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DEVELOPMENT OF A NEW CARBON FURNACE FOR ATOMIC ABSORPTION SPECTROMETRY. STUDIES ON SPECIATION OF LITHIUM IN BLOOD

The Louisiana State University and Agricultural and Mechanical Col. Ph.D. 1984

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DEVELOPMENT OF A NEW CARBON FURNACE FOR ATOMIC ABSORPTION SPECTROMETRY. 
STUDIES ON SPECIATION OF LITHIUM IN BLOOD.

A Dissertation

Submitted to the Graduate Faculty of the 
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requirements for the degree of 
Doctor of Philosophy

in

The Department of Chemistry

by

Thomas Arthur Ekman 
B.A., Arkansas College, 1978

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DEDICATION

TO: Melissa Ann Seay Ekman

"You're My Best Friend"

- Queen
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ABSTRACT

PART ONE. DEVELOPMENT OF A NEW CARBON FURNACE FOR ATOMIC ABSORPTION SPECTROMETRY.

A new, multipurpose carbon furnace was designed and tested for quantitative atomic absorption spectrometry. The furnace had two separately controlled heating chambers, one for vaporization of the sample and the other for atomization of the sample.

Basically, three modes of furnace operation were investigated. Quantitation was investigated with (a) the atomization section hot and (b) the atomization section cold, for trapping before atomization. The vaporization section was heated quickly in each case. Speciation of lead compounds was carried out by slowly heating the vaporization section, while the atomization section was hot. Variations on these basic methods (including the use of a carbon rod sampling device) were also studied. Elements investigated included lead, mercury, zinc, copper, nickel, tin, arsenic, and magnesium. The new furnace design was shown (i) to eliminate sample loss, (ii) to reduce molecular background absorption, (iii) to be capable of many different modes of operation and (iv) to be capable of speciation. It was much more versatile than commercially available models.

PART TWO. STUDIES ON SPECIATION OF LITHIUM IN BLOOD.

The use and efficacy of lithium in the treatment of certain mental disorders is well known, but its mode of action is not known. Several studies were carried out
with the goal of detecting two or more lithium species in the blood serum of mental patients undergoing lithium treatment. "Coupled" techniques investigated included liquid chromatography - furnace atomic absorption, liquid chromatography - inductively coupled plasma atomic emission, liquid chromatography - flame atomic emission and evolved gas analysis - flame atomic emission. For various reasons, data obtained with these techniques were inconclusive. Li - 7 Fourier transform/nuclear magnetic resonance was used to detect two lithium peaks, which indicated the possible presence of two lithium species in the blood serum of two mental patients undergoing lithium treatment.
PART ONE

Development of a New Carbon Furnace for Atomic Absorption Spectrometry
I. INTRODUCTION

In order to understand better the significance of the work presented in Part One of this dissertation, it is necessary to review some of the major advances in the field of electrothermal atomic absorption spectrometry (or carbon furnace atomic absorption spectrometry), as well as some of the problems associated with the technique.

A. DEVELOPMENT OF ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Since first introduced by Walsh in 1955 [1], atomic absorption spectrometry (AAS) has become the most widely used method for determining trace levels of metals. The hollow cathode lamps and flame atomizers, used in his pioneering work, are still the most popular light sources and atomizers.

Flames do have some serious disadvantages as atomization cells, however:

1) Flames present a hostile environment for atoms. Many elements are converted very quickly to an oxide, which cannot undergo atomic absorption. 2) Nebulizers for flame atomizers have been found to have a transport efficiency of only 6 - 7% [2]. Therefore, most of the sample is lost and never reaches the flame, decreasing sensitivity. 3) The sample is effectively diluted by the flame gases, reducing sensitivity. 4) Relatively large sample volumes are required, on the order of several milliliters. 5) Solids must be dissolved before they can be analyzed. 6) Work at short wavelengths is difficult because the flame gases absorb strongly near the vacuum ultraviolet region.

Many of these problems were overcome by electrothermal atomization. The
first practical electrothermal atomizer for analytical spectroscopy was reported by
L'vov in 1961 [3]. The device, shown in Figure 1, consisted of a tantalum foil lined
carbon tube. The tube, through which the light path passed, was heated
resistively by passing electrical current through it. Sample was placed on the end
of a carbon electrode and dried. The sample electrode was inserted into the
preheated furnace tube and heated by an electrical arc from a secondary electrode.
Atomization took place as the sample vaporized from the hot electrode surface and
entered the hot furnace environment. A pulse of atoms entered the light path. The
absorption peak height was related to the absolute mass of analyte inserted into
the furnace.

The L'vov furnace provided excellent sensitivity, but rather poor precision and
accuracy. In addition, the furnace, as originally designed, was inconvenient to
use and did not fit into commercial atomic absorption instruments.

Massman [4] and West [5] introduced electrothermal atomizers which were
eventually adapted for use with commercial atomic absorption instruments. The
quartz "T" simultaneously introduced by Robinson [6] was not developed because of
the cumbersome radio frequency generator used.

The Massman furnace consisted of a hollow tube of carbon, through which
the light path passed. Liquid sample was placed on the wall of the unheated
furnace. Then, the furnace was quickly heated, vaporizing and atomizing the
sample. This atomizer was made available commercially by the Perkin-Elmer
Corporation [7] for use with their atomic absorption instruments (Figure 2).

The West atomizer consisted of a carbon filament, which was 2 mm in
Figure 1
Early Carbon Atomizer Designs

L'vov Furnace

West Carbon Filament Atomizer

Mini - Massman Atomizer
Figure 2
Commercial Carbon Atomizers

Perkin - Elmer Heated Graphite Atomizer

Varian Carbon Rod Atomizer
diameter (Figure 1). A liquid sample was placed on the surface of the unheated carbon filament. The filament was heated rapidly, releasing an atomic cloud into the light path, just above the filament. The West carbon filament atomizer was the prototype for a wide variety of carbon and metal filament atomizers [8 - 13].

The area immediately above the carbon filament did not provide a good environment for atomic stability. This problem prompted Amos [14] to drill a hole through the carbon rod (Figure 1). A liquid sample was placed inside the hole, which also served as the light path. The carbon rod was quickly heated, sending the atomized sample into the light path. This "mini-Massman" atomizer was offered, with modifications, by Varian Instruments, for use with their atomic absorption instruments (Figure 2).

Even though the commercial furnaces were inspired by the L'vov furnace, they differed in one major way. The L'vov furnace offered an isothermal environment in which to atomize the sample. The commercial furnaces utilized a cyclic heating program. Sample was placed in the unheated furnace, which was then quickly heated to a high temperature. The analyte was vaporized into an environment which had a constantly changing temperature.

More importantly, the temperature at which the analyte was released was highly dependent upon the sample matrix. This phenomenon was known as the matrix effect. The sample matrix consisted of the solvent, dissolved solids and any organic material, (all of the sample - except for the analyte). The temperature at which the analyte was vaporized had a great effect on the sensitivity, which usually increased with increasing temperature. Since standards and samples
frequently had very different matrices (eg. aqueous standards and urine samples),
the matrix effect was a serious problem.

Several different approaches have been proposed to overcome matrix effects. The easiest way was to dilute the sample in order to approximate the pure water matrix of the aqueous standards. Often, when the sample was diluted enough to eliminate the matrix effect, the analyte was too dilute to be detected.

An obvious way to correct for the matrix effect was to matrix match the sample and standards. For example, standards used for urine analyses would have the same concentrations of major salts (and perhaps proteins) as the sample itself. A not so obvious problem, was the wide variety of matrices possible for the same type of sample. In the case of urine samples, salt concentrations could vary widely, especially for ill patients.

The time-honored method of standard addition had been applied with success to furnace AAS. Unfortunately, this extended an already lengthy analysis time from 1 - 2 min to 3 - 10 min. The long analysis time negated some of advantages of furnace AAS, because flame AAS required only a few seconds of analysis time.

No reasonable method for dealing with the matrix effect in furnace AAS was available until 1975, when Ediger introduced the concept of matrix modification [15]. This method utilized the addition of one or more reagents to the sample. Matrix modification worked in one of several ways. 1) The analyte could be trapped in the salt lattice of the matrix modifier. This would allow a higher ashing temperature to be used to drive off the native sample matrix [16]. The only matrix left would be the added matrix, which should be the same from sample to sample.
2) Sample matrix could be removed, before vaporization of the analyte, by chemical reaction with the matrix modifier. An example was the volatilization of chloride as HCl [17]. 3) Various reducing agents, used as matrix modifiers, have increased analyte sensitivity [18, 19], presumably by providing a better reducing environment inside the furnace. However, a disadvantage was that matrix modification increased the possibility of contamination of sample and/or standards, through the use of impure reagents. When working at trace levels, this was a serious problem.

In 1978, L'vov proposed another method for dealing with the matrix effect [20]. He suggested that a thin, rectangular plate of carbon be placed inside commercial furnaces, Figure 3. This device became known as the L'vov platform. The platform was heated only by radiation from the surrounding furnace. A sample placed on the platform was heated more slowly than the furnace itself. The analyte vaporization was delayed until the furnace was at a high, nearly stable temperature. Under these conditions, matrix effects have been, reportedly, reduced [21, 22]. Together with matrix modification, the L'vov platform has been able to completely overcome matrix effects in certain systems [23 - 25]. However, the above platform did not totally eliminate matrix effects by itself. If matrix modification was used, in conjunction with the L'vov platform, then the possibility of contamination of sample and/or standards was enhanced.

The success of the L'vov platform inspired the development of two related techniques. Lawson and Woodriff designed a double walled furnace that delayed analyte vaporization until the furnace temperature was high and nearly constant
Figure 3

Atomization with the L'vov Platform and the Probe

Atomization with the L'vov Platform

Probe Atomization
Holcombe and Sheehan developed a furnace technique termed "second surface atomization" [27]. The analyte was trapped on a cool carbon plug during the charring step. The large mass of the carbon plug prevented it from heating as quickly as the furnace itself. Thus, during atomization, the vaporization and atomization of the analyte was delayed, until the furnace reached a high, nearly stable temperature. Both designs, like the L'vov platform, resulted in reduced matrix effects.

L'vov also proposed the use of "probe atomization" or "constant temperature atomization" [28]. In this method, the sample was placed on the end of a tungsten or carbon filament. The filament was placed near a heated furnace to dry and char the sample. After the commercial furnace had been heated to the atomization temperature, the probe was plunged in. The analyte was vaporized into a constant temperature furnace, in a manner similar to the L'vov furnace. Several workers have worked with probe atomization and many have reported decreased matrix related interferences when the probe was used [29 - 37].

The success of the L'vov platform and the carbon probe resulted from the utilization of a constant temperature (or nearly constant temperature) furnace. L'vov [3, 20, 28, 38], Woodriff [39 - 44] and Robinson [45 - 54, 62 - 86] have used and advocated the use of constant atomization temperature furnaces, because of the lack of matrix effects exhibited by these furnaces.

Commercial furnaces suffer from two major problems. The most easily recognized problem is that of molecular absorption. When a liquid sample (aqueous or organic) is vaporized inside a carbon furnace, a large number of molecules and
molecular fragments are generated. These species usually absorb UV radiation at the analytical wavelength, at least to some degree. With a standard hollow cathode lamp, it is impossible to distinguish between atomic absorption and molecular background absorption. There are several different methods of background correction, which are currently available on commercial instruments [55–57].

Unfortunately, no commercial background correction method is capable of completely eliminating the background problem. In order for the background correction systems to work, the background absorption must be reduced to a manageable level through an intricate temperature program. After the sample is placed in the furnace, the furnace temperature is raised to 80 – 120 °C. This removes the solvent. Next, the furnace temperature is increased to 500 – 1500 °C in order to vaporize and decompose the rest of the sample matrix, whether it is organic or inorganic. Finally, the furnace temperature is increased to 1800 – 3000 °C. The analyte, relatively free of its solvent and matrix, is vaporized and atomized. As the above discussions on matrix modification and the L’vov platform indicated, the temperature program approach does not remove all of the sample matrix. However, the method is sufficient to reduce background absorption to acceptable levels for many samples, especially aqueous ones. If the sample is atomized before it is dried and ashed, the molecular species resulting from the decomposition of the solvent and matrix completely absorbs the hollow cathode radiation. For this reason, the three step heating program is absolutely necessary when commercial furnaces are used.
The temperature program method reduces background absorption, but it frequently creates another problem. Many volatile elements are easily lost during the drying and/or ashing steps, especially mercury [58]. Since the loss occurs before the atomization temperature is reached, the loss goes undetected. Such a loss causes gross inaccuracy and imprecision.

B. DEVELOPMENT OF THE DOUBLE STAGE FURNACE

1. Quartz "T" Atomizer

At the International Atomic Absorption Conference held at Sheffield, England in 1960, Robinson announced the development of a new electrothermal atomizer [5]. The quartz "T" (or carbon bed) atomizer, shown in Figure 4, consisted of a hollow, inverted "T" shaped device, fabricated from quartz. The cross piece of the "T" served as the light path for the instrument. A bed of carbon chunks, contained in a quartz holder, was suspended in the vertical "T" stem. The carbon bed was heated, inductively, by a radio frequency (RF) coil, wrapped around the stem of the "T".

Samples, of μL size, were dropped onto the heated carbon bed. As the sample was drawn through the carbon bed, by a vacuum pump, it was decomposed and atomized, before it reached the light path. Since the atomization process took place outside of the light path, the elaborate heating program, characteristic of commercial atomizers, was unnecessary. This was because most of the molecular species were reduced to atomic state before they reached the light path. Sample loss was made impossible because the analyte could only exit the
Figure 4
Quartz "T" Atomizer

- RF Coils
- Carbon Bed
- Quartz Window
- Frit
- Heating Blanket
- Exhaust Ports
- Light Path
atomizer through the light path, and the drying and ashing steps were avoided.

The quartz "T" atomizer has been used with a wide variety of complex matrices [48 - 54] and has demonstrated excellent sensitivity for many elements. In almost all cases, the sample matrix was broken down completely and gave little or no interference. There were two reasons for the exceptional matrix reduction capability and high sensitivity exhibited by the quartz "T". First of all, the sample vapor was in contact with the hot carbon, over a wide surface area, for a relatively long period of time, as much as several seconds. This provided ample time for the sample to be completely atomized before it entered the light path. Another factor which contributed to the high atomization efficiency was the high concentration of carbon monoxide and hydrogen in the atomizer. These gases were formed by the well known water - gas reaction:

\[
\begin{align*}
H_2O + C & \xrightarrow{900 \degree C} CO + H_2 \\
C_xH_y + O & \rightarrow CO + H_2
\end{align*}
\]

Carbon monoxide and hydrogen are excellent reducing agents at high temperatures. They contributed to the high atomization efficiency and maintenance of the atom population after atomization. Since the atomizer and light path were at a constant temperature, the advantages of the L'vov and Woodriff constant temperature furnaces were also present in the quartz "T" atomizer.
The quartz "T" atomizer had one major flaw. It could not be operated at temperatures above 1500 °C. At higher temperatures, the quartz began to soften and the "T" was easily damaged or destroyed. The 1500 °C temperature limit did not hinder the sensitivity of the volatile elements, such as lead, cadmium and mercury. More refractory elements, with low volatilities, such as platinum and gold, could not be easily detected. Other materials were available for use at temperatures above 1500 °C, but their use was not practical for physical or economic reasons.

2. Carbon "T" Atomizer

The next development was that of the carbon "T" atomizer. This device consisted of a hollow "T" fabricated from carbon tubes (or carbon rods). As with the quartz "T", the cross piece of the "T" served as the light path, while the stem served as the atomization chamber. This atomizer design went through several modifications [47, 59 - 66], some of which are shown in Figure 5. These atomizers were quite successful. One carbon "T" atomizer has been used quite successfully as an element specific detector for gas chromatography [62, 64 - 66]. The carbon "T" exhibited the same high sensitivity and background reduction capabilities as did the quartz "T". In addition, the carbon could be raised to temperatures of 3000 ° - 3200 °C, which made the determination of the refractory elements much easier.

3. Double Stage Furnace

In order to use the carbon "T" for speciation studies, a modified version, called the double (or two) stage furnace was developed. The double stage furnace consisted of two, separately controlled, heating chambers. As originally designed, the
Figure 5
Carbon "T" Atomizer Designs
Figure 6
Early Double Stage Furnace Design

Furnace Housing

Carbon Supports

Sample

Vaporization Section

Atomization Section

Light Path

Argon

Brass Electrodes

To Vacuum
furnace consisted of two tubes (Figure 6). One tube contained the atomization chamber and the light path. The other tube contained the vaporization section.

The principle of operation of the double stage furnace for speciation was as follows. The sample was placed in the vaporization section. The atomization section was heated to the atomization temperature. Next, during several minutes, the temperature of the vaporization section was slowly increased. The different compounds vaporized as their boiling points were reached, leaving behind the higher boiling components. Each vapor state compound passed through the hot atomization section, where it was atomized, and then into the light path where the atomic absorption measurement was made. In this way, speciation was accomplished by utilizing the differences in volatilities of the various compounds in the sample. Only compounds that contained the element of interest were detected by the atomic absorption system.

In the work with the first version of the double stage furnace [46, 50], which used carbon tubes, the designs of the connecting electrodes were varied for optimum results. The furnace housing was designed and built. The first furnace design demonstrated the feasibility of using the double stage furnace for speciation, though further development was needed.

The introduction of the first version of the double stage furnace by Robinson and Rhodes in 1980 [46] was followed by the development of double stage furnaces by other workers [67, 68]. These furnaces, though similar in concept, were quite different in design from the double stage furnace of Robinson and Rhodes. They were used for quantitative analysis rather than speciation and did not have
versatility of the Robinson-Rhodes furnace design.

The second double stage furnace design, reported by Robinson and Jowett [45] was designed and built using the results obtained from the first design. Molybdenum tubes were substituted for the carbon tubes, to eliminate the porosity problem encountered with the carbon. To facilitate convenient tube replacement, the electrode connections and furnace housing were redesigned. To increase the atomization efficiency, the interior diameter of the atomization section was reduced.

These changes made the double stage furnace easier to operate and brought significant improvements in its performance.

The remainder of Part One of this dissertation describes the design and use of a third generation double stage furnace. This design enabled the device to be used for quantitative analysis, while still retaining the desirable speciation capabilities.

4. A Note on Terminology

It should be noted that in common usage, when referring to atomic absorption, the terms "atomizer" and "furnace" are used interchangeably. This is because virtually all commercial carbon atomizers are furnaces (a semi-enclosed, heated tube). Throughout the remainder of this dissertation, the term "atomizer" will not be used, in order to avoid possible confusion of the terms "atomizer" (which could refer to the entire double stage furnace) and "atomization section" (only one part of the double stage furnace).
II. EQUIPMENT

A. FURNACE COMPONENTS

1. Modified Electrodes

   a. First Modification

   Beginning with the earliest carbon furnace designs [3, 4], the electrically heated carbon tube was connected to metal electrodes at both ends by way of carbon supports. These carbon supports provided a thermal barrier to heat flow between the graphite tube and the electrodes. This enabled the carbon to be heated to high temperature with a minimum expenditure of energy and gave added protection to the, relatively, low melting metal electrodes. However, the atomization and vaporization took place in one step - a serious disadvantage. To improve on this, a two stage system was developed.

   In the early double stage furnace designs [45, 46, 59, 69], practical problems were encountered with the carbon supports which were very difficult to machine properly. If the fit was poor between the electrode and support, or between the tube and support, then arcing resulted. The arcing quickly eroded the metal and/or carbon surfaces. Over time, this broke the electrical connection. Several different carbon support configurations were used [69], none of which were entirely successful. They all suffered from one or more of the following problems: difficult to machine, difficult to install, poor electrical connection and poor physical connection. It should be noted that commercial instruments utilize carbon supports. These are successful because of the superior machining precision available to the instrument manufacturers.
The problem of physical connection was the most severe. It proved difficult, if not impossible, to produce a gas-tight connection, especially between the carbon supports and electrodes. Because of the gas leaks, the argon flow through the tube was not as high as was thought. Lack of knowledge concerning the actual argon flow rate probably contributed to imprecision.

The front and back electrodes, as well as the tube itself, were redesigned to eliminate the need for the carbon supports. Figure 7 shows the old and new electrode designs. The new electrode design had been conceived by a previous worker, but never tried.

Collets were used to clamp the tube directly to the electrode in the new design. The collet design allowed the use of one long tube rather than two short tubes as had been used previously. A hose clamp was placed around the collet. Tightening the hose clamp tightened the grip of the collet on the tube. This provided a better and less complicated electrical connection between the electrode and the tube than provided by carbon supports.

The top and bottom electrodes were not changed as drastically. Since a heat sink at the center of the new furnace design would have a detrimental effect on performance, the carbon supports were retained. The carbon support itself was altered, however. A single tube was used in the new furnace design. Thus, it was possible to divide the center carbon electrode into two parts, as shown in Figure 7. These carbon supports were positioned above and below the tube to connect the tube with the top and bottom brass, water-cooled electrodes. The contact area between the supports and the tube was minimized. This was to further reduce the
Figure 7

Old and new designs for the front electrode, showing the old carbon support and new collet, and old and new center carbon electrode designs.
heat sink effect and allow the center of the tube to attain the highest possible
temperature.

b. Second Modification

When the furnace was brought to its maximum temperature the collets were
heated to a temperature close to the melting point of brass. This caused the collets
to be deformed and electrical contact was lost.

An attempt was made to use steel collets, but the high resistance and the low
thermal conductivity of the steel caused it to melt.

The design of the brass collets was changed to allow for water cooling. Two
"fingers" were used for each collet instead of four. The interior of each "finger" was
hollowed out to allow cooling water from the interior of the electrode to enter. It
was anticipated that localized heating at the ends of the collets could cause boiling.
Boiling would probably cause the electrode to vibrate, which would shorten the
lifetime of the thin carbon furnace.

2. Carbon Furnace

a. Choice of Furnace Material

As was mentioned in the Introduction, one of the original double stage
atomizer designs used molybdenum tubes. Molybdenum was ideal for the
speciation studies carried out at that time because the metal surface did not
become porous after it was heated repeatedly, as did carbon. A porous surface
allowed the liquid sample to soak in. This was undesirable because the analyte
required a longer period to vaporize and pass out of porous surface. The results
were broader peaks, poorer resolution and poorer sensitivity. The use of
molybdenum avoided these problems.

Carbon was chosen as the furnace material over molybdenum for several reasons. 1) The new furnace design, outlined in this section would require two to three times the mass compared with previous designs. 2) Molybdenum rod is rather expensive and there was a limited amount of it available. 3) Carbon could be machined by the author in the laboratory, while molybdenum could be machined only by the experienced machine shop personnel. 4) A large number of furnaces would be needed during the course of this research. This reinforced the three reasons mentioned above. 5) A large stock pile of carbon rods was available for use. 6) The porosity of carbon would be less problematic during quantitative studies, which make up the bulk of this research, than during speciation studies.

Thus, the advantages of using carbon for the furnace material outweighed the disadvantages.

b. First Furnace Design

When the new electrode and collets were designed, the interior diameter of the collets were specified to be 0.25 inch (0.635 cm). This provided a good fit with the one-quarter inch carbon rods which were available.

Upon delivery of the new electrodes, it was discovered that the carbon rods which were reportedly “1/4 inch” in diameter were in fact 0.242 inch (0.615 cm). The collets were not flexible enough to clamp down on a rod of such small diameter.

Thus, it was necessary to begin with a carbon rod of larger diameter, 0.365 inch (0.927 cm), and reduce the diameter by machining. Electrode connections at the ends of the vaporization and atomization sections were machined to about 0.25
inch in outside diameter (O.D.) to match the collet inside diameter (I.D.), as seen in Figure 8. These electrode O.D.'s were critical. If the O.D. was wrong by about 0.005 inch (0.013 cm), then the carbon would not fit in the collet properly. A large O.D. did not allow the carbon to slip into the collet. A small O.D. resulted in a loose fit and a poor electrical connection.

The electrode connection for the center electrodes was left at the original O.D. The carbon supports were machined to fit this O.D. snugly.

The O.D.'s of the atomization and vaporization sections were reduced. This increased the resistances of these sections and allowed a higher temperature to be attained when the furnace was heated.

Finally, the atomization section was drilled out to an I.D. of 0.0625 inch (0.158 cm). The vaporization section and the furnace extension were drilled out to 0.125 inch (0.318 cm).

There were several problems with this furnace design. Because the exterior of each furnace required so much machining, their manufacture was difficult and very time consuming. Installation of the furnace into the furnace housing was quite complicated: the front electrode had to be completely removed from the furnace housing and then replaced by carefully screwing it back into the housing. It was not uncommon for the furnace to break as the front electrode was screwed back into place. One additional disadvantage of this furnace design was that machining the exterior of the furnace tube seemed to weaken the carbon more than was expected. The furnace usually broke where the atomization section met the center electrode connection.
Figure 8
New Furnace Designs

Furnace Extension
Vaporization Section
Atomization Section
Light Path

Electrode Connections
First Furnace Design

Electrode Connections
Second Furnace Design

Electrode Connections
Third Furnace Design

Argon Inlet
Teflon Adaptor
This first design was used for quite some time. The majority of the studies on lead was done with it.

c. Second Furnace Design

After using the first furnace design for quite some time, it became apparent that its disadvantages were too severe to continue with it. The slits in the collets were lengthened. This allowed the collets to grip the smaller 0.242 inch (0.615 cm) O.D. carbon rods. The new furnace design was based on these rods, as seen in Figure 8.

There were several advantages over the first furnace design. 1) The exterior required no machining, greatly reducing the time necessary for their manufacture. 2) Installation was faster and easier because the furnace was simply slid through the front electrode and clamped into place.

A cross piece was added to this furnace design in order to extend the light path. This was advantageous because the atomic absorption signal for a given sample concentration was greatest when all of the analyte atoms were in the light path simultaneously. The cross piece was constructed of a 5.0 cm length of 0.365 inch (0.927 cm) O.D. carbon rod that had been drilled out to 0.25 inch (0.635 cm) I.D. A 0.25 inch hole was drilled through the center of the cross piece. This allowed the cross piece to be positioned over the light path of the furnace.

Initially, a mixture of furfuryl alcohol and concentrated HCl was used to cement the two carbon tubes together. If this procedure was carried out after the furnace and cross piece had been installed, the HCl fumes corroded parts of the exposed metal components. If the parts were installed after being cemented
together, the front and back electrodes had to be removed. Both of these procedures were undesirable. It was determined that no loss of sensitivity occurred if the cross piece was allowed to simply rest on the furnace, without being cemented into place. This method was used throughout most of this work. The furnace with cross piece and electrode connections are illustrated in Figure 9.

d. Third Furnace Design

A new furnace design was needed for constant temperature atomization. That procedure is discussed in a later section.

This furnace design was similar to the second design except that the furnace extension was slightly longer, as illustrated in Figure 8. A short side-arm was added to the inlet end of the furnace tube. This allowed the argon to be introduced into the furnace through the side-arm rather than from the end.

A Teflon adapter was attached to the furnace tube with a short length of Tygon tubing. This adaptor accepted the second carbon rod sampling device design, described below.

3. Carbon Rod Sampling Device (CRSD)

a. First Carbon Rod Sampling Device Design

The carbon rod sampling device (CRSD), illustrated in Figure 10, was a carbon rod approximately 12.7 cm long and slightly less than 0.38 cm in diameter. Each CRSD was machined from a carbon rod of 0.242 inch (0.615 cm) diameter.

One end, called the sample head, was slightly larger in diameter and had a flat face. A small depression carved into the sample head held 2 – 5 µL of sample. These carbon rods were easy to machine but were fragile, due to the small
Figure 9

View of the Interior of the Furnace Housing

front brass electrode

thermocouple
top brass electrode
carbon electrode
atomization section

vaporization section

bottom brass electrode

back brass electrode
Figure 10

Carbon Rod Sampling Device Designs

**First CRSD Design**

- Sample Depression
- Sample Head

**Second CRSD Design**

- Teflon Adaptor
- Sample Head
diameter, and had to be carefully handled. They were designed to be slid into the vaporization section from the furnace inlet.

b. Second Carbon Rod Sampling Device Design

This design was much like the first. As can be seen from Figure 10, the end of the rod opposite the sample head was left at the original 0.242 inch (0.615 cm) diameter. This end fit inside a Teflon adapter.

The second CRSD design was meant to be used with the third furnace design for constant temperature atomization, which is discussed in a later section.

4. Furnace Housing

The carbon furnace rapidly deteriorated if it was heated in the presence of oxygen. Thus, it was necessary to isolate the furnace in a housing purged with an inert gas, such as argon. The furnace housing described below was originally designed by a previous worker [45, 69]. The housing was made of aluminum and had channels to provide water cooling. There was an argon inlet. An exhaust port was vented to a hood via a length of Tygon tubing.

Electrodes in the front, back, and bottom screwed into the housing. The end of each electrode was positioned precisely by carefully screwing the electrode in or out of the housing. Unlike the other electrodes, the top electrode was spring loaded.

Access to the housing interior was provided by removable panels, or doors, which formed the two sides of the housing. Each door had two windows. A small quartz window allowed the source radiation to pass through the housing. The second, larger window was made of glass. It allowed the operator to observe the
housing interior without obstructing the light path. A grid of aluminum foil was placed just inside this window. This allowed the operator to see in but prevented the intense heat from cracking the glass.

All openings were sealed through the use of rubber "O" rings.

5. Electrical Components

The electrical system described was essentially the same as that used by previous workers [45, 46, 59, 69]. Figure 11 illustrates the electrical system used.

The atomization and vaporization sections were heated by two separate electrical systems. In both cases, power was supplied from 208 V, 45 A fuse boxes.

Electrical power for the vaporization section was regulated through two 20 A ganged auto variable transformers (Variac, General Radio Co.) connected in parallel. Two 12 V, 500 A stepdown transformers (Signal Transformer Co.), connected in series were used. The two isolated primary windings of each were connected in parallel. An ammeter located between the variac and stepdown transformers indicated the line current drawn. A switch installed between the fuse box and variac allowed a preset current to be switched on and off easily. Welding cables were used to connect the transformer secondaries to the furnace electrodes.

The electrical system for the atomization section was essentially the same as outlined above, except a single 18 A auto transformer (Variac, General Radio Company) and a single 9 V, 500A stepdown transformer (Signal Transformer Company) were used.
Figure 11
Electrical System

[Diagram of electrical system with labels and connections.]
B. **OPTICAL COMPONENTS**

As can be seen from the schematic diagram in Figure 12, the spectrometer is a single beam instrument. The major optical and electronic components are listed in Table I.

1. **Sources**

   a. **Demountable Hollow Cathode Lamp**

   The demountable hollow cathode lamp (DHCL) used was similar in design to the ones which have been used in these laboratories for years. These lamps were all manufactured by college machine shop personnel. Figure 13 shows the major components of the DHCL.

   Filler gas for the DHCL was provided by a helium gas cylinder. The gas passed through a regulator to the gas scrubbers. Activated charcoal removed organic compounds and silica gel removed water vapor. The oxygen scrubber was a Pyrex tube filled with copper turnings. The copper was heated by Nichrome wire wrapped around the tube and connected to a variable auto transformer (Powerstat, Superior Electric Co. 7.5 A). Scrubbed filler gas was metered into the DHCL housing with a needle valve. A single stage, oil vacuum pump (Welch Scientific Company) pulled the filler gas out of the DHCL housing. The DHCL pressure was monitored with a vacuum gauge tube (Veeco, type DV-4AM).

   These lamps were less expensive to use than sealed, commercial hollow cathode lamps (HCL's). Since the removable cathode could easily be replaced, changing from one element to another was a rapid process. The cathodes were machined from the metal of interest or one of its salts. This was done in house.
Figure 12
Optical and Electronic Components of the Double Stage Furnace

Chopper with Magnetic Reed Switch

HCL

Power Supply

Lens

Furnace and Housing

PMT

Power Supply

Amplifier

Monochromator

Recorder
**TABLE I**

Major Spectrometer Components

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Hollow Cathode Lamps</td>
<td>From Perkin-Elmer and Westinghouse</td>
</tr>
<tr>
<td>Hollow Cathode Lamp Power Supply</td>
<td>Varian Techtron AA - 5 HCL power supply, modified for DC operation</td>
</tr>
<tr>
<td>Deuterium Lamp</td>
<td>Beckman model 6280</td>
</tr>
<tr>
<td>Deuterium Lamp Power Supply</td>
<td>Beckman model B</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Fisher - Jarrel Ash model 82 - 020 scanning 0.5 m Ebert monochromator with a 1180 line/mm grating, blazed for 300 nm and adjustable slits</td>
</tr>
<tr>
<td>Detector</td>
<td>Hamamatsu model R106 - UH PMT</td>
</tr>
<tr>
<td>Photomultiplier Tube Power Supply</td>
<td>Hewlett Packard model 6515A high voltage DC power supply</td>
</tr>
<tr>
<td>Amplifier</td>
<td>GCA/McPherson photometric readout model EU-703-31, modified for phase lock operation</td>
</tr>
<tr>
<td>Recorder</td>
<td>Beckman model 1005 10 - inch recorder</td>
</tr>
<tr>
<td>Vacuum Pump</td>
<td>Welch Scientific Co. single stage, oil pump</td>
</tr>
<tr>
<td>Step Down Transformers</td>
<td>Signal Transformer Co. 12 V, 500 A and 9 V, 500 A transformers</td>
</tr>
<tr>
<td>Variable Auto Transformers</td>
<td>General Radio Co. 20 A and 18 A Variacs, Superior Electric Co. 7.5 A Powerstat</td>
</tr>
</tbody>
</table>
Figure 13
Demountable Hollow Cathode Lamp

Diagram showing the components of a demountable hollow cathode lamp. Key features include:
- Electrical Connections
- Hollow Cathode
- Anode
- Window
- To Vacuum
- Helium In
- Retaining Ring
- Cooling Water

Materials used:
- Glass
- Ceramic
- Steel
- Brass
- 'O' Ring
- PUC
- Aluminum
Thus, the expense of having removable cathodes for many elements was negligible compared to an equal number of HCL's, which cost several hundred dollars each.

Another, analytically more important, advantage to the DHCL was that self-reversal was reduced. In a sealed, commercial HCL, the atoms that are formed during the sputtering process tend to remain in the atomic state, occupying space in the lamp between the hollow cathode and the exit window. This is especially true of very volatile elements, such as mercury. These atoms are free to absorb the atomic emission from the hollow cathode. This process is termed "self-reversal".

It can be shown that self-reversal causes decreased sensitivity and poor linearity of calibration curves [70].

Because the DHCL constantly had the filler gas pumped through it (as opposed to being a sealed, self-contained system), atoms formed in front of the hollow cathode were swept out of the lamp. In this way, self-reversal was greatly reduced. Self reversal was reduced even further by operating the DHCL in the "flow through" mode. As Figure 14, indicates, a Teflon seal placed between the anode or cathode forced the filler gas to flow through the cathode. This forced the removal of atoms as they were formed in the cathode. The atom population inside the lamp, and thus self-reversal, were further reduced.

There were disadvantages to the use of DHCL's. These lamps required more operator intervention than commercial HCL's. They had to be taken apart and cleaned periodically. The lifetime of the cathode itself, was much shorter than for the commercial HCL's and new cathodes had to be manufactured from time to time.
Figure 14
Demountable Hollow Cathode Lamp in Flow Through Mode

- Electrical Connections
- Retaining Ring
- Cooling Water
- Teflon Adaptor
- Anode
- Window
- Hollow Cathode
- To Vacuum
- Helium In

Materials:
- Glass
- Ceramic
- Steel
- Brass
- 'O' Ring
- PVC
- Aluminum
The filler gas pressure and lamp current were critical for stable DHCl operation. These conditions were optimized for each element and monitored quite closely during operation.

b. Commercial Hollow Cathode Lamps

For various reasons, it was necessary to use commercial hollow cathode lamps for a few of the elements investigated. Manufacturers included Perkin-Elmer Corporation and Westinghouse.

c. Deuterium Lamp

Molecular background absorption was measured by replacing the hollow cathode lamp with a deuterium lamp (Beckman model 6280 powered by a Beckman model B deuterium lamp power supply). The sample was run using the hollow cathode lamp and then using the deuterium lamp. The difference in the two absorbances was the atomic absorption signal.

2. Other optical components

The source radiation was modulated by a mechanical chopper (chopper motor by Hinds Mueller Engineering Company, Inc.). Two quartz plano-convex lenses focused the source radiation through the furnace housing and then onto the slit of the monochromator. A scanning 0.5 m Ebert monochromator (Fisher-Jarrel Ash model 82-020) with adjustable slits was used. The grating had 1180 lines/mm and was blazed for 300 nm. Detection was provided by a photomultiplier tube (Hamamatsu, model R106-UH).

3. Optical bench

The optical bench used was similar in concept to one reported by Winefordner,
et al. [71]. The bench top was a painted, 0.95 cm thick sheet of iron. Instrument components were attached to magnetic mounts which clamped to the iron. This arrangement, which had been used in these laboratories previously, proved easier to use and more versatile than conventional optical rails.

C. ELECTRONIC COMPONENTS

Figure 12 is a diagram showing the electronic and optical components. Major components are listed in Table I.

1. Hollow Cathode Lamp Power Supply

The power supply for the DHCL and commercial HCL's was a Varian Techtron AA-5 HCL power supply, modified to provide direct current.

2. Detection and Readout

Power for the photomultiplier tube (PMT) was supplied by a high voltage, direct current power supply (Hewlett Packard model 6515A).

The PMT signal was amplified by a GCA/McPherson photometric readout (model EU-703-31). A modification to the amplifier allowed it to be phase locked to the signal generated by a magnetic reed switch on the chopper. This permitted the amplification of only the chopped source radiation.

Traces were made on a Beckman 10-inch potentiometric recorder (model 1005).

D. GAS HANDLING EQUIPMENT

A diagram of the gas handling system is shown in Figure 15.
Argon was used to purge the furnace housing and as a flow gas through the furnace. In order to minimize gas phase reactions and deterioration of the carbon furnace, the argon was scrubbed. Activated charcoal, silica gel and hot copper turnings were used to remove organic materials, water vapor and oxygen, respectively.

Methane was occasionally mixed with one or both of the argon streams. The methane was obtained from in-house gas lines and passed through activated charcoal and silica gel scrubbers.

Nitrogen was sometimes used to purge the monochromator when wavelengths below 200 nm were used. The nitrogen was passed through activated charcoal and silica gel scrubbers.

The gases were metered using needle valves and rotometers. Table II indicates which rotometer flow tubes were used with which gas streams.

Gas mixing took place, between the rotometers and the housing or furnace, by merging the argon and methane gas streams using glass “T” pieces.

Nearly all tubing used throughout the gas handling system was polyethylene or Tygon tubing. A short length of surgical-type latex hose was slipped over the end of the furnace extension to introduce the flow gas into the furnace.

A three-way stopcock was installed between the rotometers and the furnace inlet. In one valve position, the gas flowed through the valve to the furnace. The other position allowed the gas to be vented to the atmosphere. This enabled the flow gas to the furnace to be stopped without adjusting the needle valves at the rotometers.
<table>
<thead>
<tr>
<th>Gas Stream</th>
<th>Rotometer Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Housing Argon</td>
<td>J.T.Baker model 588274</td>
</tr>
<tr>
<td>Furnace Argon</td>
<td>Matheson model 600</td>
</tr>
<tr>
<td>Housing Methane</td>
<td>Matheson model 602</td>
</tr>
<tr>
<td>Furnace Methane</td>
<td>Matheson model 610</td>
</tr>
<tr>
<td>Monochromator Nitrogen Purge</td>
<td>Matheson model 201A</td>
</tr>
</tbody>
</table>
E. TEMPERATURE MEASURING EQUIPMENT

An iron-constantan thermocouple was positioned about 5 mm over the center of the vaporization section. Direct contact with the vaporization section was not possible because the maximum temperature of the vaporization section would exceed the melting point of the thermocouple metals.

The temperatures measured above the vaporization section were correlated to the actual temperature of the furnace. Vaporization section temperatures of 800 °C or less were measured with another iron-constantan thermocouple placed at the center of the vaporization section. At temperatures above 800 °C an optical pyrometer (Leeds and Northrup Co., model 8632-0) was used to measure the temperature.

The thermocouple was rarely used to measure the temperature of the vaporization section since a small change in distance between the two would cause a large difference in temperature measured. Usually, the optical pyrometer was used to measure the temperature of the vaporization and atomization sections.

F. SAMPLE DISPENSING DEVICES

Two devices were used to dispense the liquid sample. A microliter syringe (Hamilton model 701 - RN) with a 10 cm removable needle was used to place sample directly on the furnace wall or on the carbon rod sampling device (CRSD).

A 1.0 - 5.0 μL adjustable micropipet (Ky Pinpipette) was used to place sample on the CRSD.
III. EXPERIMENTAL AND RESULTS

A. CHEMICALS

1. Deionized Distilled Water

Deionized Distilled Water (DDW) was obtained by passing distilled water, from
the chemistry building's distilled water system, through a mixed bed deionization
column (Illinois Water Treatment Company Research IonXchanger model 2). The
DDW was stored in a large, polyethylene carboy.

2. Standards

Stock standards of 1000 µg/mL were prepared by dissolving the appropriate
mass of the element or its salt in deionized distilled water (DDW) or an appropriate
acid. Most stock standards were made up in DDW unless a stabilizing reagent was
required. Selenium, tin and arsenic standards required stabilization. Selenium
and tin standards were made up in 10% HCl. Arsenic standards were made up in 3%
sulfuric acid.

Chemicals used for stock standards were of reagent grade or better. Suppliers
included J.T. Baker Chemical Company; Fisher Scientific Company; Mallinckrodt
Chemical Works and Matheson, Coleman and Bell Manufacturing Chemists.

Stock standards were stored in polyethylene bottles. Dilute standards were
made up daily for quantitative work.

3. Gases

Argon, nitrogen and helium were supplied by Lincoln Big Three Industries,
Incorporated. Methane was obtained from the in-house natural gas lines. The
natural gas supplier was Gulf States Utilities Company.

B. PYROLYSIS

1. Introduction

From the first use of GFAAS [3] came a warning that the porous nature of the graphite allowed part of the atomic vapor to diffuse through the furnace wall and go undetected. L'vov lined his furnace with tantalum foil to avoid this problem.

There was another problem associated with the porosity of carbon furnaces. A liquid sample soaked into the porous carbon surface. When the furnace was heated, sample vapor diffused back out of the carbon. The peak broadened because of the extra time required for diffusion to take place. The resulting peak height and sensitivity decreased.

A third problem associated with carbon furnaces resulted from the fact that many elements form stable carbides. The carbon furnace provides, of course, the perfect environment for carbide formation. Since metal carbides are rather non-volatile and difficult to atomize, their formation would result in decreased sensitivity.

One way, first proposed by L'vov [38], to overcome the problems mentioned above was to coat the carbon furnace with a thin layer of pyrolytic carbon. This was done by heating the carbon in the presence of methane, or certain other hydrocarbon gases [38, 72 - 76]. Upon coming in contact with the hot carbon, the methane decomposed to carbon and hydrogen. A layer of dense, non-porous carbon built up.
A pyrolytic coating reduced the porosity of a carbon tube to essentially zero [72]. Thus, the problems attributed to carbon porosity were eliminated. In addition, since pyrolytic carbon is less reactive than standard carbon, carbide formation was reduced. As would be expected, the use of pyrolytically coated carbon tubes gave increased sensitivity over non-coated tubes [73].

2. Procedure

Various workers reported that a pyrolytic coating was obtained by heating carbon to about 1000 °C in the presence of natural gas [38] or by heating the carbon to 2200 °C in an atmosphere of 10% methane and 90% nitrogen or argon [73, 76]. At temperatures in between, a sooty deposit was formed.

Several different procedures were studied before the pyrolysis method used during this research was finalized. After each trial, the furnace was broken open to observe how well the pyrolysis procedure had worked. The final procedure adopted follows: A carbon furnace was installed in the furnace housing and connected to all electrodes. After the housing was closed, it was purged with argon at about 250 mL/min. Both sections of the furnace were brought to about 1000 °C. Then, natural gas was allowed to flow through the furnace at about 30 mL/min for 60 minutes.

The exterior of the furnace was continuously pyrolyzed in a way similar to previously reported procedures [74, 75]. The furnace housing was constantly purged with a mixture of argon with about 3% natural gas at a rate of 200 - 250 mL/min. This procedure was followed any time the furnace was used, except during the analysis of arsenic and selenium. Resonance lines for arsenic and selenium (193.7
nm and 195.1 nm, respectively) are in the vacuum ultraviolet region. Some of the pyrolysis products absorbed strongly in this region. After pyrolysis had occurred during several heating cycles, a large fraction of either of the resonance lines were absorbed, which made quantitation difficult.

3. Results

The interior of the furnace could not be seen without it being broken open, precluding its further use. Thus, during actual operation, it was impossible to tell whether the interior of the furnace had been pyrolyzed.

Occasionally during pyrolysis, under apparently ideal conditions, black soot has been reported to form instead of the desired pyrolytic carbon [72]. Such results indicated that conditions must be more rigorously controlled than was sometimes possible. During this work similar phenomena were observed. Occasionally, a plug of soot built up inside the furnace. This could be seen, if the furnace interior was viewed from the inlet while the carbon was red hot. This was especially true in the section between the atomization and vaporization sections, which was 200 - 300 °C cooler than the other two sections. More often, the soot was not noticeable until a sample was placed in the furnace and the syringe needle was covered with soot.

When pyrolysis failed, two options were available; removal of the furnace and pyrolyzation of a fresh one, or continuation of work with the non-pyrolyzed furnace. The latter option was usually chosen.

For most of the elements investigated, the use of pyrolytically coated furnaces seemed to have little or no effect on sensitivity. Because pyrolysis was such a time-
consuming procedure, uncoated furnaces were used, once it was determined that pyrolyzed furnaces held no advantages for the atomization of a specific element.

In contrast, the pyrolysis of the exterior of the furnace was entirely successful. After a few heating cycles, the atomization and vaporization sections would have a uniformly shiny coating of pyrolytic carbon. The portion of the furnace between the atomization and vaporization section, because of its lower temperature, would not usually become coated. Pyrolytic carbon covering most of the furnace exterior probably greatly reduced the fraction of sample that would have escaped by diffusing through the carbon.

Even though the pyrolytic coating was constantly being renewed, and it probably protected the carbon underneath it from early deterioration, the protection did not last indefinitely. On more than one occasion, it was discovered that the carbon had deteriorated to such an extent as to render it non-conductive. All of the current was carried through, and the heat generated by, the pyrolytic carbon coating. This was easily detected because temperature, electrical current and sensitivity all dropped off drastically.

C. EXPERIMENTAL PARAMETERS FOR QUANTITATIVE ANALYSIS WITH DOUBLE STAGE FURNACE

1. Furnace Temperature

The maximum temperature attainable for the double stage furnace varied from 2400 - 2800 °C, depending on how good the electrical connections were. A temperature of about 2500 °C was most common. This compared to an atomization
temperature of 2800 °C recommended by a commercial instrument vendor for many of the elements investigated [77].

Also, it was well known that, for the vast majority of elements, the atomization efficiency increased as the temperature increased. This means that, for a fixed mass of analyte, the absorbance value increased with increasing temperature, up to a point. Eventually, a point was reached where a large temperature rise had little or no effect on absorbance values. Thus, it was nearly impossible to adversely affect the analytical sensitivity for an element by atomizing at a very high temperature. This is illustrated in Figure 16.

With these two factors in mind, it was decided, for the purposes of this work, to always run the atomization section at its highest possible temperature.

The vaporization section was also run at its highest temperature, though for a different reason. The vaporization section needed to be heated at the fastest possible rate so that the absorption peak would be as narrow and tall as possible. With the equipment available, the only feasible way of doing this was to set the power to its maximum level. Thus, maximum heating rate and maximum temperature were used.

2. Atomization Warm-up Time

The atomization section usually required about 30 s to reach its maximum temperature. In the case of a few elements, a 30 s warm-up time was either too long or too short. The relationship between atomization section warm-up time and sensitivity was studied if preliminary data for an element indicated that the 30 s time period was inappropriate.
Figure 16
Typical Plot of Absorbance versus Atomization Temperature for Furnace Atomic Absorption Spectrometry
3. **Flow Rate of Furnace Housing Purge Gas**

In order to prevent the rapid deterioration of the carbon furnace, it was necessary to purge the furnace housing with inert gas. The argon flow rate was usually 200 - 250 mL/min. The methane flow rate was usually about 4 mL/min. These flow rates provided adequate protection for the carbon furnace.

4. **Flow Rate of Gas Through the Furnace**

Perhaps, the most important variable was the flow rate of gas through the furnace. This variable controlled the time the sample vapor was inside the heated carbon furnace.

There were at least four factors to be considered in relation to the furnace flow rate. First, the longer the analyte was in contact with the hot carbon, the more efficient the atomization process became. From this point of view, the flow rate was slowed to allow the sample to be totally atomized. Second, there were gas phase interactions that decreased the free atom population. A well known example of this was the vapor phase formation of lead chloride [78, 79]. These interactions required a fast flow rate to minimize the time necessary to get the analyte through the atomization section and then into the light path. The third factor was diffusion. If the gas flow rate was too slow, the analyte vapor diffused throughout the furnace. This caused the atomic absorption peak to broaden and shorten, resulting in poorer sensitivity. A fourth factor to be considered was the instrument response time. If the instrument electronics failed to record a fast evolving peak, then a loss of sensitivity resulted.
Thus, efficient atomization and instrument response factors were optimized when a low flow rate was used. Diffusion and gas phase interactions were minimized at elevated flow rates. As might be expected, the factor or factors that predominated depended on the element of interest. It was necessary to determine the optimum furnace gas flow rate for each element studied.

5. Miscellaneous Parameters

There were a number of other parameters that were element-dependent. These included HCL or DHCL current, DHCL pressure, monochromator slit width and the photomultiplier tube voltage.

The lamp current had to be adjusted to provide adequate intensity for the instrument to operate properly. Each element required a different current, depending on its conductivity and its excitation energy. In addition, if the lamp current was too high, self-reversal occurred, which reduced the sensitivity for a particular element.

Each element used in the demountable hollow cathode lamp required a different gas pressure inside the lamp. The lamp pressure required to provide a stable operation was, again, dependant on the element's conductivity and excitation energy. High pressure would also cause self-reversal.

The monochromator slit width and photomultiplier tube (PMT) voltage settings were directly related. It was desirable for the slit width to be as narrow as possible, to provide the best possible spectral resolution. However, as the slit width was decreased, the PMT voltage had to be increased to compensate for less light passing through the monochromator. If the PMT voltage was increased too
much, the recorder baseline would become very noisy, making detection of small signals very difficult. The slit width and PMT voltage, in turn, depended on the intensity of the lamp.

Thus, all of these parameters were adjusted to give an adequate instrumental response for the element of interest. The operating conditions for each of the elements studied are summarized in a table in the discussion of the particular element.

D. METHODS FOR QUANTITATION WITH THE DOUBLE STAGE FURNACE

1. A (hot) V Method

The name of the method indicates that the atomization section was hot when the sample was injected into the vaporization section. Then the vaporization section was heated. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The atomization section was heated to approximately 2500 °C, if it was not already hot.

2) The rubber hose, which served as the argon supply to the furnace interior, was removed from the argon inlet.

3) Sample was placed in the vaporization section.

4) The argon supply hose was replaced.

5) The vaporization section was heated quickly to its maximum temperature of 2500 - 2600 °C. In a very short period of time (seconds or less), the sample vaporized. Pushed by the argon, the vapor flowed into the atomization section
### TABLE III

**A Brief Outline of Methods Used**

<table>
<thead>
<tr>
<th>Method</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(hot)V</td>
<td>atomization section heated, sample inserted, vaporization section heated</td>
</tr>
<tr>
<td>AV</td>
<td>sample inserted, atomization section heated, vaporization section heated</td>
</tr>
<tr>
<td>AV with Reverse Flow</td>
<td>sample inserted (argon supply hose not reattached - argon flowed backward through furnace), atomization section heated, argon supply hose reattached, vaporization section heated</td>
</tr>
<tr>
<td>AV (warm)V(hot)</td>
<td>sample inserted, atomization section heated, vaporization section heated to 600 - 700 °C, vaporization section heated to maximum temperature</td>
</tr>
<tr>
<td>VA</td>
<td>sample inserted, vaporization section heated, atomization section heated</td>
</tr>
<tr>
<td>VA Trapping</td>
<td>sample inserted, vaporization section heated - analyte trapped in atomization section, atomization section heated</td>
</tr>
<tr>
<td>VA Trapping with Reverse Flow</td>
<td>sample inserted (argon supply hose not reattached - argon flowed backward through furnace), atomization section heated, argon supply hose reattached, atomization section cooled, vaporization section heated - analyte trapped in atomization section, atomization section heated</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Method Modifications</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple VA Trapping</td>
<td>sample inserted, vaporization section heated, vaporization section cooled, first two steps repeated, heat atomization section</td>
</tr>
<tr>
<td>Simultaneous Heating</td>
<td>sample inserted, both sections heated</td>
</tr>
<tr>
<td>Constant Temperature</td>
<td>sample was placed on CRSD, both sections were heated. CRSD with sample was plunged into heated furnace.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method Modifications</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRSD</td>
<td>Carbon rod sampling device w/sample was placed in the vaporization section</td>
</tr>
<tr>
<td>Reaction Gases</td>
<td>Water vapor or methane was added to furnace argon flow</td>
</tr>
<tr>
<td>Multiple Sample Drying on the CRSD</td>
<td>sample was placed on CRSD and dried, more sample added and dried, etc., CRSD was placed in the vaporization section</td>
</tr>
</tbody>
</table>
where the high temperature decomposed the molecules into atoms. The atomic vapor was pushed, by the argon, into the light path where atomic absorption took place. An absorption peak was measured as the atomic vapor passed through the light path.

6) Power to the vaporization section was turned off and the section was allowed to cool for 30 - 60 s before the next sample was run.

2. AV Method

The name indicates that after the sample was injected, the atomization section was heated, then the vaporization section was heated. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The argon supply hose was removed from the furnace argon inlet.

2) Sample was placed in the vaporization section.

3) The argon supply hose was reconnected to the furnace argon inlet.

4) The atomization section was heated to its maximum temperature, usually about 2500 °C. By conduction, the vaporization section was heated to 100 - 150 °C. This dried the sample. After 25 - 30 s, the atomization section temperature stabilized.

5) The vaporization section was heated to its maximum temperature of 2500 - 2600 °C. The sample was vaporized, atomized in the atomization section and pushed into the light path where the atomic absorption measurement was made.

6) Power to both sections was turned off. The furnace was allowed to cool for 30 - 60 s before the next sample was run.
3. AV Method with Reverse Flow

The name of the method indicates that the AV method was used but that, during the atomization section warm-up period, the argon was allowed to flow backwards through the furnace. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The argon supply hose was removed from the argon inlet. Purge gas from inside the furnace housing was then able to pass into the furnace, through the light path. It flowed, backward, through the atomization section, then through the vaporization section and then out the argon inlet. This reverse flow is depicted in Figure 17.

2) Sample was placed in the vaporization section.

3) The atomization section was heated to its maximum temperature of about 2500 °C. Since the argon supply hose had not been replaced, the purge gas from the interior of the furnace housing was still flowing backward through the furnace. The purge gas was heated as it passed through the atomization section. Consequently, the vaporization section was heated to 600 - 700 °C by the hot gases passing through.

4) The argon supply hose was reattached to the argon inlet, which reestablished the normal argon flow pattern.

5) The vaporization section was heated to its maximum temperature of 2500 - 2600 °C. The sample was vaporized, atomized in the atomization section and pushed into the light path, where the atomic absorption measurement was made.

6) Power to both sections was turned off. The furnace was allowed to cool for
Figure 17

Furnace and Furnace Housing Flow Patterns

Normal Argon Flow Pattern

Reverse Argon Flow Pattern
30 - 60 s before the next sample was run.

4. **AV (warm) V(hot) Method**

The name of the method indicates that, after the sample was placed in the vaporization section, the atomization section was heated. Then the vaporization section was heated to only 600 - 700 °C for a few seconds. The vaporization section was then heated to its maximum temperature. This method recreated the temperature effects of the reverse flow method, without having the reverse flow of gases through the furnace. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The argon supply hose was removed from the furnace argon inlet.

2) Sample was placed in the vaporization section.

3) The argon supply hose was reconnected to the furnace argon inlet.

4) The atomization section was heated to its maximum temperature of about 2500 °C for 30 s.

5) The vaporization section was heated to 600 - 700 for 30 s.

6) The vaporization section was heated to its maximum temperature of 2500 - 2600 °C. The sample was vaporized, atomized in the atomization section and pushed into the light path, where the atomic absorption measurement was made.

7) Power to both sections was switched off. The furnace was allowed to cool for 30 - 60 s before the next sample was run.

5. **VA Method**

The name of the method indicates that, after the sample was placed in the vaporization section, the vaporization section was heated. Then the atomization
section was heated. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The sample was placed in the vaporization section and the argon supply hose reattached to the furnace argon inlet.

2) The vaporization section was heated to its maximum temperature of 2500 - 2600 °C. For volatile, easily atomized elements, this was enough to vaporize and atomize the sample. The analyte passed through the unheated atomization section and into the light path, where the atomic absorption measurement was made.

3) The atomization section was then heated to release the small amount of analyte that might have been adsorbed to the surface of the atomization channel.

4) Both furnace sections were cooled for 30 - 60 s before the next sample was run.

6. VA Trapping Method

The name of the method indicates that, after the sample was placed inside the vaporization section, the vaporization section was heated. Analyte was vaporized and trapped in the atomization section. Next, the atomization section was heated to release and atomize the analyte. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The sample was placed in the vaporization section and the argon supply hose was reattached to the furnace argon inlet.

2) The vaporization section was heated to its maximum temperature of 2500 - 2600 °C. The sample was vaporized and pushed by the argon flow into the unheated atomization section. There, the non-volatile components of the sample vapor
condensed on the walls of the atomization section. Volatile components of the sample matrix, including the solvent, did not condense and were pushed out of the furnace through the light path.

3) The atomization section was heated to its maximum temperature of about 2500 °C. Condensed portions of the sample were revaporized, atomized and pushed into the light path, where the atomic absorption measurement was made.

4) Both furnace sections were cooled for 30 - 60 s before the next sample was run.

7. VA Trapping Method with Reverse Flow

The name indicates that the VA method, described above, was used. During a preliminary atomization warm-up period, the argon was allowed to flow backward through the furnace. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The argon supply hose was removed from the furnace argon inlet. Purge gas from inside the furnace housing was then able to pass into the furnace, through the light path. It flowed, backward, through the atomization section, then through the vaporization section and then, out the argon inlet. This reverse flow is depicted in Figure 17.

2) Sample was placed in the vaporization section.

3) The atomization section was heated to its maximum temperature of about 2500 °C. Since the argon supply hose had not been replaced, the purge gas from the interior of the furnace housing was still flowing backward through the furnace. The purge gas was heated as it passed through the atomization section.
Consequently, the vaporization section was heated to 600 - 700 °C by the hot gases passing through.

4) The argon supply hose was reattached to the argon inlet, which reestablished the normal argon flow pattern.

5) The atomization section was turned off and allowed to cool for 60 s.

6) The vaporization section was heated to its maximum temperature of 2500 - 2600 °C. The sample was vaporized and pushed by the argon flow into the unheated atomization section. There, the non-volatile components of the sample vapor condensed on the walls of the atomization section. Volatile components of the sample matrix, including the solvent, did not condense and were pushed out of the furnace through the light path.

7) The atomization section was heated to its maximum temperature of about 2500 °C. Condensed portions of the sample were revaporized, atomized and pushed into the light path, where the atomic absorption measurement was made.

8) Both furnace sections were cooled for 30 - 60 s before the next sample was run.

8. Multiple VA Trapping Method

The name of the method indicates that the VA trapping method was used to trap several aliquots of sample in the unheated atomization section before that section was heated to release the analyte. This allowed the sample to be concentrated in the atomization section before it was released. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.
1) The sample was placed in the vaporization section and the argon supply hose was reattached to the furnace argon inlet.

2) Sample was placed in the vaporization section.

3) Power to the vaporization section was cut off and the furnace was allowed to cool for 30 - 60 s.

4) Steps 1 - 3 were repeated one or two times to concentrate the sample by two or three fold, respectively. The last time the first three steps were repeated, the vaporization section was left on.

5) The atomization section was heated to its maximum temperature of about 2500 °C. Condensed portions of the sample were revaporized, atomized and pushed into the light path, where the atomic absorption measurement was made.

6) Power to both sections was turned off. The furnace was allowed to cool for 30 - 60 s before the next sample was run.

9. Simultaneous Heating Method

The name of this method indicates that, after the sample was placed in the vaporization section, both sections were heated simultaneously to vaporize and atomize the sample. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The sample was placed in the vaporization section and the argon supply hose was reattached to the furnace argon inlet.

2) The atomization and vaporization sections were heated, simultaneously, to their maximum temperatures of about 2500 °C and 2500 - 2600 °C, respectively. The sample was vaporized, atomized and then pushed into the light path, where
the atomic absorption measurement was made.

3) Power to both sections was turned off. The furnace was allowed to cool for 30 - 60 s before the next sample was run.

10. Constant Temperature Method

The name of the method indicates that both sections of the furnace had been heated to a constant temperature before the sample, placed on a carbon rod sampling device (CRSD), was thrust into the furnace.

Attempts to study some of the more volatile elements, such as mercury and selenium, revealed a problem with the AV method, mentioned above. When the atomization section was heated, the temperature of the vaporization section rose, through conduction, to 100 - 150 °C. This temperature was high enough to volatilize a sizeable fraction of the volatile analyte. The analyte loss did not go undetected, however. It passed through the atomization section and then into the light path, where the atomic absorption measurement was made. So, even though some of the analyte was lost, it was still detected. The initial loss caused the second (major) peak to be smaller and this, in turn, caused the sensitivity to be decreased.

It was desired that all of the analyte enter the gas phase simultaneously. The second CRSD design and the third furnace design were used. The exact procedure is described in detail below. A brief outline of the method is presented in Table III.

1) The sample, 2 - 5 μL, was loaded onto the CRSD sample head with a microliter syringe or pipet.

2) Both atomization and vaporization sections of the furnace were heated to their maximum temperatures of 2500 °C and 2500 - 2600 °C, respectively. An
interval of 20 - 30 s was allowed for thermal equilibrium to occur.

3) The CRSD, with sample, was thrust into the heated furnace. Two Teflon adapters, as shown in Figure 15, provided a gas tight seal before the sample reached the heated portion of the furnace. As the sample head slid into the hot vaporization section, the sample was instantly vaporized, pushed by the argon through the atomization section and into the light path where the absorption measurement was made.

4) Power to both sections was turned off.

5) An interval of 30 - 60 s allowed the furnace and CRSD to cool before the next sample was run.

11. Method Modification by the use of the Carbon Rod Sampling Device (CRSD)

Any of the methods mentioned above (except the constant temperature method) could be modified by the use of the CRSD.

The precision associated with some of the above methods was rather poor at times, on the order of 20 - 30 % relative standard deviation (RSD). It was hypothesized that part of the imprecision resulted from irreproducible placement of sample on the furnace wall. As stated above, the needle tip was placed quite precisely in the same position before the sample was ejected. But, after the sample was ejected from the syringe, it is likely that the sample was smeared along the furnace wall as the needle was withdrawn. The carbon rod sampling device (CRSD) was designed to overcome this problem.
Figure 18
Second CRSO Design and Third Furnace Design used for the Constant Temperature Method
A microliter syringe or pipet was used to place 2 - 5 μL of sample onto the CRSD sample head. The CRSD was then slid into the vaporization section and the rest of the steps in the method were carried out with the CRSD inside the vaporization section. This avoided the smearing problem encountered with the needle.

If the CRSD had not been used in several hours, or longer, it was placed in the furnace and put through several cycles. This removed any material that may have adsorbed to it.

12. **Method Modification by the Use of Multiple Sample Drying on the CRSD**

Any of the methods described above could be modified by the use of multiple sample drying on the CRSD.

A microliter syringe or pipet was used to load 2 - 5 μL of sample onto the sample head of the CRSD. The sample was dried by heating the CRSD to about 80 °C with a heat lamp. After the sample was dry, another aliquot was added to the CRSD and the procedure was repeated two or three times, as desired.

This concentrated the sample by increasing the absolute amount of analyte on the CRSD. Now, detection of an analyte in a dilute sample was easier.

13. **Method Modification by the Use of Water Vapor or Methane as Reaction Gases**

Any of the methods described above could be modified by the addition of one of the two reaction gases to the furnace argon flow.

The purpose of adding either reaction gas to the furnace argon flow was to provide a greater reducing atmosphere inside the furnace. This would increase the
atomization efficiency and the sensitivity.

Methane was decomposed to hydrogen and elemental carbon, both of which were good reducing agents, inside the hot furnace. The water vapor was converted to carbon monoxide and hydrogen via the water gas reaction, discussed in the Introduction. Carbon monoxide and hydrogen also provided an excellent reducing atmosphere inside the furnace.

Methane was added to the furnace flow gas through the gas handling system, shown in Figure 15. Water vapor was added to the furnace flow gas by passing the argon through a water sparger, just before the argon passed into the furnace. Both gases could not be added to the furnace flow gas simultaneously, because the high back pressure from the water sparger prevented the methane from flowing.

E. Lead Studies

1. A(hot)Y Method

   a. Conditions

   The conditions used with this method are similar to those listed in Table III.

   b. Results

   When this method was used, a peak frequently occurred immediately after the sample was injected into the vaporization section. Concurrently, a "sizzle" emanated from inside the furnace. This occurred even though the vaporization section was not heated electrically. Apparently, the vaporization section, heated to 100 - 150°C by conduction, was hot enough to boil the sample solution as soon as it left the needle. Part of the analyte was carried through the hot atomization
section by the generated steam and into the light path, where the atomic absorption was measured. This was confirmed by running the same sample with the deuterium lamp, which showed that the absorption was due to atomic lead and not molecular species.

Another peak occurred when the vaporization section was heated. Because part of the analyte was lost before the vaporization section was heated, the sensitivity was reduced. The amount of analyte initially lost was not reproducible. Consequently, the peak generated when the vaporization section was heated was not reproducible.

The A(hot)V method was considered unusable for lead analyses because of the imprecision and reduced signal height caused by the initial sample loss.

2. AV Method

a. Conditions

A furnace argon flow rate of about 11 mL/min was used. This was the optimum flow rate, as indicated by a flow study (Figure 19).

The other instrumental conditions used for lead are listed in Table IV.

b. Results

A typical calibration curve for lead is illustrated in Figure 20. From the slope of the calibration curve, the sensitivity (by convention, defined as the mass of analyte required to give 1% absorption or 0.0044 absorbance units) was estimated to be 70 pg Pb. The literature sensitivity value for lead, using a commercial Massman-type atomizer [7], has been reported to be 23 pg Pb. Even though the
Figure 19

Flow Study Using 500 pg Pb

Absorbance

Furnace Argon Flow Rate (mL/min)
<table>
<thead>
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<th>Instrumental Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Wavelength</td>
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<tr>
<td>DHCL Current</td>
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<tr>
<td>DHCL Pressure</td>
<td>0.9 torr (120 Pa)</td>
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<tr>
<td>Monochromator Slit Width</td>
<td>20 μm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>330 V</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>275 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>16 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate - (Without CRSD)</td>
<td>11 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate - (With CRSD)</td>
<td>17 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
Figure 20
Calibration Curve for Lead Using the AV Method

Absorbance vs. ng Lead
sensitivity reported for this work was poorer, it was still of the same order of magnitude.

The calibration curve did not appear to be linear. Not all of the points fell on the least squares line, as shown in Figure 20. Part of the reason for this was the poor precision obtained, illustrated in Figure 21. For 2 ng of lead, an average absorbance 0.21A with a relative standard deviation of 22% was attained (11 trials). The reason for this poor precision is described below.

3. AV Method with the CRSD

a. Conditions

A furnace argon flow rate of about 17 mL/min was used. This was the optimum flow rate, as indicated by a flow study (Figure 22). Other instrument parameters are listed in Table IV.

b. Results

Imprecision resulted when the sample was placed in the vaporization section with the 10 cm syringe needle. It was possible that the sample was smeared along the vaporization chamber as the needle was withdrawn. The CRSD was designed, specifically to overcome this problem. Using this technique, sample placed on the CRSD was placed in the vaporization section reproducibly and without smearing.

Using an aliquot containing 2 ng of lead, an average absorbance of 0.10 A with a relative standard deviation of 8.7% was obtained when the CRSD was used (nine trials). When the CRSD was not used, a relative standard deviation of 22% was attained, (for eleven trials). Therefore, the precision was greatly increased when the CRSD was used. Unfortunately, peak broadening and consequent peak
Figure 21

Data Used for Lead Calibration Curve
Figure 22

Flow Study using 2 ng of Pb on the CRSD
shortening occurred, when the CRSD was used, leading to a decrease in sensitivity. This was a result of the decreased heating rate experienced by the sample, due to the increased mass of carbon (i.e., the CRSD) which had to be heated to vaporize the sample.

The precision study, above, was carried out before the furnace argon flow rate was optimized. A calibration curve made while using the CRSD, (Figure 23) indicated that the sensitivity (60 pg Pb) was virtually the same as when the CRSD was not used. This showed that, probably, the use of the CRSD did not greatly affect the sensitivity for lead, if all conditions were optimized.

4. AV Method with Multiple Sample Drying on the CRSD

a. Conditions

Conditions used are listed in Table IV.

b. Results

By placing a 2 µL aliquot of sample on the CRSD, drying it in the vaporization section and then placing 2 µL more sample on the CRSD, a two fold increase in signal was obtained, (Figure 24). Thus, some degree of sample concentration was achieved. This effectively increased the concentration sensitivity values, though not the absolute (mass) sensitivity values.

5. Effect of Furnace Design

a. Comparison of the Sensitivity of the First and Second Furnace Designs

The first and second furnace designs were described in the equipment section and illustrated in Figure 8.
Figure 23

Calibration Curve for Lead Using the AV Method with the CRSD
Figure 24
Absorption Signals for Lead Using the AU Method with Multiple Sample Drying on the CRSD

two aliquots
average = 0.174 A

one aliquot
average = 0.065 A

Absorption

Time

5 min
There was no significant difference in sensitivity for lead between the two furnace designs.

b. Effect of Atomization Channel Inside Diameter

The first time the second furnace design was used the results were very disappointing. A 5 ng aliquot of lead gave little or no signal. Usually, such a large quantity would result in at least 50% absorption. It was quickly discovered that the atomization section had been mistakenly drilled out to the wrong diameter. A drill bit of 5/64 inch (0.20 cm) diameter had been used instead of the usual 1/16th inch (0.16 cm) diameter drill bit. The larger diameter atomization channel did not allow the intimate contact between sample and hot carbon experienced with the smaller diameter atomization channel. What was most remarkable was that such a small difference in diameter could make such a large difference in atomization efficiency. When an atomization section inside diameter of 1/16th inch was used, roughly the same sensitivity as for the first furnace design was attained.

c. Effect of Extending the Furnace Light Path with a Cross Piece

A cross piece was added to the second furnace design in order to extend the light path. The design of the cross piece was described in the equipment section and illustrated in Figure 10.

The advantage of extending the light path with the cross piece was that it enabled more atoms to be in the light path at one time. Because more atoms were in the light path, the atomic absorption and sensitivity increased. The addition of a 4 cm cross piece resulted in a four fold increase in sensitivity for lead, as compared to the furnace without the light path.
F. COPPER STUDIES

1. A(hot)V Method
   a. Results

   As with the lead studies, when the aqueous sample came into contact with the hot vaporization section, the water boiled rapidly and part of the analyte was forced into the vapor phase. Two peaks resulted, one upon injection and one when the vaporization section was heated. This was undesirable for two reasons. First, the presence of two peaks resulted in lower peak heights and reduced sensitivity. Second, the first peak was extremely irreproducible, which resulted in poor precision.

   This method was not investigated further.

2. AV Method
   a. Results

   Copper, which has a boiling point of 2567 °C, required a longer period of time than lead to be released from the vaporization section. This section was only heated to about 2500 °C. Consequently, the copper absorption signals were 15 - 30 s wide at the base. This was much wider than for lead. Because the peaks were very wide, the peak heights were very small, resulting in poor sensitivity. This figure was 80,000 pg Cu. This was poorer than with the AV method with reverse flow.

3. AV Method with Reverse Flow
   a. Conditions

   It was shown that for the reverse flow method the maximum signal was obtained after the atomization section had heated for 45 s, as seen in Figure 25.
After this was ascertained, the atomization section was heated for ca. 50 s.

A flow study was conducted, as shown in Figure 26. It indicated that the furnace argon flow rate had little effect on the absorption peak height above about 25 mL/min. Other conditions are listed in Table V.

b. Results

No other method investigated was as sensitive as this one. It was never understood exactly why this particular method worked better than other methods. At first, it was suspected that methane in the housing purge gas was providing a better reducing atmosphere as it passed through the furnace. Such was not the case, however. When the methane was eliminated from the purge gas, the effect was the same. Later, it was discovered that soot had built up in the vaporization section after repeated cycles. It is possible that this soot was somehow responsible for the phenomenon, by providing sites for the reduction of the copper cation or formation of a more volatile copper compound, etc.

This hypothesis was strengthened by a report that carbon black increased the atomization efficiency of molybdenum and vanadium in furnace AAS [18]. The estimated sensitivity for copper was 150 pg Cu. This was poor compared to the literature sensitivity value of 45 pg Cu [7].

4. AV(warm)IV(hot) Method

a. Conditions

Conditions used with the AV(warm)IV(hot) method were similar to those listed in Table V.
Figure 25

Atomization Section Warm-Up Time Study Using 5 ng Cu
Figure 26
Flow Study Using 5 ng Cu
### TABLE V

**Typical Instrumental Conditions Used for Copper Studies**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
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<tr>
<td>DHCL Current</td>
<td>20 mA</td>
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<tr>
<td>DHCL Pressure</td>
<td>0.5 torr (67 Pa)</td>
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<tr>
<td>Monochromator Slit Width</td>
<td>30 μm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>330 V</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>275 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>4 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate</td>
<td>32 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
b. Results and Discussion

This method resulted in a sensitivity of 350 pg Cu, poorer sensitivity than the reverse flow method.

In terms of the temperature program, this method was very similar to the reverse flow method. The only difference was that the gases from the furnace housing did not flow backward through the furnace.

5. VA Trapping Method

a. Conditions

Conditions used with the VA trapping method were similar to those listed in Table V. Various furnace argon flow rates were studied to find the optimum flow rate.

b. Results

The VA trapping method resulted in a sensitivity value of 900 pg Cu. This was poorer than obtained with the AV method with reverse flow.

6. VA Trapping Method with Reverse Flow

a. Conditions

Conditions used with the VA trapping method with reverse flow were similar to those listed in Table V. Various furnace argon flow rates were studied to find the optimum flow rate.

It was hoped that by utilizing the reverse flow method the trapping efficiency would be increased. However, the method provided a sensitivity of 1000 pg Cu, poorer than the AV method with reverse flow and the VA trapping method.
7. Other Methods

a. Methods

At least two other methods, described below, were investigated for use with copper.

In one method the sample was placed in the furnace, the argon supply hose left unconnected, and the atomization section was heated. After 45 - 50 s, the vaporization section was heated and the argon supply hose reconnected to the furnace.

The other method used the three-way stopcock that had been installed in the argon supply system just before the furnace. Initially, the argon was shut off at the stopcock. The sample was placed in the furnace and the argon supply hose left unconnected. After the atomization section was heated for 30 - 60 s, the argon supply hose was reconnected. Then the vaporization section was heated for ca. 15 s. Next, the stopcock was turned to allow argon to flow through the furnace.

The object of both of the above methods, was to increase the time the sample spent in the vaporization section and thus increase the analyte atom concentration in the gas phase, before the sample was pushed through the atomization section and into the lightpath.

b. Results

The use of the first method resulted in an absorption signal when the argon supply hose was reconnected to the furnace. An estimated sensitivity of 300 pg Cu was obtained, as compared to 150 pg Cu for the AV method with reverse flow. The precision was very poor because it was difficult to time the various steps precisely.
The second method provided better reproducibility, because there were fewer critical steps. But the sensitivity was 200 pg ca, poorer than the AV method with reverse flow.

G. NICKEL STUDIES

The second furnace design was used throughout the nickel studies.

1. AV Method

a. Conditions

A flow study, illustrated in Figure 27, showed that the atomic absorption increased with increasing furnace argon flow rate. Since no maximum or plateau in the curve was seen, the flow rate was set to the maximum flow measurable by the rotometer, about 130 mL/min.

Other conditions utilized for the nickel studies are listed in Table VI.

b. Results

i. Sensitivity

A calibration curve made while using the AV method is shown in Figure 28. The slope of the curve indicated that the sensitivity was about 300 pg Ni. The literature sensitivity value was 330 pg Ni [7]. These values were essentially equivalent.

It was noted that as the carbon aged, the sensitivity for nickel decreased. A two or three fold decrease in sensitivity was sometimes noted, depending on the number of heating cycles the carbon had undergone.
Figure 27

Flow Study Using 50 ng of Ni
TABLE VI

Typical Instrumental Conditions Used for Nickel Studies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
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<td>Monochromator Slit Width</td>
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<td>Photomultiplier Tube Voltage</td>
<td>320 V</td>
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<td>Housing Argon Flow Rate</td>
<td>275 mL/min</td>
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<tr>
<td>Housing Methane Flow Rate</td>
<td>10 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate</td>
<td>122 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
ii. Precision

From six trials using 25 ng of nickel, an average signal of 0.30 A was obtained with a relative standard deviation of 35 %.

2. AV Method with the use of Reaction Gases
   a. Results

   Neither of the reaction gases (water vapor and methane) affected the sensitivity for nickel. Part of the failure of the water vapor may have rested on the low argon flow through the water sparger. Because the flow rate was relatively slow, the bubbles passing through the sparger were rather large. This decreased the efficiency of the sparger so that the argon was not saturated with water vapor.

3. AV method with Reverse Flow Method
   a. Conditions

   The conditions used were the same as listed in Table VI.

   b. Results

   No change in the atomic absorption signals was seen when the reverse flow method was used, as compared to when the basic method was used.

4. AV Method with the CRSD
   a. Conditions

   The conditions used were the same as listed in Table VI.

   b. Results

      i. Sensitivity

   A calibration curve, shown in Figure 29, was run. The sensitivity, as calculated from the slope, was about 200 pg Ni. This was slightly better than the
Figure 28
Calibration Curve for Nickel Using the AV Method

Absorbance

ng Nickel

0.0  0.05  0.10  0.15  0.20

0  5  10  15  20  25  30
Figure 29

Calibration Curve for Nickel Using the UA Trapping Method with the CRSD
Figure 30

Precision Study for Nickel Using the AU Method with and without the CRSD

- 15 ng Ni on CRSD: 6.6% RSD
- 25 ng Ni w/o CRSD: 35% RSD

Absorption vs. Time

5 min
sensitivity value obtained with the AV method without using the CRSD, which was 300 pg.

ii. Precision

Aliquots with 15 ng nickel (Figure 30) provided an average signal of 0.25 A with a relative standard deviation of 6.6 % (6 trials). This precision was much better than the 35 % RSD obtained without the use of the CRSD.

5. VA Trapping Method

a. Conditions

The conditions used are listed in Table VI.

b. Results

When the VA trapping method was used, the sensitivity of about 600 pg Ni was obtained. This represented a two fold loss of sensitivity over the AV method. The sensitivity loss did not seem to be due to peak broadening. When comparing peaks obtained while using the AV and VA trapping methods, no difference in peak widths was noticed. Thus, the loss of sensitivity was probably due to poor trapping efficiency, rather than peak broadening.

H. MERCURY STUDIES

The second furnace design was used throughout the mercury studies.

1. AV Method

a. Conditions

Conditions typically used for mercury are listed in Table VII. Several variables, notably the furnace argon flow rate and the atomization section
warm-up time, were changed to investigate the effect on the atomic absorption signal.

b. Results

As can be seen in Figure 31, as soon as the atomization section was heated, a mercury peak was generated. After 20 - 30 s, the vaporization section was heated, another mercury signal was seen.

It was apparent that by heating the atomization section, the vaporization section was heated (by conduction) enough to volatilize part, though not all, of the mercury standard. Thus, when the vaporization section was switched on, the peak that resulted was not as high as it might have been, because of the lost analyte. This illustrated the extreme volatility of mercury and its salts.

The method itself, was judged unsuitable, based on the evolution of two peaks, rather than one.

2. VA Method

a. Conditions

Typical conditions used for mercury are listed in Table VII.

b. Results

As can be seen in Figure 31, a peak occurred after the vaporization section was heated. When the atomization section was heated, another, smaller peak resulted. The second peak resulted from the small amount of mercury trapped inside the atomization section.

i. Sensitivity

The estimated sensitivity value was 600 pg Hg.
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<td>Housing Methane Flow Rate</td>
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<td>4 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
Figure 31
Mercury Absorption Signals Obtained from Various Methods

A - AV Method
50 ng Hg

B - VA Method
50 ng Hg

C - Simultaneous Heating Method
50 ng Hg

D - VA Method with CRSD
20 ng Hg

Absorption

Time

2 min
The first peak was much larger than the second, indicating that most of the mercury passed through the atomization section without being trapped.

When the height of the first peak was measured and compared to peaks representing the same amount of mercury, generated by other methods, it was obvious that this method was the most sensitive of all the methods that did not use the CRSD.

ii. Precision

The precision for seven trials using 25 ng of mercury was 34 % relative standard deviation.

iii. Cold Furnace Results

If a sample was placed in the furnace and allowed to sit for several minutes with argon passing over it, an atomic absorption signal would result. As can be seen from Figure 32, the peak was very broad, requiring two or three minutes to reach its maximum and subside. A large portion of the peak was due to atomic absorption even though the deuterium lamp showed that a small part of it was due to molecular absorption. If the peak was allowed to return to the baseline, the peaks that resulted from the heating of the vaporization and atomization sections were very small. This indicated that a large fraction of the analyte was being lost without even heating the furnace.

This phenomenon was noticed only when the furnace was new. Probably, when the carbon surface was aged and pitted, the sample soaked in and was not as easily volatilized. At least one manufacturer reported poorer sensitivity for mercury when pyrolytically coated furnaces were used [77]. Since the speed and/or
degree of loss depended on the porosity of the carbon surface, this process could lead to long term imprecision in quantitating mercury.

Once again, the volatility of mercury and its compounds was demonstrated. What was most remarkable, however, was that the mercury (II) chloride was not only volatilized, but also atomized in the cold furnace before it reached the lightpath.

3. VA Method with CRSD

a. Conditions

A flow study (Figure 33) indicated that a very low flow was optimum. Higher flow rates caused the atoms to pass through the light path faster than the electronics could process the signal. A furnace argon flow rate of 10 mL/min was typical. Other conditions are listed in Table VII.

b. Results

i. Sensitivity

A calibration curve (Figure 34) was run. The slope of the curve indicated a sensitivity value of 220 pg Hg. This was better than the value for the ordinary VA method, which was 600 pg Hg, and orders of magnitude better than the literature value of 15000 pg Hg [7].

The poor literature sensitivity value was a result of the loss of analyte during the drying and ashing steps necessary for commercial instruments.

The reason for the improved sensitivity over the ordinary VA method was probably due to the slower heating rate experienced by the sample on the CRSD. (Because the CRSD was heated only by radiation and conduction from the hot
Figure 32

Mercury Absorption Signals Obtained When the Furnace was not Heated

50 ng Hg

HCL
Deuterium Lamp

Absorption

Time

5 min
Figure 33
Flow Study Using 14 ng Hg and the UA Method with the CRSD
Figure 34
Mercury Calibration Curve with the CRSD and the VA Method
furnace, its temperature increased more slowly than that of the furnace.). The signal was slowed enough for the electronics to process it adequately.

ii. Precision

Using 10 ng aliquots of mercury, an average absorbance of 0.30 A with a relative standard deviation of 9.9 % was obtained (7 trials). This precision was considerably better than the 34 % obtained when the VA method was used without the CRSD.

4. AV and VA Methods with Matrix Modification

a. Method

As mentioned in the introduction, the use of matrix modifiers prevented the volatilization of easily vaporized analytes. One instrument manufacturer [77] recommended that matrix modification be carried out for mercury analyses. This was done by making up all of the samples and standards so that they contained 1000 µg/mL of tellurium and 10 % HCL.

For the purposes of this study, all of the standards were made up to contain 600 µg/mL of tellurium and 1 % HCL. The VA method or the AV method was then used for all of the samples.

b. Results

With matrix modification, the sensitivity for mercury was found to be 100 pg Hg for the VA method and 200 pg Hg for the AV method. Both of these values are better than those obtained without matrix modification, but not much better than when the CRSD was used (220 pg Hg). Also, these values were about the same as the commercial vendor's claimed sensitivity value of 150 pg Hg, attainable when
matrix modification was used. The results indicated that the use of the CRSD and the double stage furnace provided excellent sensitivity without the risk of added reagents.

It should be noted that when the AV method was used with matrix modification, only one peak resulted after the vaporization section was heated. This indicated that the matrix modifier greatly reduced the mercury loss, while the atomization section was being heated and the sample was dried.

5. Simultaneous Heating Method

a. Conditions

Typical conditions used are listed in Table VII.

b. Results

The estimated sensitivity value was 800 pg Hg. As can be seen from Figure 31, only one peak resulted. It was expected that this peak would be larger than any one peak in the other methods used for mercury, because no analyte loss occurred before the analytical signal was generated. In fact, the peak was smaller than with any other method. There were at least two explanations. First, it might have been that the absorption signal came off much faster than with the other methods and was distorted much more. The result was a drastically shortened peak. The other explanation was that when both sections were heated simultaneously, the currents set up by the rapidly expanding gas impeded the analyte flow into the light path. In support of this, the peaks did not rise and fall as smoothly for this method as they did with some of the other methods.
6. Other Methods

a. Methods and Conditions

Several other methods were investigated for use with mercury. Most of these involved changing the furnace argon flow rate or rearranging the order of the steps in the heating cycle.

b. Results

None of the other methods had results as good as those obtained for the methods used for mercury mentioned previously in this section.

I. Tin Studies

The second furnace design was used throughout the tin studies.

1. Demountable Hollow Cathode Lamp

The tin DHCL proved to be rather troublesome. Several different hollow cathodes were made by different methods. The tin was pounded into a foil, cut to size, rolled up and slipped into a brass or carbon cup. Another method for manufacturing hollow cathodes was to melt tin pellets in a brass or carbon cup (an oven at 300 °C was used). After the metal had cooled, it was drilled out to form the hollow cathode.

Several cathodes were made by the above methods, but they did not produce a strong tin resonance emission line. Finally, a cathode was made (tin pellets melted in a carbon cup) that emitted the 224.6 nm tin resonance line. The emission line was strong enough to use, only if the DHCL was operated in the flow through mode, as explained in the equipment section.
Even this hollow cathode was far from satisfactory. The emission line was rather weak and unstable. Fluctuations in the emission line intensity made it difficult to keep the recorder pen on scale.

2. AV Method

a. Conditions

A flow study, Figure 35, indicated that the optimum furnace argon flow rate was about 60 mL/min. The effect of atomization section warm-up time on the tin signal was also studied, Figure 36. It indicated that the atomization section should be allowed to heat for 30 s before the vaporization section was heated. Other conditions are listed in Table VIII.

b. Results

As can be seen in Figure 37, the linearity of the calibration curve was poor beyond about 30 ng of tin. The slope of the linear portion of the curve indicated a sensitivity value of about 2500 pg Sn. This was better than the literature sensitivity value of 5500 pg Sn [7].

J. ARSENIC STUDIES

1. Hollow Cathode Lamp

A Westinghouse sealed hollow cathode lamp was used for most of the arsenic studies.

A few hollow cathodes were initially available for the demountable HCL, but they were old and soon ceased to function. The only arsenic containing materials available were elemental arsenic powder and arsenic trioxide. Both of these
Figure 35
Flow Study Using 50 ng Sn
Figure 36

Atomization Section Warm-Up Study

Using 50 ng Tin
**TABLE VIII**

**Typical Instrumental Conditions Used for Tin Studies**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>224.6 nm</td>
</tr>
<tr>
<td>DHCL Current</td>
<td>&gt; 30 mA</td>
</tr>
<tr>
<td>DHCL Pressure</td>
<td>0.96 torr (128 Pa)</td>
</tr>
<tr>
<td>Monochromator Slit Width</td>
<td>20 µm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>430 V</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>275 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>4 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate</td>
<td>65 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
Figure 37

Calibration Curve for Tin Using the AV Method
materials sublime at temperatures below their respective melting points. Thus, they could not be melted in a cathode cup and drilled out, as could some of the arsenic halides, for example.

2. AV Method

a. Conditions

A flow study, using the basic method, shown in Figure 38, indicated an optimum furnace argon flow rate of about 55 mL/min. Other conditions are listed in Table IX.

b. Results

i. Preservatives for Standards

Originally, all of the standards were made up with 3% sulfuric acid as a preservative [77]. It was soon discovered that the sulfuric acid created a serious background absorption problem. As much as 95% of the HCL radiation was absorbed, through molecular absorption, by a 5 µL aliquot of 3% sulfuric acid in DDW. Thus, all standards more dilute than 1000 µL/mL As were made to have 5% hydrochloric acid. Hydrochloric acid has been used by other workers to preserve arsenic standards [80]. This reduced the background problem considerably.

ii. Sample Loss

A signal was generated as soon as the atomization section was heated. Most of the peak represented molecular background absorption, as measured with the deuterium lamp, but part of it was due to the volatilization of arsenic. The majority of the arsenic was released when the vaporization section was heated. This result was very similar to the result noted for the mercury study using the AV
Figure 38

Flow Study Using 5 ng As
<table>
<thead>
<tr>
<th><strong>Typical Instrumental Conditions Used for Arsenic Studies</strong></th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>193.7 nm</td>
</tr>
<tr>
<td>HCL Current</td>
<td>16 mA</td>
</tr>
<tr>
<td>Monochromator Slit Width</td>
<td>70 μm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>420 V</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>325 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate</td>
<td>55 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
method. Part of the analyte was lost during the atomization warm-up process.

iii. Sensitivity and Precision

The analyte loss mentioned above contributed greatly to a loss in sensitivity and poor precision. Arsenic sensitivity was estimated to be 256 pg As. This was compared to a literature sensitivity value of 160 pg As.

3. Other Methods

a. Methods

Other methods investigated for use with arsenic included the AV method with the CRSD, the AV method with reverse flow method, the AV method with reaction gas (methane), the simultaneous heating method, and the VA trapping method.

b. Results

None of these methods gave better results than did the AV method. The AV method with the CRSD, the AV method with reaction gas (methane) and the AV method with reverse flow methods did not improve the precision or sensitivity. The VA trapping and simultaneous heating methods provided poorer sensitivity.

K. MANGANESE STUDIES

1. Hollow Cathode Lamp

A combination magnesium/calcium hollow cathode lamp, manufactured by the Perkin-Elmer Corporation, was used.

2. Determination of Molecular Background Absorption

As will be discussed below, it was necessary to remove the cross piece from the light path of the furnace. When the cross piece was removed, radiation from
the hot atomization section was allowed to reach the monochromator. This was not a problem when the HCL was used.

The deuterium lamp, normally used for background determination, was not very intense in the region of the magnesium resonance line (285.2 nm). It required that the voltage to the photomultiplier tube (PMT) be increased in order to set the electronics to 0% absorption.

Ultraviolet radiation coming from the hot atomization section did not directly interfere with the measurement of absorption signals, since the electronics discriminated against all UV radiation except that from the modulated deuterium lamp. But the combination of high intensity UV radiation from the furnace and the high PMT voltage caused the PMT to become "fatigued". The result was a great deal of electronic noise. The baseline noise sometimes encompassed as much as 10% of the recorder scale. Clearly, this condition made the measurement of molecular background absorption difficult.

In order to avoid this problem, an off-resonance magnesium emission line from the hollow cathode lamp, was used for background determination. A magnesium emission line (280.3 nm) near the resonance emission line (285.2 nm) was chosen. This emission line was much more intense than the deuterium lamp. A lower PMT voltage was used to eliminate the PMT fatigue. The non-resonance line could not be absorbed by magnesium atoms (or any other atoms). Any absorption of the non-resonance line was a good measure of the broad band molecular absorption in the spectral neighborhood of the resonance line. The
difference in absorption of the two emission lines was the net atomic absorption signal.

3. AV Method

a. Method and Conditions

The AV method described in the methods section was used. The atomization section was allowed to heat for 10 s before the vaporization section was heated.

A flow study, Figure 39, indicated that a furnace argon flow rate of 50 - 60 mL/min was optimum. Other conditions are listed in Table X.

b. Results

i. High Atomic Background

When the atomization section was heated, with no sample, a slow increase in absorption took place. This absorption would increase to a certain value, level off and then decrease. The entire cycle could take as long as 10 min. Normally, it would be suspected that such a phenomenon was caused by some organic material volatilizing out of the carbon. In this case, that was not the cause.

When the deuterium lamp was used, it became evident that the phenomenon was caused by atomic, not molecular, absorption. Apparently, minute amounts of magnesium, present as an impurity in the carbon, were vaporizing and entering the light path. Such small amounts were a problem because of the high sensitivity of atomic absorption for magnesium.

Because the cross piece was heated to only about 1200 °C it could retain a volatile element, such as magnesium, much longer than the furnace itself. For
Figure 39
Flow Study Using 0.5 pg Mg and the AU Method

Absorbance

Furnace Argon Flow Rate (mL/min)
TABLE X

**Typical Instrumental Conditions Used for Magnesium Studies**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>285.2 nm</td>
</tr>
<tr>
<td>(for background measurement)</td>
<td>280.3 nm</td>
</tr>
<tr>
<td>DHCL Current</td>
<td>12.5 mA</td>
</tr>
<tr>
<td>Monochromator Slit Width</td>
<td>30 μm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>290 V</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>275 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>10 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate - AV Method</td>
<td>55 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate - VA Trapping Method</td>
<td>80 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
this reason, the cross piece was considered the primary source of the background magnesium.

The atomic background decreased dramatically after the cross piece was removed. It was later shown that the removal of the cross piece did not greatly decrease the sensitivity for magnesium.

ii. Sensitivity

Only one peak resulted. It occurred when the vaporization section was heated.

The AV method gave an estimated sensitivity value of 0.8 pg Mg, which was not as sensitive as the trapping method, discussed below.

4. VA Trapping Method

a. Method and Conditions

The method used was essentially the same as described in the methods section. The vaporization section was heated for 15 s before the atomization section was heated. A flow study, Figure 40, indicated that the optimum furnace argon flow rate was 75 - 85 mL/min. Other conditions are listed in Table X.

b. Results

1. Contamination

It became apparent that magnesium was present in the laboratory environment in rather high concentrations. No other element studied, showed a significant "blank" concentration in the deionized distilled water. Magnesium was present in concentrations high enough to produce 5 - 10% absorption signals for 5 µL sample of DDW.
Figure 40

Flow Study Using the UA Trapping Method and 2.5 pg Mg
Figure 41
Magnesium Absorption Signals from DDW Stored in Four Different Volumetric Flasks

Flask A
Flask B
Flask C
Flask D

Absorption

Time

5 min
In addition, magnesium leached out of the volumetric glassware (if magnesium concentrations were low) or adsorbed onto the glassware (if concentrations were high). The former problem was most severe.

It proved impossible, because of leaching, to prepare accurate standards for a calibration curve. Different volumetric flasks would contribute different amounts of magnesium to their contents. Thus, each flask had its own blank value, which even varied over time. This is illustrated in Figure 41, where DDW stored for one hour in four different acid washed volumetric flasks was analyzed for magnesium. The DDW from each flask had a different concentration of magnesium.

ii. Sensitivity

To combat the leaching problem, a different method for making a calibration curve was devised. A volumetric flask was filled with DDW and allowed to sit for an hour. The "blank" magnesium absorption measurement was made for a 5 µL aliquot. A 1 ppb Mg standard was made up in the same flask and was allowed to sit for one hour. Then, 5 µL, 10 µL, and 15 µL aliquots of the standard were placed in the furnace and analyzed. The resulting signals were corrected for the blank by subtracting the blank value multiplied by a factor of 1, 2 or 3, depending on whether a 5 µL, 10 µL, or 15 µL aliquot of standard had been used.

Figure 42, shows both the corrected and uncorrected calibration curves. The blank correction method described was not entirely successful because the two curves did not have similar slopes. In hindsight, it would have been more accurate to measure blank absorptions for 5 µL, 10 µL and 15 µL aliquots of DDW and subtract those values from the standard absorptions obtained.
Nevertheless, the slope of the corrected curve gave a conservative estimate of the sensitivity. The value was 0.3 pg mg. This compared well with the sensitivity range of 0.3 - 0.6 pg mg claimed by a commercial instrument manufacturer [77].

iii. Precision

For five aliquots of 5 pg mg, the average absorbance value was 0.0714 A with 14% relative standard deviation.

5. Multiple Trapping Method

a. Conditions

Conditions used are summarized in Table X.

b. Results

Calibration curve data were obtained by trapping aliquots totaling 5 µL, 10 µL, and 15 µL of the 1 ppb Mg standard. The absorbance values obtained were corrected by subtracting the blank value for 5 µL, 10 µL, and 15 µL of DDW stored in the same flask, as described above.

As was the case with the VA trapping method, the slopes of the two curves did not agree. Again, this indicated that the blank correction method was not entirely correct.

The slope of the corrected curve indicated a sensitivity value of 0.6 pg mg for the multiple VA trapping method, slightly poorer than for the simple VA trapping method. This difference was expected because there were more opportunities for sample loss when the trapping was performed in stages.
Figure 42

Calibration Curve for Magnesium
Using the UV Trapping Method

pg Magnesium
6. Simultaneous Heating Method

a. Conditions

Conditions for magnesium are listed in Table X.

b. Results

The sensitivity for this method was estimated to be 0.9 pg Mg. This was a factor of three poorer than for the AV method.

7. Trapping Method with the CRSD

a. Conditions

Conditions used are listed in Table X.

b. Results

The CRSD adsorbed magnesium from the atmosphere. The amount adsorbed was large and irreproducible. This made the use of the CRSD impossible outside of a laboratory "clean room". Such facilities were not available.

L. CALCIUM STUDIES

The second furnace design was used throughout this study.

1. Hollow Cathode Lamp

A commercial, combination calcium/magnesium hollow cathode lamp (Perkin-Elmer Corporation) was used.

2. Methods and Conditions

The AV method and the VA trapping method, described in the methods section, were used. Typical instrument parameters for calcium are listed in Table XI.
3. Results and Discussion

The VA trapping method resulted in no apparent atomic absorption signal for 5 ng of calcium. Several furnace argon flow rates were investigated with identical results.

When the AV method was investigated, using 5 ng of calcium, a very broad peak (about 60 s wide at the base) resulted. Figure 43 illustrates the wide absorption peaks, which were obtained at several different furnace argon flow rates. Based on peak height, an estimated sensitivity value for calcium was 300 pg Ca. This compared rather poorly with the literature sensitivity value of 3.1 pg Ca [7].

Calcium is one of the most easily atomized elements studied, as indicated by the low literature sensitivity value. Unfortunately, it also forms a stable carbide when heated in the presence of carbon [133]. The calcium atoms, formed in the vaporization chamber, probably reacted with the hot carbon to form calcium carbide. Since calcium carbide has an extremely high boiling point (melting point is > 2000 °C [81]), a relatively long period of time was required for it to vaporized completely from the furnace, which had a temperature of about 2500 °C.

Another possible explanation of the peak broadening involved a dynamic equilibrium between calcium atoms and calcium carbide. Calcium atoms in the vapor phase constantly formed calcium carbide, which had a low vapor pressure and was adsorbed to the carbon. The calcium carbide was decomposed by the hot carbon, releasing calcium atoms, which began the cycle again. Such a
### TABLE XI

**Typical Instrumental Conditions Used for Calcium Study**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>242.7 nm</td>
</tr>
<tr>
<td>HCL Current</td>
<td>13 mA</td>
</tr>
<tr>
<td>Monochromator Slit Width</td>
<td>20 µm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>310 V</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>275 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>9 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate</td>
<td>64 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
Figure 43
Typical Absorption Signals for 5 ng Calcium
pseudo-chromatographic process would explain the calcium retention by the furnace.

M. ZINC STUDY

It was found that the carbon, from which the furnace was machined, was too contaminated with zinc to be used. When the furnace was heated, the zinc resonance line was almost totally absorbed. Even heating the carbon furnace for an hour or longer did not remove the zinc and reduce the absorption to an acceptable level.

The reasons for this result, included the high sensitivity for zinc by atomic absorption and the high levels of zinc in the carbon.

N. SELENIUM STUDIES

1. Problems with the Demountable Hollow Cathode Lamp

Selenium proved to be an especially difficult element from which to make an operable hollow cathode. The element was brittle, difficult to machine and, most importantly, non-conductive.

A selenium hollow cathode was made by melting selenium powder in a brass cathode cup. When the cathode had cooled, it was mounted on a lathe and carefully drilled out. Care had to be taken to avoid shattering the fused selenium. The inside diameter was critical, though difficult to control because of the material's brittleness. If the coating of selenium inside the cathode cup was too thick, the resistance was too great to allow current to flow through the lamp. If the coating
was too thin, the volatile selenium was quickly lost and a new cathode had to be made.

Getting the selenium hollow cathode to fire, once inside the lamp, was also problematic. Best results were obtained when the lamp was evacuated to about 0.01 torr (1.3 Pa) for 10 - 14 hours. At this point, the lamp usually would not fire. The polarity was reversed and the lamp was fired "anodically". This was easier to accomplish because the discharge was then centered on the stainless steel anode, rather than the nonconducting selenium. After the lamp was fired 5 - 10 min., with the polarity reversed, the lamp polarity was returned to normal. Usually, the lamp would then fire in the correct manner.

The fact that a cathode could be made to fire was no assurance that it could be used. Out of three or four apparently identical cathodes, usually, only one would exhibit the selenium emission lines. Many cathodes would exhibit only broad emission bands rather than the narrow selenium atomic emission lines.

An attempt was made to use the DHCL in the flow through mode, as discussed in the equipment section. The attempt only decreased the intensity of the atomic emission lines.

At the end of each working day, the DHCL had to be disassembled. Selenium oxide, which had built up during the day, was rinsed out of the cathode cup with DDW. The water caused the formation of elemental red selenium, indicating the reduction of the selenium oxide. To rid the cathode cup of water, it was rinsed with absolute ethanol. The cathode cup was returned to the DHCL and placed under reduced pressure over night.
These cathodes were very temperamental, unstable, (due to selenium oxide formation) and short lived.

2. Effect of Selenium Plating onto the Syringe Needle

Over a period of time, the stainless steel syringe needle became coated with a layer of selenium. The selenium was, apparently, plating onto the needle from the standard solutions used.

This process almost certainly had an adverse effect on the precision and accuracy of the technique for several reasons. When selenium plated out of the standard solutions, then with time, the standards would no longer have the proper concentration of selenium. Also, some of the selenium which had plated on the needle was probably scraped off the needle and onto the inside of the vaporization section, when the sample was deposited. This resulted in irreproducibly elevated selenium signals. Thus, possibilities existed for sample contamination and sample loss.

When the importance of this phenomenon was realized, the use of the syringe was halted. Methods involving the CRSD were used. The CRSD was loaded with sample from a microliter pipet fitted with plastic pipet tips to avoid the selenium plating problem.

3. AV Method with the CRSD

a. Method and Conditions

The AV method described in the methods section was used. The atomization section heating time was 15 s, instead of 30 s. The CRSD was used to place 3 μL of sample in the vaporization section. Typical conditions used are listed in Table XII.
b. Results

This method gave an estimated sensitivity of 600 pg Se. This was less sensitive than the trapping method, discussed below.

4. VA Trapping Method with the CRSD
   a. Conditions

   A flow study, Figure 44, indicated that the optimum furnace argon flow rate was about 30 mL/min. Other instrument operating parameters are listed in Table XII.

   b. Results

   A calibration curve is shown in Figure 45. Using the linear part of the curve, the slope indicated a sensitivity value of 300 pg Se. This value was not much worse than literature sensitivity value of 100 pg Se [73].

   It should be noted that pyrolysis decreased the sensitivity for selenium. The reason for this may have been that the surface area in the atomization section was decreased, which decreased the trapping efficiency.

5. Constant Temperature Method
   a. Conditions

   Operating conditions are summarized in Table XII.

   b. Results and Discussion

   The calibration curve obtained is shown in Figure 46. From the linear portion of the curve, (the lowest three points) the slope indicated a sensitivity value of 300 pg Se. This value was exactly the same as for the trapping method. The two explanations for this were, that the constant temperature atomization method did
TABLE XII

Typical Instrumental Conditions Used for Selenium Studies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Wavelength</td>
<td>196.1 nm</td>
</tr>
<tr>
<td>DHCL Current</td>
<td>20 mA</td>
</tr>
<tr>
<td>DHCL Pressure</td>
<td>1 torr (133 Pa)</td>
</tr>
<tr>
<td>Monochromator Slit Width</td>
<td>50 µm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>380</td>
</tr>
<tr>
<td>Housing Argon Flow Rate</td>
<td>350 mL/min</td>
</tr>
<tr>
<td>Housing Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
<tr>
<td>Furnace Argon Flow Rate</td>
<td>30 mL/min</td>
</tr>
<tr>
<td>Furnace Methane Flow Rate</td>
<td>0 mL/min</td>
</tr>
</tbody>
</table>
Figure 44

Flow Study Using 50 ng Se and the UR Method with the CRSD

Absorbance vs. Furnace Argon Flow Rate (mL/min)
Figure 45

Calibration Curve for Selenium

Using the Ua Trapping Method with the CRSD

Absorbance

ng Selenium
not work as planned, or that no sample loss occurred with the VA trapping method.

After reviewing the data, it was concluded that the sample loss initially noted for selenium had been eliminated through the careful control of the operating parameters. Therefore, the two methods should have obtained the same sensitivity values. Such a result indicated that each method was operating with very high efficiency.

However, the precision for the constant temperature atomization method was rather poor, compared to other CRSD methods. From eight trials using 3 ng of selenium, the relative standard deviation was 17%. Most of the other CRSD techniques had relative standard deviations of about 10% or less.

It was noticed that the peak height for a certain mass of analyte depended on how fast the CRSD was pushed into the hot furnace. The faster the CRSD was pushed in, the higher the peak was. This was almost certainly caused by the difference in heating rate experienced by the sample, which depended on how fast it entered the furnace. If an automatic device had been available to push the CRSD into the furnace at a reproducible speed, the precision could have been improved. Such a device was reported to have improved the operation of a graphite probe atomization system [33].

The graphite or carbon probe has been reported by several authors in connection with carbon furnace atomic absorption [29 - 35] and atomic emission [35, 36]. The CRSD and the graphite probes were similar in construction and use.
Figure 46
Calibration Curve for Selenium
Using Constant Temperature Atomization
A sample was placed on the graphite probe. The sample was dried, and charred, (if necessary), usually outside of the atomizer. Then the probe was plunged into the hot Massman-type furnace, where atomization and absorption took place. The most important difference between the two methods was that, for the Massman-type furnace and the graphite probe, the atomization process took place in the optical light path of the instrument. Thus, the samples had to be dried and ashed before they were inserted into the hot furnace. For example, if an aqueous sample were thrust into the hot furnace, the steam generated would completely absorb the hollow cathode radiation. No atomic absorption could be measured and the analytical signal would be lost. This was not the case with the CRSD and the double stage furnace. As Figure 47 clearly illustrates, an aqueous sample, inserted into the double stage furnace (already heated), gave a large absorption signal while only a small part of it represented molecular background absorption. Reduced background absorption was one of the advantages of atomization of the sample outside of the light path, as in the double stage furnace.

6. **Multiple VA Trapping Method and VA Trapping Method with Multiple Sample Drying on the CRSD**

   a. **Conditions**

   Typical conditions used are listed in Table XII.

   b. **Results**

   For both cases, the two-fold drying or trapping process increased the signal by 80 - 90%. This was similar to the results obtained for magnesium. When the three-fold drying or trapping process was attempted, only a negligible increase
Figure 47

Absorption Traces from 15 ng Selenium Using the Constant Temperature Method
was noted. Thus, these two methods were used to increase the selenium signal by about two-fold, but not much more.

7. Other Methods

a. Methods and Conditions

The simultaneous heating method with the CRSD was used. The reaction gases, methane and water vapor, were used with the VA trapping method. Conditions used are listed in Table XII.

b. Results

The simultaneous heating method gave small atomic absorption signals compared to the trapping methods. The estimated sensitivity value was 500 pg Se.

The use of methane and water vapor did not improve the sensitivity for selenium by the trapping method.

8. SPECIATION STUDIES

1. Introduction

The speciation of a metal is sometimes just as important as its quantitation. The double stage furnace was originally designed specifically for speciation.

In order to show that the speciation capabilities had not been adversely affected by the new furnace designs, some speciation work was performed. Lead was chosen for this work because of the large amount of data obtained with earlier designs [45, 46, 59, 69], which could be used for comparison.

The second furnace design was used throughout the speciation studies.
2. Methods and Conditions

The microliter syringe was used to deposit 2 - 5 µL of sample in the vaporization section. After the argon supply hose was reattached, the atomization section was heated to its maximum temperature for 30 s. Then the temperature of the vaporization section was slowly increased.

As the temperature increased to near the boiling point of a certain compound, that compound would vaporize, leaving behind all of the other compounds that had higher boiling points. In this way, a separation was accomplished by differences in boiling points. The gaseous compound was swept, by the argon flow, through the atomization section and into the light path, where the atomic absorption measurement was made.

The vaporization section heating program was accomplished manually. As explained in the equipment section, the voltage (and thus current) going to the vaporization section was controlled by two ganged auto transformers (Variac). To implement a temperature program, the Variac setting was increased by a certain amount at selected intervals. For example, one temperature program increased the voltage from 0 to 130 V by 5 V intervals every 5 s. This gave a net heating rate of about 1250 °C/min. Rates of 250 °C/min to 5000 °C/min were investigated. The 1250 °C/min rate was one of the more common heating rates used.

Since different temperature programs were used at different times, the instrument results (called thermograms), illustrated in the figures in this section, differed somewhat, even for the same sample. The thermograms differed in width (time) from beginning to end. Also, "spikes" appeared in some thermograms.
When the interval between voltage settings was too large, the temperature of the vaporization section would increase in steps, rather than as a smooth increase, as desired. As the temperature increased quickly, material vaporized more quickly, until the temperature stabilized. The result was a set of spikes rather than the smooth curve which indicated smooth heating and vaporization.

It is important to note that in these temperature programs, it was the voltage which increased linearly with time, not temperature. At low temperatures, the temperature of the carbon changed only slightly with an increase in voltage. At high temperatures, the carbon temperature increased a great deal with a small increase in voltage. Because of this, the temperature increased slowly at the beginning of the temperature program and it increased quickly at the end. The electronic equipment needed to set up a true, temperature-based program was not readily available. Thus, the voltage-based programs described above, were used.

A flow study was performed which indicated that a furnace argon flow rate of about 10 mL/min gave the best sensitivity. However, it also indicated that a flow rate of about 120 mL/min resulted in the smallest amount of molecular background absorption. The 120 mL/min flow rate was used.

All of the other instrument parameters were similar to those in Table IV.

3. Results for Lead Nitrate and Lead Chloride

The lead nitrate thermogram exhibited one peak at about 1500 °C (Figure 48). This peak was not the result of the vaporization of lead nitrate, however. Lead nitrate decomposed at about 400 °C to lead monoxide. The lead monoxide then vaporized at 1500 °C to give the peak seen in the thermogram.
Lead chloride exhibited two peaks at about 300 °C and about 1500 °C. The first peak represented the vaporization of lead chloride. The temperature of the second peak corresponded to that of lead monoxide, which indicated that that specie had vaporized. The exact mechanism for the conversion of lead chloride to lead monoxide is not known. In solution, lead is ionic and hydrated. It has been suggested that the drying process converts a large amount of the hydrated lead to lead monoxide [45].

The results presented here agree well with previous workers results [45].

4. Effects of Added Halides on the Lead Nitrate Thermogram
   a. Iodide and Bromide

   Solutions were made up with 100 μg Pb/mL (as the nitrate) and 100 μg iodide or bromide/mL (as the potassium or sodium salt, respectively).

   The thermograms of these solutions closely resembled that of lead chloride, as seen in Figure 49. This indicated that the lead halide was formed when the solution was dried in the furnace, as would be expected.

   Increasing the amount of halide to 500 μg/mL did not increase the size of the first peak relative to the second peak, however.

   b. Chloride

   1. As Hydrochloric Acid

   Solutions of 100 μg Pb/mL (as the nitrate) were made up with approximately 500, 1000, and 5000 μg HCl/mL.

   A typical thermogram is shown in Figure 50. It was very similar to that obtained for lead chloride. Increased amounts of hydrochloric acid had no
Figure 48
Absorption Traces for Lead Chloride and Lead Nitrate
noticeable effect on relative peak heights.

ii. As Sodium Chloride

Solutions of 100 μg Pb/mL (as the nitrate) were made up with 100, 500, 1000, 5000 μg chloride/mL (as the sodium salt).

Resulting thermograms are shown in Figure 51. Only a very small chloride peak was seen at high chloride concentrations. It was absent at lower chloride concentrations.

A very sharp peak was present at a very low temperature in the thermogram for the 5000 μg chloride/mL sample. It was suspected that water, trapped in the matrix, explosively forced part of the solid into the argon stream. Thus, this peak was probably due to the fine powder passing through the atomizer, rather than a vaporized lead compound.

5. Effects of Furnace Age and Pyrolysis

It was noticed that as the furnace aged, the separation between the halide and oxide peaks deteriorated. The peaks broadened also, making peak differentiation difficult, if not impossible. As shown in Figure 52, the thermogram for 100 μg Pb/mL and 500 μg iodide/mL was improved considerably after the furnace was pyrolyzed for 30 min. This indicated that the porosity of the interior surface of the vaporization section was of critical importance for reproducible results.

6. Summary

This, rather cursory, study indicated that the new furnace design had not hindered the speciation ability of the double stage furnace. As noted above, the
Figure 49
Absorption Traces for 100 μg/mL Pb with Added Bromide and Iodide

\[ \text{Pb(NO}_3\text{)}_2 + \text{Br}^- \]

\[ \text{Pb(NO}_3\text{)}_2 + \text{I}^- \]

Time (Temperature)

2 min
Figure 50

Absorption Traces of Lead (as Nitrate) with Various Amounts of Added Hydrochloric Acid
Figure 51
Absorption Traces for 100µg/mL Pb with Various Amounts of Added Chloride
results obtained compared favorably with previously reported results [45].

The study results emphasized the need to use a non-porous material for the furnace if speciation work was to be performed. Thermograms, even for the same sample, were not entirely reproducible, as illustrated in Figure 53. This was because the nature and porosity of the carbon surface was constantly changing.

Study results also indicated that a former explanation for the formation of lead monoxide from a solution of lead chloride [45] was probably incorrect. The assertion was that lead is ionic and hydrated in solution. When the solution was dried, mostly hydrated lead ions along with some lead chloride was deposited on the furnace walls. Upon heating, the hydrated lead decomposed to lead oxide. If this theory were correct, then added chloride should have forced, by mass action, the formation of a larger fraction of lead chloride. However, added chloride had no effect on the lead thermograms, indicating no change in the system.

An alternate explanation might be that, on heating, most of the lead chloride decomposed directly to lead monoxide. A related explanation was that on melting, at 550 °C, part of the lead chloride was vaporized, but most of it decomposed. Elemental lead released during decomposition scavenged the warm furnace environment for the traces of oxygen present. Lead monoxide was produced. A trace concentration of about 10 ppm oxygen in the argon, used over a period of 15 s, converted all of the lead present to lead monoxide. Such low levels of oxygen were very difficult to eliminate. To support this explanation, lead chloride was heated above its melting point in a muffle furnace. After 30 - 40 min., much of the white lead chloride had been converted to yellow lead monoxide.
Figure 52
Absorption Traces of a Solution of Lead and Iodide
Before and After Pyrolysis of the Furnace

Before

After

Absorption

2 min

Time

(Temperature)
Figure 53

Three Consecutive Absorption Traces of a Solution of PbCl and HCl
IV. CONCLUSION

A. EVALUATION OF METHODS

Table XIII summarizes which techniques were used with which elements. It indicates the preferred method and the sensitivity obtained. The other important methods used are also indicated.

1. A(hot)V Method

The original method, as described in the discussions of the lead and copper studies, was unsuccessful. Heat, conducted from the atomization section caused analyte loss when sample was placed in the vaporization section.

2. AV Method

The AV method was the most consistently successful method investigated. For five of the nine elements, for which data were obtained, the AV method (including CRSD use) provided the best sensitivities.

3. VA Trapping Method

The trapping method proved to be the best for only two elements, magnesium and selenium. Other elements investigated probably were too volatile to trap or were not released efficiently when the atomization section was heated. The latter problem was caused by the uneven heating of the atomization section. Since the center of the atomization section heated more quickly than did the ends, analyte trapped at the center was vaporized first. As the temperature of the ends of the section heated, more analyte was vaporized. This caused the absorption signals to be broadened and consequently shortened. The apparent sensitivity was decreased.
Only those elements which were vaporized at low temperatures, such as magnesium and selenium, were quickly and efficiently released from the atomization section.

This method was similar, in principle, to a flame atomic absorption method, reported by Khalighie, Ure and West [82 - 85]. With this method, the analyte was trapped and concentrated on a water cooled length of tubing held in the flame. When the water cooling was discontinued, the concentrated analyte was vaporized into the flame where the absorption measurement was made.

The trapping method was even more closely related to the use of second surface atomization [27] and the L'vov platform [20 - 25]. These methods were discussed in the general introduction.

4. AV Method with Reverse Flow

This method, as described in the discussion of the copper studies, was the most sensitive method for copper. Its efficiency was never understood, however. The method did not improve the sensitivities for arsenic or nickel.

5. Simultaneous Heating Method

This method was not successful for any of the four elements with which it was used. The problem arose from the rapidly expanding gases in the heating vaporization and atomization sections, which interfered with the normal argon gas flow through the furnace.

6. VA Method

The VA method, which was used only for the mercury studies, was procedurally the same as the trapping method. This method, when used with the
CRSD, provided the best sensitivity for mercury.

7. Multiple VA Trapping Method and Method Modification by Multiple Sample Drying on the CRSD

The purpose of the multiple VA trapping method and the method modification by multiple sample drying on the CRSD was to concentrate the sample. It was successful. By concentrating two aliquots together, the concentration sensitivity value was improved by 80 - 100 %, as expected. The absolute sensitivity value was unchanged, of course.

These results were not surprising. Similar methods have been reported for commercial instruments [66].

8. CRSD Methods

The various CRSD methods improved, at least slightly, the sensitivity values for three of the elements studied.

Most importantly, the precision increased dramatically when the CRSD was used, even when the same heating method was used. Using the same heating method, the precision for lead, selenium and mercury increased from 22 %, 14 % and 34 % relative standard deviation to 8.7 %, 6.5 % and 9.9 % relative standard deviation, respectively.

9. Constant Temperature Method

The data concerning the constant temperature method, used for selenium, were not as conclusive as was hoped. This method had no better sensitivity than did the CRSD/trapping method for selenium. As discussed, this probably indicated that both methods had high efficiency.
TABLE XIII

Selected Methods and Sensitivity Values for Elements Investigated

( in pg/0.0044 A )

<table>
<thead>
<tr>
<th>Method</th>
<th>As</th>
<th>Ca</th>
<th>Cu</th>
<th>Hg</th>
<th>Mg</th>
<th>Ni</th>
<th>Se</th>
<th>Sn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(hot)V</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AV</td>
<td>260'</td>
<td>300'</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td>300</td>
<td>-</td>
<td>2500'</td>
<td>70</td>
</tr>
<tr>
<td>AV with reverse flow</td>
<td>600</td>
<td>150'</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>AV(warm)V(hot)</td>
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<tr>
<td>VA trapping</td>
<td>1100</td>
<td>-</td>
<td>900</td>
<td>-</td>
<td>0.3'</td>
<td>600</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>AV with reaction gases (methane)</td>
<td>300</td>
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<tr>
<td>(water vapor)</td>
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<tr>
<td>VA</td>
<td>-</td>
<td>600</td>
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<td>300</td>
<td></td>
<td></td>
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<tr>
<td>simultaneous heating</td>
<td>280</td>
<td>800</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>multiple VA trapping</td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>AV with matrix modification</td>
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<td>100</td>
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<tr>
<td>Methods with the CRSD</td>
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<tr>
<td>AV</td>
<td>350</td>
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<td>200'</td>
<td>600</td>
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<td>60'</td>
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<tr>
<td>VA</td>
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<td>220'</td>
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<tr>
<td>VA trapping</td>
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<td></td>
<td>300'</td>
<td>-</td>
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<tr>
<td>constant temperature</td>
<td></td>
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<td></td>
<td></td>
<td>300</td>
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<tr>
<td>multiple sample drying</td>
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<td></td>
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<td></td>
<td></td>
<td>60</td>
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<tr>
<td>multiple VA trapping</td>
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<td></td>
<td></td>
<td>300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>simultaneous heating</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>VA trapping with reaction gases</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>(methane)</td>
<td></td>
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<td></td>
<td>300</td>
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<td></td>
<td></td>
<td>300</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* indicates that this is the preferred method for this element.

** indicates that no useful data for this element was obtained through the use of this method.
The method had a few problems, however. Poor precision resulted from a dependency on the speed at which the CRSD was inserted into the furnace. The faster the insertion was made, the sharper and higher the peak was. Another problem was the fragility of the CRSD's used. These were longer than the normal CRSD's and were easily broken when hurriedly inserted into the furnace.

10. Reaction Gases

Water vapor and methane were used as reaction gases with three of the elements investigated. These gases provided a better reducing atmosphere inside the furnace and should have increased the atomization efficiency and sensitivity. However, the gases neither hurt nor helped the sensitivities for those elements investigated.

The failure of the water vapor might be traced to the inefficient water sparger used, which did not adequately saturate the argon with water vapor.

11. Speciation

The new furnace design did not adversely affect the speciation capability of the double stage furnace.

B. SENSITIVITY

Sensitivity data are summarized in Table XIV. The data presented in the table are from the most sensitive methods investigated in this work, excluding data collected with the use of matrix modifiers. Reference sensitivity values are shown for comparison purposes. These data were taken from work that did not use matrix modifiers or other sample pretreatment.
For most of the elements investigated, the sensitivity values obtained were comparable to the reference values, not deviating by more than two or three fold. However, for calcium and mercury, the differences in sensitivity were much more significant. The sensitivity for calcium was two orders of magnitude poorer than the reference value. As noted before, calcium formed a stable carbide. Since the carbide was probably only slowly vaporized at the furnace temperatures available, it caused the absorption peak to be broadened excessively. The use of a metal furnace would eliminate carbide formation and increase the calcium sensitivity markedly.

For mercury, the sensitivity value for mercury was nearly two orders of magnitude better than the reference value. As was shown in the discussion on the mercury studies, the element would vaporize at very low temperatures or, in the case of a new carbon surface, without heating at all. Thus, much of the mercury is lost in a commercial instrument during the drying and ashing steps.

C. FURNACE LIFETIME

The average carbon furnace, operating under ideal conditions, would last an average of 150 heating cycles. Under extreme conditions, however, furnace lifetime would be reduced to only 30 - 50 heating cycles.

The weakest part of the furnace was where the carbon was initially the thinnest. This was where the light path cut through the atomization section. The carbon directly above and below the hole formed by the light path was only 0.06 in. (1.5 mm) thick.
Since this section of carbon was the thinnest, it also was heated the most, because of the high electrical resistance. As a result, this section of carbon deteriorated faster than the rest of the furnace. In addition, any vibration caused by water boiling, in the nearby electrode, encouraged deterioration of this section of carbon. The lifetime of the carbon furnace could very likely be increased by increasing the thickness of the carbon surrounding the light path through the furnace.

D. ADVANTAGES OF THE DOUBLE STAGE CARBON FURNACE

1. No Sample Loss

Volatile elements, such as mercury, are easily lost (and not detected) from commercial carbon furnaces during the drying and/or ashing steps [58]. The design of the double stage furnace made this impossible. If the analyte was vaporized at any time, it was pushed, by the argon flow, through the hot atomization section and then into the light path, where it was detected.

2. Reduction of Molecular Background Absorption

The atomization process took place in the atomization section, outside the light path. The water vapor and organic compounds were broken down to carbon monoxide, hydrogen, and carbon, which did not absorb very strongly in the ultraviolet region. Since this occurred before the vapor reached the light path, the molecular background absorption was greatly reduced.

3. Speciation

None of the atomic absorption systems in wide use allow speciation by
### TABLE XIV

**COMPARATIVE SENSITIVITY VALUES**  
(in pg/0.0044 A)

<table>
<thead>
<tr>
<th>Element</th>
<th>This Research</th>
<th>Reference Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>As</td>
<td>256</td>
<td>160</td>
<td>[7]</td>
</tr>
<tr>
<td>Ca</td>
<td>300</td>
<td>3.1</td>
<td>[7]</td>
</tr>
<tr>
<td>Cu</td>
<td>150</td>
<td>45</td>
<td>[7]</td>
</tr>
<tr>
<td>Hg</td>
<td>220</td>
<td>15000</td>
<td>[7]</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3</td>
<td>0.3</td>
<td>[77]</td>
</tr>
<tr>
<td>Ni</td>
<td>300</td>
<td>330</td>
<td>[7]</td>
</tr>
<tr>
<td>Se</td>
<td>300</td>
<td>100</td>
<td>[73]</td>
</tr>
<tr>
<td>Sn</td>
<td>2500</td>
<td>5500</td>
<td>[7]</td>
</tr>
<tr>
<td>Pb</td>
<td>60</td>
<td>23</td>
<td>[7]</td>
</tr>
</tbody>
</table>
thermal analysis, as does the double stage furnace. If a slow temperature ramp is applied to a conventional carbon furnace, any analyte specie vaporized below the atomization temperature is lost as the molecular vapor and not detected [69]. This was not possible with the double stage furnace because the atomization section was always heated to insure atomization and detection of the analyte.

4. Solid Sampling Capability

Solid sampling was not investigated during this research, primarily because of the difficulty in the preparation of solid state standards. However, the possibility of using the CRSD with solid samples existed. A few milligrams of solid could have been placed on the CRSD and introduced into the furnace.

Conventional instruments are not easily adaptable to the analysis of solid samples. The major problem is the blockage of the light path by the solid sample or its residue left in the furnace. This would not be a problem with the double stage furnace since the vaporization and atomization processes take place outside of the light path.

5. Versatility

The double stage furnace was capable of speciation, solid sampling and quantitation using a wide variety of methods. Such versatility was unrivaled by commonly used atomic absorption instruments.

E. DISADVANTAGES OF THE DOUBLE STAGE CARBON FURNACE

1. Carbide Formation

The design of the double stage carbon furnace encouraged the formation of
metal carbides. As was seen in the case of calcium, carbide formation greatly reduced sensitivity. This problem could be overcome by the use of a metal furnace rather than a carbon one.

Carbide formation is probably not a problem with commercial instruments because the atoms are created in the light path and are detected before carbide formation can occur.

2. Uneven Furnace Heating

A relatively cool zone existed between the atomization and vaporization sections when the furnace was heated. Because of the heat sink effect of the two center electrodes, the temperature of the zone was 200 - 300 °C lower than the other two sections. This cool zone could provide an excellent area for the collection of material with very high boiling points. This was not an obvious problem for any of the elements investigated, but it may be a problem for some of the more refractory elements, such as tungsten.

Unfortunately, the center electrodes could not be eliminated and still retain the desirable characteristics of the double stage furnace.

F. PROPOSED IMPROVEMENTS

Because the double stage carbon furnace was a prototype instrument, improvements were always sought. Many improvements were implemented during the course of these studies. Other improvements could not be implemented because of the expense in time and/or money. Some of those proposed improvements are listed below.
1. **Improve Electrode Design**

Two aspects of the electrodes, described in the equipment section, were undesirable. First, the water-cooled electrodes were excellent heat sinks. Thus, the furnace did not get as hot as it might have. Sensitivity probably suffered. The other problem was that, over time, the metal "fingers" of the collets became deformed. They would not "relax" when the clamp was removed. For this reason, it became very difficult to remove the used furnaces from the persistent grip of the collets.

New electrode clamps, which employed carbon, would solve both of these problems.

2. **Faster Electronics**

It has been reported that if the response time of an atomic absorption instrument's electronics is too long, then severe signal distortion can occur when a carbon furnace is used [87 - 89]. The very fast signal generated by a carbon furnace was not followed by the electronics and the peak height was diminished. Loss of sensitivity resulted.

A similar situation almost certainly existed with the electronic equipment used for the double stage furnace, because of its age. Thus, newer electronics, with shorter time constants, would very likely increase the sensitivity of the technique.

3. **Peak Integration**

Measurement of integrated peak area (in absorbance), is reportedly more accurate and reproducible than measurement of peak height [89 - 91]. Also, Frech, et al. [92] used an isothermal atomization system and found that sensitivity
derived from peak height for lead was not influenced greatly by several factors.
When peak area was used, instead of peak height, to calculate sensitivity, it
increased by four fold when the same factors were varied.

Therefore, the addition of electronics to allow peak integration would probably
improve precision and (together with faster electronics) sensitivity.

4. Increase Heating Power

The electrical equipment available could deliver enough power to heat the
double stage furnace in about 30 s. Commercial furnaces are heated faster, in 5 - 10
s, to higher temperatures, up to 3000 °C. If more heating power was applied to the
double stage furnace, higher peaks and better sensitivity could result.

5. Automatic Background Correction

Background correction was carried out by analyzing replicate samples, first
with the hollow cathode lamp and then with the deuterium lamp. The difference
between the two signals obtained was the net atomic absorption. The poor
precision exhibited during some of these studies made this process of limited
worth. It would be far more valid to use the same type of automatic background
correction systems available on commercial instruments. They simultaneously
measure total and molecular absorption, but display only the net atomic
absorption.

6. Supplemental Cooling

It would be possible to cool the atomization and/or the vaporization sections
by directing a stream of cold nitrogen or argon against the outside surface of the
furnace. Trapping efficiency should be increased by cooling the atomization section
during the first part of the trapping process. Premature vaporization of analyte might be avoided, if the vaporization section were cooled during the first step in the AV method.

7. **Automatic Temperature Control**

At least one feed-back circuit for automatic control of furnace temperature has been reported [93]. Such control for the double stage furnace would increase reproducibility by insuring that the same furnace temperatures were achieved during each heating cycle.

8. **Heated Light Path**

The light path extension, or cross piece, was heated only by radiation from the atomization section and achieved a maximum temperature of about 1200 °C. A higher light path temperature would improve the atomic lifetime for some elements and thus increase the sensitivity. This could be achieved by heating the light path with a separate electrical circuit. Another way to increase light path temperature would be to provide a better physical connection between the cross piece and the atomization section so that the cross piece could be heated by conduction.

9. **Computer Interface**

A small microcomputer system interfaced to the double stage furnace would have a wide variety of uses. It could carry out some of the functions proposed above, such as automatic temperature control and peak integration. It could be used to automatically optimize lamp conditions. In addition, it could eliminate hours of tedious calculating and curve plotting.
PART TWO

Studies on Speciation

of Lithium in Blood
I. INTRODUCTION

A. LITHIUM AS A PSYCHOACTIVE DRUG

The Australian psychiatrist John F. J. Cade reported in 1949 that doses of lithium citrate calmed acutely manic patients and certain schizophrenic patients [94]. Since that first report, lithium treatment has been applied to a wide range of other illnesses, with varying success, including: depression [95, 96], epilepsy [97], schizophrenia and schizoaffective illness [98, 99], asthma [100] and cyclic neutropenia [101]. However, lithium has been found to be most effective in the treatment of mania or the manic phase of manic-depression.

Lithium levels in human tissue are reportedly in the range 1 - 300 ng/g with a level of 4 - 8 ng/g in blood [102]. Therapeutic use of lithium raises blood serum levels to approximately 6 - 8 μg/g (0.8 - 1.2 mEq/L) [103]. A bewildering array of studies has been performed to determine what effect lithium has on many biochemically important substances and systems. Research has involved the influence of lithium on neurotransmitters [104 - 107], the functioning of calcium [108, 109] and magnesium [108], carbohydrate metabolism [110], adenylate cyclase [109, 111, 112] and ATPase [113, 114], among others. The results have been voluminous and, in many instances, contradictory. The reason for the efficacy of lithium is still not known, though many theories have been proposed. Several reviews and compendia on lithium treatment have been published [115 - 118].

In relation to lithium as a psychoactive agent, most of the analytical research has been concerned with the determination of lithium in serum [119, 120].
plasma [121], and erythrocytes [121].

According to early workers, lithium is not protein-bound [122, 123]. It can, however, compete quite effectively with calcium for calcium binding sites on proteins involving carboxyl groups [124]. This is not surprising since lithium has been shown to form complexes with ethylenediaminetetraacetic acid [125, 126] and nitrilotriacetic acid [127].

The chemical form of the lithium in the blood has not been determined, although it is generally assumed to be ionic. However, it is difficult to predict the effect that lithium will have in previously untreated patients, either from the lithium levels in the blood, or the form of the lithium because it is assumed to be ionic. It is conceivable that lithium exists in two forms, one of which is biologically active and the other less active or inactive. Such a proposal would demand that the lithium exists in at least two chemical forms in the body.

Knowledge of the normal levels of two or more lithium species might be used to predict which mental patients will respond to lithium treatment, to differentiate between different mental illnesses responsive to lithium, to help diagnose certain mental disorders, and to elucidate lithium efficacy and differences in lithium metabolism between "normal" and mentally ill persons, etc. The possibilities are numerous.

Part Two of this dissertation describes several studies which attempted to detect two or more lithium species in human blood serum.
B. INSTRUMENTAL METHODS OF METAL SPECIATION

In order to put the work presented in Part Two of this dissertation in its proper perspective, a brief discussion of some metal speciation techniques is presented here.

1. Metal Specific Detectors for Chromatography

The use of metal specific detectors for chromatography has been one of the most popular methods used for speciation. Such coupled techniques are ideal for metal speciation. The chromatograph is used to separate the metal species then the column effluent is fed to a detector which is sensitive only to the metal interest. Van Loon reviewed the work performed in this area prior to 1979 [128]. Because relatively few metal compounds are volatile enough to pass through a gas chromatographic column, only liquid chromatography (LC) systems will be discussed below.

a. Flame Atomic Emission (Flame Photometry)

Flame emission burners normally utilize liquid samples. Thus, interfacing an LC with a flame emission burner only requires that a short length of tubing transfer the sample from the LC column to the burner aspirator. However, flame emission does not demonstrate good sensitivity for most metals. The majority of LC - flame emission work has involved the speciation of non-metals, such as phosphorous [129, 130].

b. Flame Atomic Absorption

Flame atomic absorption (flame AA) is the metal specific detector of choice for LC, for several reasons. First of all, flame AA burners have a liquid up take rate
which is similar to the LC flow rates of 0.5 - 5 mL/min. There have been some problems associated with slow LC flow rates, but several inventive methods have overcome these problems [131, 132]. Secondly, flame AA has good sensitivity for many metals.

Unfortunately, samples injected into LC systems are diluted by the eluent. Many times biological or environmental samples contain very low levels of the metals of interest, to begin with. Thus, after LC separation, flame AA is frequently incapable of detecting metals in these samples.

c. Furnace Atomic Absorption

Furnace AA would seem to be a better LC detector than flame AA, because of the improved sensitivities available with furnaces. Unfortunately, the cyclic heating programs used with commercial carbon furnaces create a compatibility problem for an interfaced LC-furnace AA instrument. A continuously flowing LC, with a furnace that is heated in cycles, is impossible to interface directly. One common alternative is to collect fractions from the LC. The fractions are then individually analyzed by furnace AA. The result is a set peaks that corresponds to the chromatographic curve. Auto-samplers can be used to automate the entire process. This approach has been used to speciate organolead and organotin compounds [133].

d. Inductively Coupled Plasma Atomic Emission

Inductively coupled plasma atomic emission (ICP) has been used as an LC detector in much the same way as flame AA. Size exclusion chromatography (SEC) has been coupled with ICP to speciate organically bound metals in coal-derived
materials [134] and non-aqueous samples [135]. SEC-ICP has also been used to
detect different calcium and magnesium species in natural waters [136].

2. Metal Specific Detectors for Evolved Gas Analysis

Evolved gas analysis (EGA) is the analysis of gases released from a sample
when it is heated. In order to perform speciation, a sample is heated slowly.
Different compounds are vaporized at different temperatures. Hence, separation of
the compounds depends on each one having a unique boiling or vaporization
temperature. At least two types of metal specific detectors have been used for
evolved gas analysis.

a. Plasma Atomic Emission

Inductively coupled plasma atomic emission spectrometry (ICP) and
microwave induced plasma atomic emission spectrometry (MIP) have both been
used as metal selective detectors for EGA. Usually, the sample is heated in a
furnace and the evolved gases transported, via a heated transfer line, to the
plasma, where atomization and emission take place. Speciation of metals in solids
has been performed by EGA-ICP [137] and EGA-MIP [138]. Metals in solid biological
samples have been speciated by EGA-MIP [139].

b. Furnace Atomic Absorption

Robinson and co-workers performed speciation studies using a double stage
furnace AA [45, 46]. This technique was described in the introduction to Part One of
this dissertation.

In related work, Robinson, et al. used a platinum loop vaporizer in
conjunction with the quartz "T" atomizer to perform speciation studies of lead,
cadmium [54] and mercury [48]. Sample was placed on the platinum loop which was lowered into the quartz "T" atomizer, just above the carbon bed. The platinum loop was slowly heated. Evolved gases were swept through the carbon bed, where atomization took place, and into the instrument light path.

3. Metal Speciation by Nuclear Magnetic Resonance Spectrometry

Nuclear magnetic resonance (NMR) has been used for many years to determine the chemical environment of hydrogen atoms (protons) and carbon atoms. Analytical and organic chemists have made extensive use of proton and carbon NMR for the identification of organic compounds.

NMR can also be used to investigate the chemical environment of many metal nuclei. Such work has been reported, but not nearly to the extent of proton and carbon NMR. For example, Al - 27 NMR has been used to investigate aluminum species in aqueous solutions [140] and aluminum binding sites on enkephalin [141].

In the case of lithium, much of the Li - 7 NMR work has centered around the investigation of lithium complexes. Investigation of lithium complexation with cryptates [142, 143], pentamethylenetetrazole [144] and nitrilotriacetic acid [145] have been reported. Li - 7 NMR has been used to show that the lithium ion can bind to the nucleosides cytidine and cytosine [146].
II. EQUIPMENT

A. LIQUID CHROMATOGRAPHY - CARBON FURNACE ATOMIC ABSORPTION SPECTROMETER (LC - AA)

1. Liquid Chromatograph

The liquid chromatography (LC) column used was a 80 ft. by 0.01 in. (24.4 m x 0.25 mm) capillary SE-30 column. Eluent was supplied to the LC column from a pressurized solvent reservoir. The solvent reservoir consisted of a 62 cm, 1.2 cm diameter copper tubing, with a capacity of about 70 mL. It was pressurized, with gas from a nitrogen tank, to pressures of about 700 kPa (100 p.s.i.).

2. Interface Between the Liquid Chromatograph and the Carbon Furnace Atomic Absorption Spectrometer

The interface between the liquid chromatograph (LC) and the carbon furnace atomic absorption spectrometer is illustrated in Figure 54.

The effluent from the LC column passed into a cross flow nebulizer, where it was broken into tiny droplets by the oxygen stream. A miniature oxy-hydrogen flame was used to burn the organic solvent before the sample passed into the carbon furnace. The flame was ignited by a small nichrome coil, which was heated to incandescence with a battery. An inlet allowed argon to be added to the combustion chamber in order to prevent air from leaking into the interface.

This LC - AA interface was designed by a previous worker, but had never been tested.
3. **Carbon Furnace Atomic Absorption Spectrometer**

   a. **Carbon Furnace**

   The heart of the LC - AA was the carbon furnace. It was similar in design to the carbon "T" atomizer used for the GC - AA, as was discussed in the introduction to Part One. The carbon furnace used for the LC - AA did not use a cross piece to extend the light path.

   As with the carbon "T" atomizers, the atomization process took place outside of the light path. By the time the sample reached the light path, it had been reduced to atomic vapor and was able to undergo atomic absorption without the presence of interfering molecular species.

   b. **Furnace Electrical Components**

   Power was supplied to the carbon furnace by a 18 A variable autotransformer (Variac). A 9 V, 500 A stepdown transformer (Signal Transformer Company) was used to decrease the voltage and increase the current going through the carbon furnace. Welding cables were used to connect the transformer secondaries to the furnace electrodes.

   c. **Furnace Housing**

   In order to prevent rapid deterioration of the carbon furnace, it was enclosed in a brass, water cooled, housing (Figure 54). Ports allowed argon to be added to the housing interior, insuring an inert atmosphere.

   Two quartz windows allowed the source radiation to pass through the light path of the furnace.

   The bottom of the carbon furnace rested on the bottom electrode, which
Figure 54

Furnace, Housing and Interface for the LC - AA

Electrical Connection

Water Out

Water In

Water Out

Light Path

Water In

Argon In

Electrical Connection

Water In

Argon In

Combustion Chamber

Column Effluent

Oxygen

Hydrogen

Electrical Connection

Water Out

Oxygen
served as the bottom of the furnace housing. The top electrode was water cooled. It
was also spring loaded, to insure good contact between the furnace and both
electrodes.

d. Optical Components

i. Source

A demountable, hollow cathode lamp (DHCL) system, similar to the one
discussed in the equipment section of Part One of this dissertation, was used as the
source for the atomic absorption spectrometer.

ii. Chopper

A mechanical chopper (motor by Arch Manufacturing Company, type U21)
was used to modulate the DHCL radiation. A magnetic reed switch was attached to
the chopper so that it and the amplifier could be phase-locked.

iii. Lenses

Plano-convex lens were used to focus the source radiation on the light path of
the furnace and on the slit of the monochromator.

iv. Monochromator, Detector and Amplifier

A Beckman (model DB-G) spectrophotometer taken from a Beckman (model
1301) atomic absorption spectrometer was used. It provided the monochromator,
photomultiplier tube (PMT), detector and amplifier. The amplifier had been
modified to be phase-locked to the signal from a magnetic reed switch on the
chopper. This allowed the monochromator to discriminate against all radiation
except that from the mechanically chopped source.

The monochromator had a manually adjustable slit. The grating had 1200
lines/mm and was blazed for 250 nm.

e. **Gas Handling Equipment**

Flow meters and needle valves were used to regulate the flow of gases to various parts of the instrument. A small vacuum pump (Dyna-Vac pump model 4K) pulled the combustion gases from the oxy-hydrogen flame, through the hot furnace and out of an exhaust port in the furnace housing.

**B. LIQUID CHROMATOGRAPHY - INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY**

A block diagram of the liquid chromatograph - inductively coupled plasma spectrometer (LC - ICP) is shown in Figure 55.

1. **Liquid Chromatograph**

   The solvent reservoir was machined from a rod of 316 stainless steel. It had a capacity of about 750 mL and could be pressurized to 6000 kPa (870 p.s.i.) with gas from a nitrogen tank. An injection port and valves, placed between the reservoir and the LC column, allowed a sample injection to be made with a microliter syringe. The sample passed into the LC column where separation of the sample components took place.

   A standard 25 cm column (Whatman, Inc.) packed with silica gel was used.

2. **Interface Between the Liquid Chromatograph and the Inductively Coupled Plasma Atomic Emission Spectrometer**

   Commonly used inductively coupled plasma atomic emission spectrometers (ICP's) frequently exhibited a memory effect [147].
This memory effect resulted from two factors. First, standard ICP nebulization chambers have large interval volumes. Since the gas flow rate through the chamber was low, it was possible for a component from the LC column to enter the chamber and not leave before a closely following component also entered the chamber. Thus, two components, which had been separated by the LC column, were partially or totally recombined.

Second, the large surface area inside the nebulization chamber, ICP torch and connecting tubing, provided a vehicle for sample deposition. The deposited sample may later be washed off the surface, contaminating later samples. This was another way that the component resolution achieved by the LC column was diminished by the standard ICP sample introduction system.

Another disadvantage of standard ICP nebulization systems was the low analyte transport efficiency, only 1 - 2% \(^{[2, 146]}\). Thus, much of the potential sensitivity was lost because most of the sample went down the drain and never reached the plasma.

Two LC-ICP interfaces were designed to overcome these problems.

a. First Interface Design

The first interface design consisted of a cross flow nebulizer (Figure 56) similar to that used with the LC-AA. This nebulizer design had proved itself capable of reducing the LC effluent to a spray of very fine droplets.

This nebulizer replaced the center (sample introduction) tube in the ICP torch.
Figure 55
Equipment for the LC - ICP

- N₂ Tank
- Solvent Reservoir
- LC Column
- RF Generator
- Plasma Torch
- Mirror
- DB-G: Monochromator, Detector, Amplifier
- Recorder
b. **Second Interface Design**

A second interface design also employed a cross flow nebulizer, originally designed by Robinson for use as part of a total consumption burner [149]. This nebulizer (Figure 56) replaced the center tube in the ICP torch.

3. **Inductively Coupled Plasma Atomic Emission Spectrometer**

a. **Plasma Torch**

The plasma torch (Figure 57) consisted of two concentric quartz tubes which were held in place by a brass base. The torch base had inlets for two argon flow streams. A tangential argon stream spiralled up through the torch, between the two quartz tubes, at a flow rate of 10 - 15 L/min. This argon provided cooling for the quartz tubes. The auxiliary argon flowed in a laminar fashion up through the center quartz tube. This flow stream provided the argon to sustain the plasma.

One of the two cross flow nebulizers, mentioned in the section above, was centered in the torch base so that the nebulized sample was sprayed into the bottom of the plasma. It was important that the sample aerosol entered the center part of the plasma in order to be exposed to the hottest part of the plasma. Otherwise, the sample would flow around the outside of the hot plasma and not be atomized or excited efficiently.

b. **Radio Frequency Generator**

The ICP was powered by a 5 kW, 5 - 8 MHz radio frequency (RF) generator. A 3 1/2 turn induction coil from the RF generator, made of 1/4 in. (0.64 cm) diameter copper tubing, was wrapped around the upper part of the plasma torch.
Figure 56
Nebulizer Designs for the LC - ICP Interface

First Nebulizer Design

Second Nebulizer Design
c. **Monochromator, Detector and Amplifier**

The spectrophotometer (Beckman model DB-G) used for the LC-AA was also used for the LC-ICP.

d. **Recorder**

A Sargent-Welch recorder (model SRLG) was used to record the emission signals.

e. **Plasma Initiator**

The spark from a Tesla coil was used to initiate the plasma, which was self-sustaining after initiation.

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C. **LIQUID CHROMATOGRAPHY - FLAME ATOMIC EMISSION SPECTROMETRY**

A block diagram of the liquid chromatograph-flame atomic emission spectrometer (LC-FAES) is shown in Figure 58.

1. **Liquid Chromatograph**

The liquid chromatograph used was described in the discussion of the LC-ICP. All of the liquid chromatography columns used were 25 cm in length. Packing materials included:

- silica gel (packed in-house)
- carboxy methylcellulose ion exchange resin (packed in-house)
- C8 reversed phase (Whatman Partisil PXS 10/25)

The LC effluent from the column passed through a short length of capillary polyethylene tubing to the flame emission burner. No other interface was used.
Figure 57
ICP Plasma Torch with LC Interface (Nebulizer)

RF Coils
Quartz Tubes
"O" Ring
Argon
Nebulizer
2. Flame Atomic Emission Spectrometer (FAES)

a. Atomizers (Burners)

i. Total Consumption Burner

Total consumption burners have traditionally been used for flame emission work. The first atomizer used was of the total consumption type (Jarrell Ash Hetco burner). The oxy-hydrogen total consumption burner was so audibly noisy that it was not used after a few trials.

ii. Pre-Mix Burner

A pre-mix burner, similar to the type used for atomic absorption, was used for the majority of the LC-FAES studies.

The burner is shown in cross section in Figure 59. The body of the burner was made of stainless steel. A pneumatic nebulizer used an air stream to break the LC effluent into tiny droplets. Acetylene was mixed with the air and the sample aerosol in the nebulization chamber. Droplets that were too big to pass through the chamber were drained into a waste container. The gases passed through the burner head into the flame where the sample aerosol was atomized and excited.

The usual 10 cm long path length burner head, used for atomic absorption, was replaced with one more appropriate for flame emission work. For flame emission, it was necessary that the flame be compact so that all of the emitted radiations were focused on the monochromator slit.

After some experimentation, a successful burner head design was found. The round burner head had 15 holes of 0.9 mm (0.035 in) diameter. The holes were 2 mm apart and arranged in two concentric circles with one hole in the center.
Figure 58
Equipment for the LC - FRES

- PMT Power Supply Amplifier
- Monochromator
- Recorder
- In House Compressed Air
- Gas Control Unit
- Burner
- LC Column
- Solvent Reservoir
- Tank Recorder
- Gas Control Unit
- Column Solvent Reservoir
- \( \text{N}_2 \) Tank
- \( \text{C}_2\text{H}_2 \) Tank
Figure 59
Cross Sectional Diagram of the Flame Emission Burner
b. Optical Components

i. Collecting mirror

A convex, front surface mirror was used to reflect and focus radiation from the flame onto the slit of the monochromator.

ii. Monochromator

A Littrow prism monochromator with a manually adjustable slit (Beckman Instruments DU model 2400) was used.

iii. Detector

A red sensitive photomultiplier tube (Hamamatsu model R456) was used as the detector.

c. Amplifier and Photomultiplier Tube Power Supply

The photomultiplier tube power supply and signal amplifier unit were manufactured by Techtron Pty. Ltd., Melbourne (type W/M).  

d. Chopper

A chopper (Eastern Engineering Company, model 4 variable speed motor) was placed in the light path, just in front of the monochromator slit. The purpose of the chopper was to modulate the atomic emission signal so that the amplifier processed it.

e. Gas Handling System

i. Compressed Air

Compressed air was obtained from the in-house compressed air line. A gas regulator was used to moderate the pressure variations of the compressed air system. The air passed from the regulator to a gas control unit (Varian Pty. Ltd.,
Melbourne, type GCUI) and then into the nebulizer.

Acetylene was obtained from a commercial vendor (Lincoln Big Three). The gas passed through a regulator and a flow meter, in the gas control unit, to the burner mixing chamber.

D. EVOLVED GAS - FLAME ATOMIC EMISSION SPECTROMETER

1. Sample Vaporizer

The device which provided the evolved gas, to be analyzed by the FAES, was an electrothermally heated platinum loop (Figure 60).

This device consisted of a short length of 0.13 mm diameter platinum wire, fashioned into a "V" shaped loop. The ends of the platinum were spot welded to two steel electrodes. Power to heat the Pt-loop was provided by a variable autotransformer (Viac). A small electric motor was attached to the Variac so that the voltage and current to the Pt-loop could be slowly increased over time. This allowed the Pt-loop to be heated smoothly and reproducibly from room temperature to 1750 °C over approximately a 7 minute period.

The steel electrodes were insulated by a ceramic covering. The ceramic piece passed through a rubber stopper. A glass adapter was made for the Pt-loop, so that it interfaced with the pre-mix burner. The adapter was a 15 cm length of glass tubing which was 2.2 cm in diameter. One end of the glass tubing was tapered to capillary size. This capillary was attached to a short length of capillary polyethylene which led to the nebulizer. The Pt-loop was inserted in the other end of the glass adapter. The rubber stopper made an airtight seal. From there, the
sample was pushed into the flame by the combustion gases. Separation of different compounds was dependent upon differences in boiling points, just as with the double stage furnace described in Part One. After the sample was placed on the Pt-loop, the loop was slowly heated by activating the motorized variac. As the boiling point of a particular compound was reached, it was vaporized, leaving behind all the compounds with higher boiling points. The remainder of the compounds were vaporized as the Pt-loop continued its heating cycle.

E. Nuclear Magnetic Resonance Spectrometer

The spectrometer used was a 200 MHz Bruker, model WP-200. A tunable probe was used at a frequency of 77.78 MHz. The constant field strength was 4.7 T.
III. EXPERIMENTAL AND RESULTS

A. CHEMICALS

1. Deionized Distilled Water

Deionized distilled water (DDW) was obtained by passing distilled water, from the chemistry building’s distilled water system, through a mixed bed deionization column (Illinois Water Treatment Company, Research Ion XChanger Model 2). The DDW was stored in a large, polyethylene carboy.

2. Lithium Standards

Reagent grade lithium chloride was dried in a 110 °C oven. An appropriate amount was weighed and dissolved in DDW to make a 1000 µg/mL standard. This working standard was stored in a polyethylene bottle. Dilute standards were prepared daily for quantitative work.

3. Saturated Lithium Carbonate Solution

Lithium carbonate was prepared by mixing concentrated solutions of lithium chloride and sodium carbonate. The lithium carbonate precipitate was washed several times with DDW. A saturated solution of lithium carbonate was prepared by mixing DDW and excess lithium carbonate in a stoppered test tube.

4. Saturated Lithium Phosphate Solution

Lithium phosphate was prepared by mixing concentrated solutions of lithium chloride and sodium phosphate. The same procedure was followed as for the lithium carbonate solution discussed above.
5. **Saline Solutions**

A saline solution was made up with the following salt concentrations: 0.115 M sodium chloride, 0.0045 M potassium chloride, 0.025 M sodium bicarbonate. This solution approximated the concentrations of sodium, potassium, chloride and bicarbonate in human blood [150].

6. **Serum Samples**

Ordinary serum samples were obtained from the Louisiana State University Student Health Service. Serum samples from mental patients undergoing lithium treatment (treated serum) were obtained from Doctor's Hospital, Baton Rouge, LA.

7. **Gases**

Acetylene, argon, hydrogen, oxygen and nitrogen were obtained from a commercial vendor (Lincoln Big Three Inc.). Compressed air was obtained from the chemistry building's in-house compressed air system.

B. **LIQUID CHROMATOGRAPHY - CARBON FURNACE ATOMIC ABSORPTION SPECTROMETRY (LC - AA )**

1. **Results**

During preliminary work with the LC - AA, a major design flaw became apparent, which made the instrument unusable.

The major product of the oxy-hydrogen flame was water vapor. Water vapor reacted with hot carbon, through the water gas reaction, to form carbon monoxide and hydrogen gases. In a matter of 15 - 30 minutes, the carbon furnace was eroded to the point that it would not operate efficiently. Within 60 minutes, the
furnace was eroded so badly that it could no longer be electrically heated.

The lifetime of the carbon furnace was so short that a maximum of three or four chromatograms could be run before the furnace had to be changed. The time involved in the machining and installation of each new carbon furnace made analysis times excessively long. Thus, the technique was abandoned as unusable.

C. LIQUID CHROMATOGRAPHY - INDUCTIVELY COUPLED PLASMA

ATOMIC EMISSION SPECTROMETRY (LC - ICP)

I. Results

Both interface designs were found to be deficient. The technique was not pursued after it was learned that the detection limit for lithium by ICP atomic emission spectrometry was not as good as by flame atomic emission spectrometry [151]. This information had not been reported previously in the literature.

a. First Interface Design

The first interface design suffered from two problems. One problem was that the end of the nebulizer was about 10 cm from the bottom of the plasma. In comparison, the standard ICP aerosol injection tube was only a few millimeters below the plasma. Because the LC - ICP interface nebulizer was so far below the plasma, it could not efficiently inject sample into the plasma. The length of the nebulizer could not be increased because the drill bits used to manufacture it were only about 3 cm long. Longer drill bits were not available.

The other problem with this nebulizer design was that the argon flow rate (about 0.5 L/min) was not sufficient to effectively nebulize the liquid. The nebulizer
argon flow rate could not be increased without extinguishing the plasma.

b. Second Interface Design

The second interface design enabled the nebulizer to be made longer so that the exit orifice was 2 - 3 cm below the plasma. This was possible because larger diameter (and longer) drill bits were used for most of the machining of the second nebulizer.

This nebulizer was also able to nebulize the LC effluent quite effectively with an argon flow rate of 0.5 L/min. Unfortunately, the aerosol stream was not perfectly vertical as it left the nebulizer tip. The aerosol struck the inside of the center quartz tube and never reached the plasma. This problem was caused by the various parts of the nebulizer not being perfectly concentric. The machine shop personnel were not able to correct the problem with the equipment available.

The second interface design was unusable because, like the first, it could not effectively deliver the sample aerosol to the plasma.

D. LIQUID CHROMATOGRAPHY - FLAME ATOMIC EMISSION SPECTROSCOPY (LC - FAES)

1. Experimental

a. Eluent

Since the goal of these studies was to separate the lithium species present in blood serum, a LC eluent was chosen which closely approximated the composition of blood serum. This was important because an eluent which was grossly dissimilar to blood serum (e.g. distilled water or an organic solvent) could disrupt
any non-ionic lithium specie present.

The eluent used for most of the LC - FAES studies was the saline solution described in the chemicals section, above.

b. Conditions

Typical conditions used for the LC - FAES studies are listed in Table XV.

2. Results and Discussion

a. Silica Gel Column

A 5 µL injection with 5 µg of lithium gave a very low, broad peak, as shown in Figure 61. The retention time was about 2 min when the column flow rate was 0.8 mL/min. The height and area of the lithium peaks were not reproducible. At this point, it was hypothesized that the lithium was undergoing an interaction with the silica gel, such as adsorption.

A Li - ethylenediaminetetraacetic acid (EDTA) complex was used to approximate organically bound lithium. The complex had a molar ratio of 2:1 lithium ion to EDTA. Half of the EDTA binding sites were occupied by lithium ions. When the complex was injected onto the LC column, it had a retention time of about 1.3 min (Figure 61). Thus, the silica gel column could separate ionic lithium from EDTA bound lithium. But, the 5 µl of Li injected as the EDTA complex produced an emission signal that was 5 or 6 times as intense as the signal produced by the same amount of ionic lithium. This indicated that the unoccupied binding sites on the EDTA were pulling adsorbed lithium off of the silica gel column.

Confirmation of lithium adsorption was obtained when an injection of an EDTA solution which contained no lithium resulted in a large lithium emission signal.
**TABLE XV**

*Typical Conditions Used for the Liquid Chromatography - Flame Atomic Emission Spectrometry Studies*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission Wavelength</td>
<td>671 nm</td>
</tr>
<tr>
<td>Background Correction Wavelength</td>
<td>674 nm</td>
</tr>
<tr>
<td>Photomultiplier Tube Voltage</td>
<td>500 - 650 V</td>
</tr>
<tr>
<td>Monochromator Slit Width</td>
<td>0.01 - 0.04 nm</td>
</tr>
<tr>
<td>Liquid Chromatograph Flow Rate</td>
<td>0.5 - 2 mL/min</td>
</tr>
<tr>
<td>Flame Conditions</td>
<td>lean, oxidizing</td>
</tr>
</tbody>
</table>
Figure 61
Liquid Chromatograms of LiCl and LiCl + EDTA Using the Silica Gel Column

5 μL 1000 μg/mL Li + EDTA (2:1 ratio)

Emission Intensity

5 μL 1000 μg/mL Li

Time (Temperature)

5 min
Apparently, the EDTA complexed lithium which had adsorbed to the silica gel and flushed it out of the column.

The silica gel column was unsuitable for lithium analyses because of its strong affinity for the lithium ion. Any molecule to which lithium was only lightly bound might not be able to retain the lithium in the presence of silica gel. In such a case, the molecular lithium specie sought would be destroyed.

b. Carboxy Methylcellulose Column

Three test solutions were injected onto this column. Solutions of lithium ion, \( \text{Li} - \text{EDTA complex (2:1)} \) and \( \text{Li} - \text{EDTA complex with excess lithium (greater than a 4:1 molar ratio)} \) all resulted in a single peak with a retention time of 6.3 minutes. These results indicated that the ion exchange resin had stripped the lithium out of the \( \text{Li} - \text{EDTA complex} \). The lithium from the complex then behaved like lithium ion, as it passed down the column.

This column packing material was unsuitable because it removed lithium from any molecule to which it was only lightly bound.

c. C8 - Reversed Phase Column

Four samples were injected onto this column: 1) a solution of ionic lithium (as the chloride), 2) a solution of the \( \text{Li} - \text{EDTA complex} \), 3) blood serum to which lithium had been added (spiked serum) and 4) blood serum from mental patients undergoing lithium treatment (treated serum). Each of the peaks gave a single peak with exactly the same retention time (Figure 62).

These results indicated several possibilities. 1) There was only one lithium specie present in the blood serum samples. 2) The column packing material
Figure 62

Liquid Chromatograms using the C8 Reversed Phase Column of LiCl, LiCl + EDTA, Doped Serum and Treated Serum

Time

Emission Intensity

100 µg/mL Li + EDTA
10 µg/mL Li
spiked serum (10 µg/mL Li)
treated serum

5 min
disrupted the bound lithium species, which resulted in only the free lithium ion moving through the column. 3) The column was unable to separate ionic lithium from EDTA bound lithium and could not separate the various lithium species in the blood serum.

The second possibility is common to all chromatography techniques. In serum, any bound lithium species would quite likely be in equilibrium with ionic lithium. The mobile to stationary phase equilibrium which takes place in chromatography could very easily disrupt the lithium equilibrium and result in the destruction of any bound lithium species. Therefore, chromatography may be an inappropriate technique for these lithium studies.

E. EVOLVED GAS - FLAME ATOMIC EMISSION SPECTROMETRY

1. Experimental

A microliter syringe was used to place 1 - 2 µL of solution on the point of the "V" shaped Pt - loop. The loop was inserted into the glass adapter. The heating cycle was begun. After the heating cycle was complete, the Pt - loop was allowed to cool for at least 30 s before the next sample was run.

2. Results and Discussion

a. Standard Thermograms

i. Lithium Chloride

The typical lithium chloride thermogram had two peaks (Figure 63). The first peak was fairly sharp. It was attributed to the vaporization and/or decomposition
of lithium chloride at a temperature just above the melting point of the salt (melting point = 605 °C). Lithium chloride has been reported to decompose very slowly with the release of chlorine gas, when heated [152]. This was supported by observing the copious fumes which arose from molten lithium chloride. During this decomposition, part of the lithium was volatilized and swept into the burner flame. The appearance temperature of the first peak corresponded roughly to the melting point of lithium chloride.

A second peak was attributed to the vaporization and/or decomposition of lithium carbonate, which was formed by action of the atmosphere on the decomposition products of the lithium chloride. This was verified by heating lithium chloride to about 700 °C. After 30 – 60 minutes, the lithium chloride was converted to the carbonate, which is one of the few insoluble lithium salts. The appearance temperature of the second peak corresponded roughly to the melting/decomposition temperature of lithium carbonate (1310 °C).

A possible route for the formation of lithium carbonate is shown in Figure 64. Lithium chloride reportedly [152] undergoes limited decomposition on heating to near its melting point, with the release of chlorine. Elemental lithium is probably also released (eqn. 1). Lithium reacts with water to form lithium hydroxide (eqn. 2). Alkali metal hydroxides are excellent trapping agents for carbon dioxide. When the lithium hydroxide traps carbon dioxide, the alkali metal bicarbonate is formed (eqn. 3). Alkali metal bicarbonates were not stable at high temperatures. Lithium bicarbonate decomposes to form lithium carbonate (eqn. 4)
Figure 63
Thermograms of Lithium Chloride, Lithium Carbonate and Lithium Phosphate
ii. Lithium Carbonate

The lithium carbonate thermogram had two peaks (Figure 63). The first peak was rather small. It was probably due to lithium chloride formed from the residual chloride ion present in the deionized distilled water (DDW).

The second peak was much larger. It was attributed to lithium carbonate. The appearance temperature of the major peak in the lithium carbonate thermogram matched that of the second peak in the lithium chloride thermogram. This strengthened the hypothesis that the second peak from the lithium chloride solution was due to lithium carbonate.

iii. Lithium Phosphate

The lithium phosphate thermogram had two peaks (Figure 63). As with lithium carbonate, the first peak was small and was attributed to lithium chloride formed by chloride contamination in the DDW.

The second peak was much larger. It was attributed to lithium phosphate. The appearance temperature for this peak was higher than for the second peak in the thermograms of the other lithium salts.

b. Effects of Complexing Agents on the Lithium Chloride Thermogram

Solutions of lithium with EDTA and nitrilotriacetic acid (NTA) were studied. As seen in Figure 65, the thermograms obtained for these solutions were dependent upon the pH. The pH was adjusted using ammonium hydroxide and hydrochloric acid.

At pH levels of 6 - 8, a more stable lithium complex was formed [126]. The
Figure 64
Proposed Mechanism for the Formation of Li₂CO₃ from LiCl

1. LiCl $\rightarrow$ Li⁺ + Cl₂
2. Li⁺ + H₂O $\rightarrow$ LiOH + H₂
3. LiOH + CO₂ $\rightarrow$ LiHCO₃
4. 2 LiHCO₃ $\rightarrow$ Li₂CO₃ + H₂O + CO₂
thermogram showed only one peak. This peak had an appearance temperature between those of the peaks in the unbound lithium chloride thermogram.

In the low pH range, the hydrogen ion displaced the lithium ion from the EDTA and NTA binding sites. The thermograms for these solutions closely resembled the thermograms of the pure lithium chloride solution.

The EG - FAES technique was able to discriminate between EDTA or NTA bound lithium and unbound lithium.

c. Effects of Changes in Atmosphere on the Lithium Chloride Thermogram

As discussed previously, the second peak in the lithium chloride thermogram was attributed to the lithium carbonate. Several different atmospheres were utilized in an effort to confirm the identity of the second peak and to eliminate it.

1. Effect of Added Water Vapor

Water vapor was added to the air entering the Pt - loop housing by passing the air through a water sparger. The resulting lithium chloride thermogram had a carbonate peak which was larger than in thermograms obtained without the water sparger (Figure 66). This indicated that the formation of lithium carbonate was enhanced by the added water vapor, as expected.

11. Effect of Removal of Water Vapor

Water vapor was removed from the air entering the Pt - loop housing by passing the air through a silica gel water sparger. The resulting lithium thermograms had a carbonate peak which was smaller than in the thermograms obtained without the water sparger (Figure 66). As expected, the lack of water
Figure 65

Thermograms of LiCl with EDTA and NTA at Various pH's

Temperature

LiCl

LiCl + EDTA

LiCl + NTA

Time (Temperature)

Emission Intensity

pH = 6 - 8

pH = 1 - 2

5 min
vapor suppressed the formation of lithium carbonate. However, the carbonate formation was not prevented altogether. This indicated that the traces of water that were able to pass through the water scrubber were sufficient to convert some of the lithium to the carbonate.

iii. Effect of an Inert Atmosphere

Argon was used to provide an inert atmosphere. The gas was scrubbed by silica gel and hot copper scrubbers to remove water vapor and oxygen, respectively. The resulting thermogram for lithium chloride was very similar to the thermogram obtained using room air. After this study was completed, the importance of the humidity of the room air became apparent. When this experiment was performed, the humidity of the room air was very low. Thus, little or no improvement could be expected of a dry argon atmosphere when compared to a dry air atmosphere. It was important that the use of an inert atmosphere did not eliminate the carbonate formation.

d. Thermograms of Lithium in Blood Serum

Typical thermograms resulting from blood serum to which lithium, as the chloride, had been added (spiked serum) are shown in Figure 67. Thermograms of blood serum from mental patients under lithium treatment (treated serum) are shown in Figure 68. In both cases, the thermograms were not very reproducible from one run to the next, but patterns were recognized in the thermograms for the same sample. Even over a time period of a few days, the same sample gave a similar thermogram. There were no distinct differences in thermograms for spiked serum as opposed to treated serum. It appeared that a greater proportion of
Figure 66

Thermograms of LiCl in Various Atmospheres

22 Jan 1982
room air
dried air
water saturated air

6 Jan 1982
room air
dried argon

Time (Temperature)
Figure 67
Typical Thermograms of Spiked Serum
Figure 68

Typical Thermograms of Treated Serum
spiked serum samples displayed a thermogram similar to that of pure lithium chloride. Too few samples were run for that difference to be statistically significant.

3. Conclusions

This technique was not pursued further for several reasons. The serum thermograms displayed observable differences from one sample to the next. However, they weren't reproducible enough for conclusions to be drawn without running each sample many times. Also, many of the blood serum thermograms had a peak that corresponded to the lithium carbonate peak. Because the formation of lithium carbonate from the decomposition of lithium chloride could not be prevented, it could not be determined whether the serum peak was due to lithium chloride, lithium carbonate or some other lithium specie.

F. LITHIUM - 7 FOURIER TRANSFORM NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

1. Experimental

All spiked and treated serum samples were kept refrigerated except during the actual NMR experiments, when room temperature was attained.

NMR tubes for all samples were 10 mm in diameter. A smaller reference tube, containing deuterated water, was inserted into the sample tube. This was to provide for the deuterium lock required by the instrument.

2. Results

A spectrum of 1 μg/mL Li in DDW was obtained and the frequency of the singlet
was used as a reference for the other spectra. The singlet obtained from a sample containing 5 μg/mL Li in saline solution was not significantly shifted from the reference.

The treated serum samples were allowed to run over night. A total of 48400 scans were accumulated for one spectrum and 10572 scans for the other. The spectra obtained are shown in Figure 69. In both cases, a large singlet was obtained at virtually the same position as the reference. Small differences in the chemical shift were judged insignificant. However, a second, much smaller, peak could be seen at approximately -0.3 ppm. It was difficult to determine whether this signal was real or simply a spinning side band.

The spectra for two spiked serum samples are shown in Figure 70. They resulted from the collection of 20300 scans for one spectrum and 29880 for the other sample. In each case, only one peak was seen, having the same position as the reference. Peaks on each side of the singlet were judged to be spinning sidebands because of their symmetry and frequency difference.

The concentration of lithium in normal blood is lower than in treated blood by three orders of magnitude. Such low levels are below the detection limit for the spectrometer used. Thus, no samples of untreated, unspiked serum were run.

3. Conclusions

The results of this limited study indicate that lithium may exist in two forms in the blood serum of some mental patients undergoing lithium treatment. When blood serum from non-patients was spiked, it showed only one form. There are at least two explanations for this second lithium specie. It may be a result of 1) a
Figure 69

$^7$Li FT - NMR Spectra of Two Treated Serum Samples

The spectra were obtained from treated blood sera (from mental patients). The top spectrum represents accumulation of 48400 scans. The bottom spectrum represents accumulation of 10572 scans. Note the small peak at -0.3 ppm (indicated by arrow) in both spectra.
The spectra were obtained from normal blood sera spiked with lithium. The top spectrum represents the accumulation of 29880 scans of serum with approximately 20 µg/mL Li. The bottom spectrum represents the accumulation of 16835 scans of serum with approximately 10 µg/mL Li.
metabolic process which takes place in mentally ill and/or normal persons, or 2) lithium binding to a compound or compounds present at a much higher concentration in the serum of certain mental patients. Further work needs to be done to confirm these data on a larger sample of patients. The data presented here are too sparse to justify firm conclusions. Even so, the results illustrated the feasibility of using Li-7 NMR for the detection of different lithium species in serum.
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PART ONE. DEVELOPMENT OF A NEW CARBON FURNACE FOR ATOMIC ABSORPTION SPECTROSCOPY.

A new, multipurpose carbon furnace was designed and tested for quantitative atomic absorption spectrometry. The furnace had two separately controlled heating chambers, one for vaporization of the sample and the other for atomization of the sample.

Basically, three modes of furnace operation were investigated. Quantitation was investigated with (a) the atomization section hot and (b) the atomization section cold, for trapping before atomization. The vaporization section was heated quickly in each case. Speciation of lead compounds was carried out by slowly heating the vaporization section, while the atomization section was hot. Variations on these basic methods (including the use of a carbon rod sampling device) were also studied. Elements investigated included lead, mercury, zinc, copper, nickel, tin, arsenic, and magnesium. The new furnace design was shown (i) to eliminate sample loss, (ii) to reduce molecular background absorption, (iii) to be capable of many different modes of operation and (iv) to be capable of speciation. It was much more versatile than commercially available models.
PART TWO. STUDIES ON SPECIATION OF LITHIUM IN BLOOD.

The use and efficacy of lithium in the treatment of certain mental disorders is well known, but its mode of action is not known. Several studies were carried out with the goal of detecting two or more lithium species in the blood serum of mental patients undergoing lithium treatment. "Coupled" techniques investigated included liquid chromatography - furnace atomic absorption, liquid chromatography - inductively coupled plasma atomic emission, liquid chromatography - flame atomic emission and evolved gas analysis - flame atomic emission. For various reasons, data obtained with these techniques were inconclusive. Li - 7 Fourier transform/nuclear magnetic resonance was used to detect two lithium peaks, which indicated the possible presence of two lithium species in the blood serum of two mental patients undergoing lithium treatment.
VITA

Thomas Arthur Ekman was born April 8, 1957 in San Francisco, California. He graduated from Searcy High School in Searcy, Arkansas in 1975, with a four year academic scholarship to attend Arkansas College, Batesville, Arkansas. He completed requirements, cum laude, with a chemistry major, in three years for the Bachelor of Arts degree. As a senior, he was awarded the college's chemistry book award. He received the William's graduate fellowship, which he used to enroll in Louisiana State University's graduate program. In August 1978, he enrolled as a chemistry graduate student at LSU and completed the requirements to obtain a computer science minor. In August 1984, he will receive a Ph.D. in Analytical Chemistry. Upon graduation, he will continue doing research with a firm located in Dobbs Ferry, N.Y.
EXAMINATION AND THESIS REPORT

Candidate: Thomas A. Ekman

Major Field: Analytical Chemistry


Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

July 9, 1984