported	% Fe Found	% Fe Reported
0	.007	0.1-10.0	.010	.01-1.0	.002	.01-0.1
3	.044	0.1-10.0	.093	.01-1.0	.004	.01-0.1
6	.116	0.1-10.0	.221	.01-1.0	.012	.01-0.1
12	.102	0.1-10.0	.220	.01-1.0	.013	.01-0.1
25	.094	0.1-10.0	.187	.01-1.0	.011	.01-0.1

From this series of runs it is evident that HCl must be used for the determination of Fe by this carbon slurry technique. The most suitable concentration was found to be between 6 and 12% by volume of concentrated HCl. Using HCl concentrations above 12% resulted in serious peak variations making the absorption difficult to read with any degree of accuracy.

Standard Addition

In an attempt to check whether or not complete readout on the Ca and Fe analyses was being obtained, the standard addition technique was tried. This was accomplished by mixing 10 ml of a given carbon slurry with 10 ml of a standard reference solution. The results were exceptionally close to the calculated values as can be seen from the data in Table 5.

Table 5

ATOMIC ABSORPTION ANALYSES USING
STANDARD ADDITION TECHNIQUE

ppm Added	ppm in Carbon Slurry	ppm Expected	ppm Found
5 ppm Fe	1.1 ppm Fe (petroleum base carbon)	6.1	6.2
5 ppm Fe	1.3 ppm Fe (wood base carbon)	6.3	6.2
2.5 ppm Ca	2.4 ppm Ca (coconut shell carbon)	4.9	5.1
5 ppm Ca	2.4 ppm Ca (coconut shell carbon)	7.4	7.2
5 ppm Ca	1.1 ppm Ca (petroleum base carbon)	6.6	6.6

The results on standard addition indicate that all the Ca and Fe was actually being read during the analyses.

Concentration Effects

In order to check the effect of concentration, slurries containing varying amounts of carbon were run, provided they would still yield values within the operating range of a given metal. The results in Table 6 show that no significant differences due to carbon concentration were found provided the analyses were carried out within the operating range for a given metal.

Table 6

Carbon Slurry Concentration	Metal Under Analysis	Type Carbon	ppm Metal Found
250 mg/100 ml	Ca	wood base	1.2
1.000 gram/100 ml	Ca	wood base	4.9
250 mg/100 ml	Fe	coconut shell	4.9
1.000 gram/100 ml	Fe	coconut shell	20.0

Addition of Interfering Metals

In order to check the effects of two elements known to be present in carbons to a large extent - Al and Si - it was decided to add calibrated amounts of these elements to the carbon slurries and standard solutions to see if interferences

could be detected and at what concentration level. For this
purpose silicic acid and $AlCl_3$ were added in varying amounts
to the slurries and standards. In each case the %La and HCl
previously found most suitable was also added. Results of
these additions are shown in Table 7.

Table 7

EFFECT OF ADDING Si AND Al ON ATOMIC ABSORPTION ANALYSIS
OF CARBON SLURRIES AND STANDARD SOLUTIONS FOR Ca AND Fe

Effect on Standard Solutions

Additive Conc.	Standard Solution	ppm Read
ppm Si	ppm Ca	
0	10	10.0
10	10	10.0
25	10	9.5
50	10	10.5
100	10	10.0
ppm Si	ppm Fe	
0	10	10.0
10	10	10.2
25	10	9.8
50	10	10.0
100	10	9.7
ppm Al	ppm Ca	
0	10	10.0
10	10	10.0
25	10	10.5
50	10	9.5
100	10	10.5
ppm Al	ppm Fe	
0	10	10.0
10	10	10.0
25	10	10.1
50	10	9.9
100	10	10.0

Effect on Carbon Slurries

Additive Conc.	Carbon Slurry	Ca ppm Read	Fe ppm Read
ppm Si			
0	coconut shell	12.0	10.0
10	"	12.5	10.0
25	"	13.0	9.8
50	"	12.5	9.6
100	"	13.0	10.2
ppm Al			
0	"	12.0	10.0
10	"	13.0	10.2
25	"	14.0	9.8
50	"	13.5	9.8
100	"	13.0	10.1

From these results it is concluded that the addition of Si and Al causes interference for the determination of Ca in the carbon slurries but does not interfere with the standard solutions. The Ca interference shows up as an _increase_ in absorption, which is rather surprising. If anything, one would expect a decrease in absorption. A second surprising anomaly is the fact that the interference reaches a maximum (at a concentration of approximately 25 ppm), and levels off regardless of further addition of Si or Al. The reason for these unexpected results is not understood at this time and will require a more detailed study for complete understanding.

IV. Method Developed

A. Preparations

Preparation of Carbon Slurries

The carbon to be analyzed was sieved (ground if necessary)
to -325 mesh or smaller. It was then oven dried at 110°C to
constant weight in order to obtain a dry carbon weight for
calculation of percent metal content.

Slurries were prepared by weighing out .0500, .1000, .2500
and 1.000 gram samples of each of the carbons, and adding a
50:50 by volume isopropanol:water (distilled and deionized)
solution to each to bring the volume up to 100 ml.

Preparation of Standard Solutions

Concentrated solutions, containing 1000 ppm of each of the
metals to be analyzed for, were prepared in accordance with
the procedure outlined on page 18 . Aliquots of each of the
concentrated solutions were used to prepare standard reference
solutions, within the operating range of each particular metal,
in order to establish absorbance versus concentration calibra-
tion curves. The following series of standard reference solu-
tions were prepared using a 50:50 isopropanol:water (distilled
and deionized) medium:

Na - Solutions of 1, 2, 4 and 5 ppm
K - Solutions of 1, 3, 6 and 10 ppm
Ca - Solutions of 2, 5, 10, 15 and 20 ppm

Mg - Solutions of 0.5, 1.0, 2.0 and 5.0 ppm

Fe - Solutions of 2, 5, 10, 15 and 20 ppm

Ni - Solutions of 3, 5, 9, 15 and 25 ppm

Cu - Solutions of 0.5, 1.0, 1.5 and 2.5 ppm

A standard solvent reference was also prepared of 50:50 iso-propanol:water to check for the presence of any of the metals in the solvent. All standard solutions were stored in rinsed and dried polyethylene bottles.

Spectro grade carbon was added to each of the standard reference solutions to simulate the effect of solid particles in the solutions, and potential absorption interferences possible with the carbon slurry samples. This was accomplished by merely weighing out samples of sieved and oven dried spectro grade carbon to correspond to the weights of carbon in the samples under analysis. To each of these slurries in polyethylene bottles was added a teflon-coated magnetic stirring bar to insure that a homogeneous sample was being taken during aspiration into the flame.

Preparation of Atomic Absorption Spectrophotometer

The setting up of the spectrophotometer followed the identical procedure for each metal, with minor variations, principally instrumental adjustments. The sharp line source lamp of the metal under analysis was inserted and the recommended amperage applied. The lamp was permitted to warm up for a

period of 30 minutes, during which time the slit opening, proper wave length, spectrum setting and energy level were adjusted. After the 30-minute warm up period, the burner was lit by first adjusting the air flow to approximately 9 liters/minute, then gradually increasing the acetylene flow while holding a flame to the burner until the acetylene flow reached approximately 8 liters/minute. Minor adjustments were made on the air and acetylene flow to regulate the flame and insure an even steady flame. The automatic absorption recorder was turned on and standard solutions, covering the entire operating range of the metal under analysis, were aspirated into the flame and the recorder adjusted to cover this entire operating range. The burner and aspirator lines were cleaned by aspirating distilled deionized water into the flame, after which the spectrophotometer was ready for the analysis.

B. Procedure

Analysis of Carbon Slurries

The analysis on the carbon slurries was carried out in an identical manner for each particular metal. The analysis was started by first aspirating the solvent being used - in all cases a 50:50 solution of isopropanol:water. This was followed with a distilled deionized H_2O blank. Each of the standard solutions was aspirated, one at a time, with a distilled deionized H_2O blank between each of the standards.

Because spectro grade carbon was added to the standards, each was stirred with a magnetic stirrer while aspirating for a period of one minute. After running the standards, the carbon slurries were run for each of the carbons under study, and as before, a distilled deionized water blank was run between each carbon slurry. After the slurries were analyzed the standard solutions were again run as previously described to insure that no change in absorption had occurred. Where a given carbon slurry showed absorption higher than the sets of standards, a less concentrated slurry was run to bring the absorption within the operating range. All slurried samples were aspirated for 1 minute using magnetic stirring to insure a homogeneous sample. In all cases where an additive was required to prevent interferences from other elements, the additive was also added in the same concentration to the standard solutions.

Interpretation of Results

Each time an absorption analysis for a given metal was run, an absorbance versus concentration calibration curve was drawn. This was accomplished by converting the % absorption, read from the automatic recorder, to absorbance, then plotting absorbance versus the concentration in ppm (mg per liter) for the standards of the given metal under consideration. A typical calibration curve for K has already been

shown in Figure III. The calibration curves for Ca and Fe were also linear for the ranges studied showing the following line slopes - Ca .030 absorbance units per ppm Ca, and Fe .029 absorbance units per ppm Fe. Using the calibration curves thus obtained, the concentration of the metals in the carbon slurries was determined by reading from the calibration curves the concentration in ppm corresponding to the absorbance, as determined from the % absorption shown on the recorder for the given carbon slurry. To determine the weight of metal in the carbon, the concentration in ppm of the slurry was multiplied by the total original volume of the slurry and divided by 1,000,000 to yield the grams of metal:

$$\text{grams of metal} = \frac{\text{ppm found by analysis x original volume of slurry in ml}}{1,000,000}$$

The percentage metal in the carbon was then calculated by multiplying the grams of metal found by 100 and dividing by the weight (in grams) of carbon originally used to form the slurry:

$$\% \text{ metal in carbon} = \frac{\text{grams of metal found x 100}}{\text{grams of carbon used to form slurry}}$$

V. Results Employing the Method

It was decided from the beginning of this research program to concentrate on the analysis of the carbons for K, Ca, and Fe, principally because these metals vary so greatly

from carbon to carbon. Once the best method was established,
no further work was conducted on the other four metals pre-
viously reported on - Na, Mg, Ni and Cu.

K Determination

Of the three metals studied, K was without any doubt the
least troublesome. Instrumental conditions and settings for
K analysis were as follows:

wave length: 383 mμ
spectrum range: visible
slit opening: 4
sharpline source: Osram
 discharge lamp - 700 m amp

acetylene - air flow: 8 1/min.-
                      9 1/min.
aspiration rate: 2 ml/min.
recorder noise suppression
 setting: 3
readout scale: x3

A repeat of the initial attempt at using a slurry produced
essentially identical results as can be seen in Table 8.

Table 8
ATOMIC ABSORPTION ANALYSIS OF CARBON SLURRIES FOR K

	Coconut Shell Carbon		Petroleum Base Carbon		Wood Base Carbon	
	% K Found	% K Reported	% K Found	% K Reported	% K Found	% K Reported
Initial Analysis	.223	0.1-1.0	.010	.01-0.1	.002	.001-0.1
Repeat Analysis	.218	0.1-1.0	.009	.01-0.1	.002	.001-0.1

A typical absorption spectrum for K in the carbon slurries is
shown in Figure VII. The results fall within the range of
the semi-quantitative spectrographic data and in general agree

K Standard
10 ppm

K Standard
6 ppm

K Standard
3 ppm

K Standard
1 ppm

Coconut Shell
Carbon Slurry

Petroleum Base
Carbon Slurry

Wood Base
Carbon Slurry

Figure VII

Typical Atomic Absorption Analysis Spectrum for K

Note: All standards contain spectro grade carbon
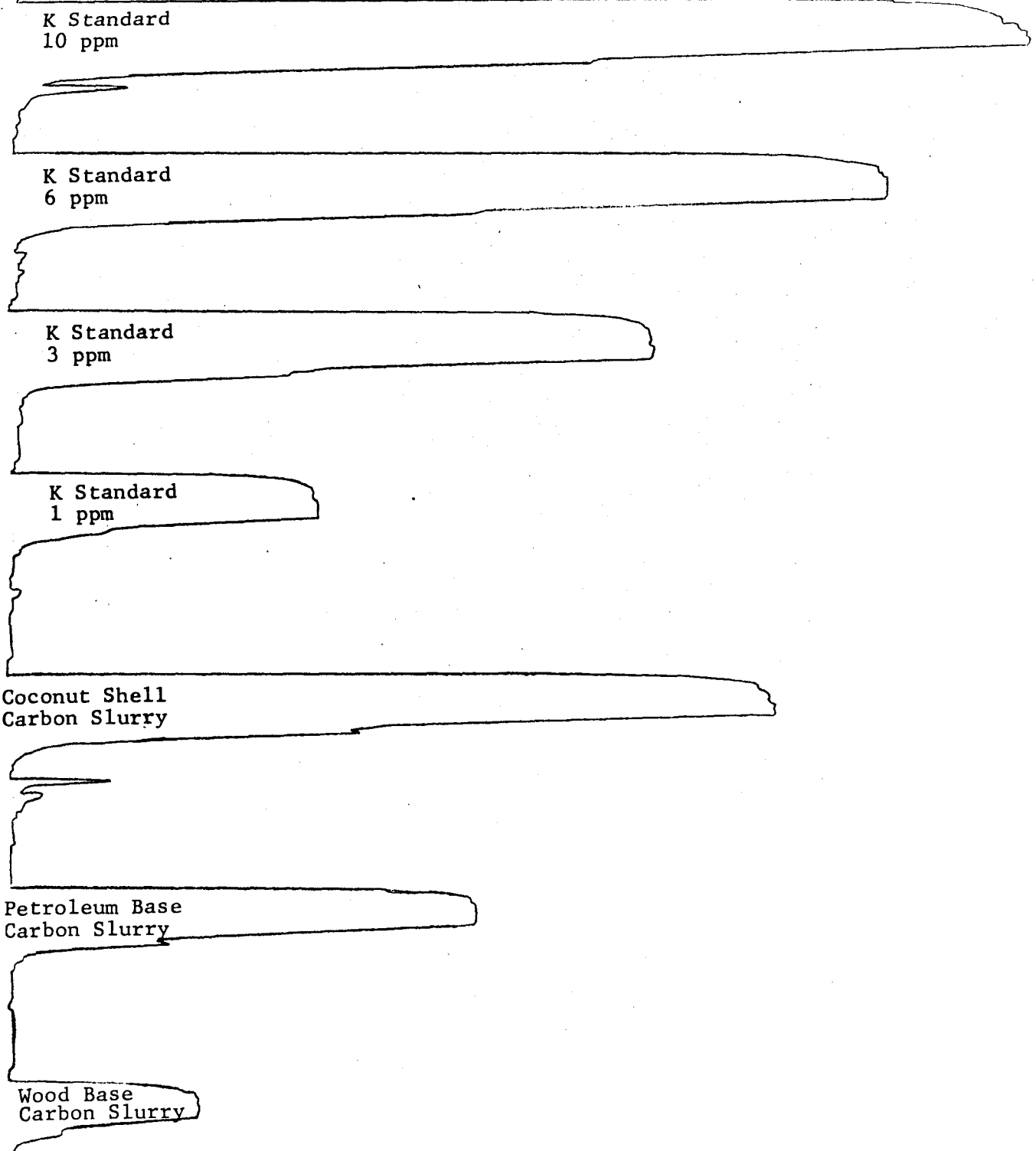
quite well with the carbon ash extraction data.

Ca Determination

The Ca analyses were carried out using 3.3% La in both the standard and carbon slurry solutions as found necessary from the Ca interference studies. The following instrumental conditions were employed in the analysis for Ca:

wave length: 212 mμ

spectrum range: visible

slit opening: 4

sharpline source: hollow cathode lamp - 10 m amp

acetylene - air flow: 8 1/min.- 9 1/min.

aspiration rate: 2 ml/min.

recorder noise suppression setting: 3

readout scale: x3

Several repeat runs showed exceptionally good reproducibility as shown in Table 9.

Table 9

### ATOMIC ABSORPTION ANALYSIS OF CARBON SLURRIES FOR Ca

Run #	Coconut Shell Carbon		Petroleum Base Carbon		Wood Base Carbon	
	% Ca Found	% Ca Reported	% Ca Found	% Ca Reported	% Ca Found	% Ca Reported
1	.095	0.1-1.0	.011	.01-1.0	.022	.01-1.0
2	.090	0.1-1.0	.012	.01-1.0	.024	.01-1.0
3	.096	.01-1.0	.010	.01-1.0	.022	.01-1.0
4	.098	.01-1.0	.014	.01-1.0	.023	.01-1.0
Average	.095	.01-1.0	.012	.01-1.0	.023	.01-1.0

A typical absorption spectrum for Ca in carbon slurries is shown in Figure VIII. As with the K determinations, these results

Figure VIII

Typical Atomic Absorption Analysis Spectrum for Ca

Note: All standards contain spectro grade carbon and 3.3% La

All carbon slurries contain 3.3% La
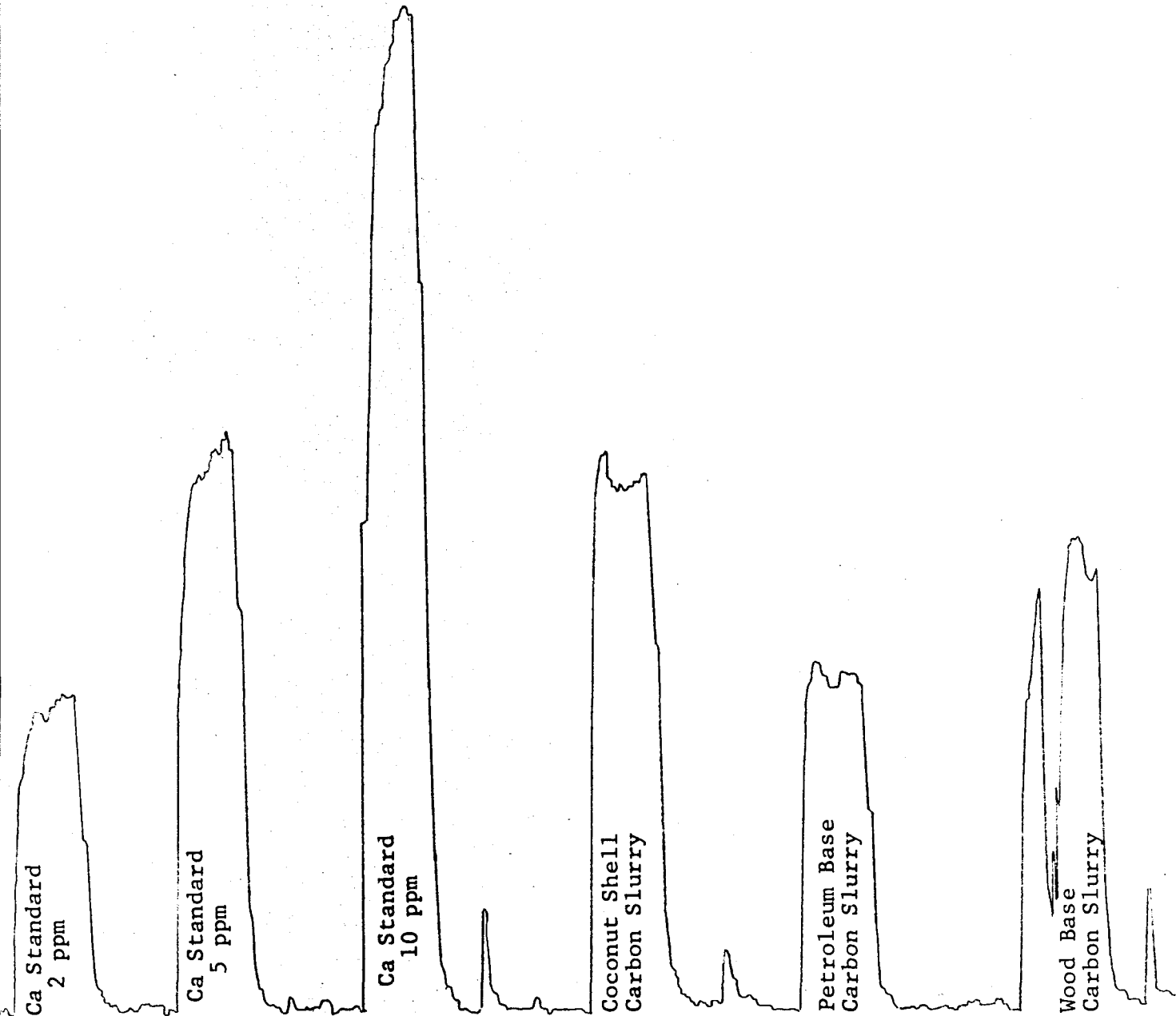
fall within the reported range found by the semi-quantitative spectrographic analysis, and show fairly good agreement with the carbon ash extraction data.

Fe Determination

For the Fe analysis 12% by volume of concentrated HCl was used in both the standard and carbon slurry solutions as found necessary from the Fe interference studies. The instrumental conditions found most suitable for the Fe analysis were as follows:

wave length: 372 mμ
spectrum range: UV
slit opening: 3
sharpline source: hollow
  cathode lamp - 20 m amp

acetylene - air flow: 8 1/min.-
                                9 1/min.
aspiration rate: 2 ml/min.
recorder noise suppression
  setting: 3
readout scale: x3

Results of several runs listed in Table 10 indicate that good reproducibility is obtainable with this slurry technique.

Table 10

ATOMIC ABSORPTION ANALYSIS OF CARBON SLURRIES FOR Fe

Run #	Coconut Shell Carbon		Petroleum Base Carbon		Wood Base Carbon	
	% Fe Found	% Fe Reported	% Fe Found	% Fe Reported	% Fe Found	% Fe Reported
1	.116	0.1-10.0	.220	.01-1.0	.013	.01-0.1
2	.112	0.1-10.0	.193	.01-1.0	.009	.01-0.1
3	.104	0.1-10.0	.201	.01-1.0	.010	.01-0.1
4	.101	0.1-10.0	.186	.01-1.0	.009	.01-0.1
Average	.108	0.1-10.0	.200	.01-1.0	.010	.01-0.1

A typical absorption spectrum for Fe in the carbon slurries is shown in Figure IX. As with the Ca and K results, these Fe results likewise fall within the reported range found by a semi-quantitative spectrographic analysis, and agree rather well with the carbon ash extraction data.

A summary of the results of the atomic absorption analyses for K, Ca and Fe by the three methods - carbon slurry, direct carbon extraction and carbon ash extraction - is listed in Table 11.

Figure IX

Typical Atomic Absorption Analysis Spectrum
for Fe in Carbon Slurries

Note: All standards contain spectro grade carbon and 12% by volume HCl
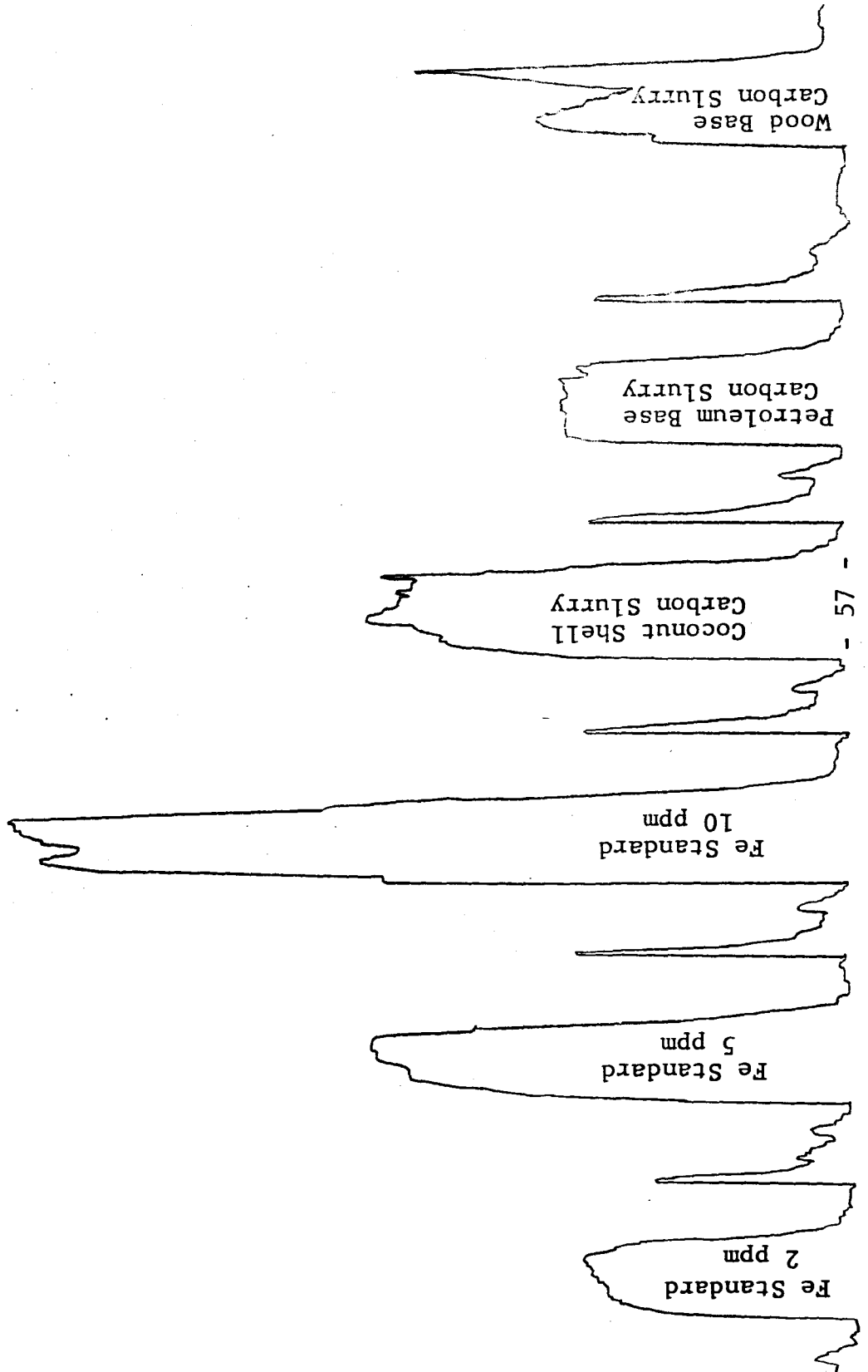   All carbon slurries contain 12% by volume HCl

Wood Base
Carbon Slurry

Petroleum Base
Carbon Slurry

Coconut Shell
Carbon Slurry

Fe Standard
10 ppm

Fe Standard
5 ppm

Fe Standard
2 ppm

- 57 -

Table 11

SUMMARY OF ATOMIC ABSORPTION ANALYSES

BY SLURRY, DIRECT EXTRACTION AND ASH EXTRACTION METHODS

Metal	Coconut Shell Carbon				Petroleum Base Carbon				Wood Base Carbon			
	Carbon Slurry	Direct Extr.	Ash Extr.	% Reported	Carbon Slurry	Direct Extr.	Ash Extr.	% Reported	Carbon Slurry	Direct Extr.	Ash Extr.	% Reported
K	.220	.207	.378	0.1-1.0	.010	.012	.009	.01-0.1	.002	.004	.002	.001-0.1
Ca	.095	.071	.096	0.1-1.0	.012	.009	.027	.01-1.0	.023	.015	.026	.01-1.0
Fe	.108	.022	.283	0.1-10.0	.200	.082	.223	.01-1.0	.010	.007	.038	.01-0.1

VI. Discussion

From the results it appears that a carbon slurry tech-
nique can be used to determine trace elements in carbons by
atomic absorption and yield fairly reproducible results.
The method completely eliminates the laborious and time con-
suming task of extracting and/or ashing while still yielding
comparative results (see Table 11). The atomic absorption
values compared very favorably, within the order of magnitude,
with results received on a semi-quantitative spectrographic
analysis of the carbons run by an independent source. The
validity and reliability of the results obtained by this
slurry method were further strengthened by the standard
addition, carbon slurry concentration, and interference studies.
The standard addition studies definitely pointed out that all
of the metal added to the slurry was read, with none being
absorbed or held by the carbon. If the carbon had been
holding a portion of a metal, permitting only a certain
amount to be read out, on standard addition of the metal one
would expect a similar lowering of reading. This was not
experienced, however, since in all cases the readings matched
very closely with the predicted calculated values (see Table 5).
The carbon slurry concentration studies further pointed out
that the read out was linear with carbon concentration, again
indicating that complete read out of the metal was obtained.

The interference studies, however, especially with Ca and Fe, leave some doubt as to complete read out using this method. Although it was shown in Tables 3 and 4 that addition of La and HCl, respectively, reached a maximum read out, then leveled off in the case of Ca and fell off at higher concentrations for Fe, this does not 'per se' mean that the maximum reached represents complete read out of the metals. The possibility of the metals being bound in a complex or matrix, thereby prohibiting read out, still exists. On the other hand, repeat analyses at the maximum read out showed that the results obtained using this method are certainly reproducible (see Tables 8, 9 and 10) and quite reliable as compared to the semi-quantitative spectrographic analysis.

The overall precision of the method is in the neighborhood of ±10%.

SUMMARY

A simple, rapid and economical method has been developed for the determination of trace amounts of metals in carbons, specifically for K, Ca and Fe. Finely ground carbon, sieved and dried to constant weight, is slurried in an aqueous-isopropanol solution, then analyzed on an atomic absorption spectrophotometer for the individual metals present. The amount of metal present is determined by direct comparison of results with values obtained for standard solutions of the metal under investigation. To insure comparability of the standards with the carbon slurries, spectro grade carbon is added to the standards in the same amounts as present in the carbon slurries under analysis. In order to insure sample homogeneity during analysis, all solutions are stirred by means of a magnetic stirrer.

This particular carbon slurry method eliminates the lengthy and cumbersome task of extracting the metals from the carbons or carbon ash residues while yielding more reproducible results. Results obtained with this method compare favorably with semi-quantitative results obtained by emission

spectroscopy.

To the author's knowledge, this is the first time a slurry or suspension of solids has been analyzed directly on an atomic absorption spectrophotometer, although it has been previously suggested as feasible by Gilbert (16) as a result of his work using flame photometry.

This method, which is essentially a method for analyzing solids directly, will not only have wide applications in many other fields, but it will also serve to increase the scope and range of the atomic absorption spectrophotometer.

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AUTOBIOGRAPHY

I, Leo Francis Meyer, was born on July 19, 1929 in McKees Rocks, Pennsylvania, where I attended elementary school, graduating in 1943. I graduated from St. Fidelis Seminary High School in Herman, Pennsylvania in 1947. In 1949 I enlisted in the U.S. Marine Corps reserve and was called to active duty in 1950 for a period of two years. In February of 1953 I enrolled at Duquesne University in Pittsburgh, Pennsylvania, graduating with a B.S. in Chemistry in June of 1956. Upon graduation I accepted a position as a research chemist with the Gulf Research and Development Center in Harmarville, Pennsylvania, and enrolled for graduate study at Carnegie Institute of Technology. In 1961 I accepted a position at the Philip Morris Research Center, having been employed there since as a research scientist.