Effects of atomization chamber size on constant temperature furnaces
by Harry Roger Howell

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemistry
Montana State University
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Abstract:
Many different graphite atomizers have been developed for flameless atomic absorption. These atomizers can be classified into two distinct groups: constant temperature furnaces and pulse type atomizers. In the constant temperature furnace a graphite tube is heated to and held at a desired atomization temperature before sample introduction. In the pulse type atomizers the sample is inserted into a cold graphite tube, which is then rapidly heated to the desired atomization temperature.

Both groups have advantages and disadvantages. Constant temperature furnaces are relatively free of matrix effects and have a higher sensitivity than the pulse type atomizers. However, they are' complex, slow, large, and not commercially available. Pulse type atomizers are small, simple, easily mounted in existing flame atomic absorption spectrophotometers, and are commercially available; however, at times are plagued by severe matrix effects.

If constant temperature furnaces could overcome the problem of size and complexity, they could become more widely accepted as a routine analytical tool replacing pulse type atomizers. In this work a smaller model of the constant temperature Uoodriff furnace was compared to the larger, established Woodriff furnace for sensitivity, resistance to matrix effects, and other operating characteristics.

The results showed that this small furnace was comparable to the larger Woodriff furnace in all aspects.

Perhaps as a result of this work, commercial atomizer corporations will give a more serious look at constant temperature furnaces as a method for non-flame atomic absorption analysis, with few known interferences.

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Date August 1, 1979

EFFECTS OF ATOMIZATION CHAMBER SIZE ON CONSTANT TEMPERATURE FURNACES

by

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A thesis submitted in partial fulfillment
of the requirements for the degree

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ABSTRACT

Many different graphite atomizers have been developed for flameless atomic absorption. These atomizers can be classified into two distinct groups: constant temperature furnaces and pulse type atomizers. In the constant temperature furnace a graphite tube is heated to and held at a desired atomization temperature before sample introduction. In the pulse type atomizers the sample is inserted into a cold graphite tube, which is then rapidly heated to the desired atomization temperature.

Both groups have advantages and disadvantages. Constant temperature furnaces are relatively free of matrix effects and have a higher sensitivity than the pulse type atomizers. However, they are complex, slow, large, and not commercially available. Pulse type atomizers are small, simple, easily mounted in existing flame atomic absorption spectrophotometers, and are commercially available; however, at times are plagued by severe matrix effects.

If constant temperature furnaces could overcome the problem of size and complexity, they could become more widely accepted as a routine analytical tool replacing pulse type atomizers. In this work a smaller model of the constant temperature Woodriff furnace was compared to the larger, established Woodriff furnace for sensitivity, resistance to matrix effects, and other operating characteristics. The results showed that this small furnace was comparable to the larger Woodriff furnace in all aspects.

Perhaps as a result of this work, commercial atomizer corporations will give a more serious look at constant temperature furnaces as a method for non-flame atomic absorption analysis, with few known interferences.

INTRODUCTION

Atomic absorption gained widespread use soon after its introduction by Walsh[1] in 1955. It was a simple, powerful, yet relatively inexpensive technique for the analysis of metals. As with any new technique considerable research was aimed at higher sensitivities and lower detection limits. Considerable improvements were realized with improved flames; however the greatest improvements were made in the development of several different flameless graphite atomizers, most of which were modeled after the work of King.[2]

The most outstanding work done with graphite atomizers was by L'vov[3,4] in Russia. L'vov's graphite atomizer consisted of a graphite tube 40 mm long with an inside diameter of 2.5 mm enclosed in a pressure chamber. With the system, up to seven samples were put on graphite rods in the pressure chamber, the chamber was evacuated of air and filled with argon, usually to a pressure greater than one atmosphere. The graphite tube was then heated to the desired temperature and the samples were inserted into it one at a time, with each being heated by a different power supply from the graphite tube. After the seven samples were analyzed the tube was cooled down and the chamber was depressurized to allow for the introduction of new samples into the chamber. L'vov has worked extensively with his graphite atomizer and has reported the best absolute sensitivities of anyone using a graphite atomizer. He also has observed few matrix effects (effects on atomization of an element due to other species in the sample) with it.

At about the same time that L'vov was developing his graphite atomizer, Woodriff,[5,6,7] at Montana State University, was developing his graphite furnace. Woodriff's furnace consisted of a graphite tube 300mm long with an inside diameter of 7mm enclosed in an insulated water-cooled shell. The air was flushed from the shell with argon, and the tube was heated to the desired temperature. The samples were then inserted into the hot graphite tube in graphite cups directly from the atmosphere. The tube was not cooled down until all the samples were run. Woodriff has obtained excellent sensitivities with his furnace, in some cases as good as that of L'vov. Very few matrix effects have been observed in a recent study by Hageman.[23]

Massmann[8] in Germany, developed a semi-enclosed graphite furnace, later adopted by Perkin-Elmer Corporation. This furnace consisted of a graphite tube 55 mm long with an inside diameter of 8 mm, supported at the ends by water cooled electrodes. The sample was inserted into the cold graphite tube, then the tube was gently heated to dry the sample, then hotter to char, and then finally rapidly heated to the atomization temperature to atomize the sample, and finally cooled down for the next sample to be introduced. Massmann has obtained good sensitivity with his furnace, which is considerably better than a flame, but not as good as L'vov or Woodriff. He did, however, observe matrix effects with his furnace. These matrix effects at times were quite severe.

Amos and Matousek[9] developed a mini-Massmann furnace for Varian Techtron. This furnace consisted of a graphite tube 9 mm long with an inside diameter of 3 mm, supported in the center by graphite electrodes. The furnace is operated in the same manner as Massmann's. It has better sensitivity than Massmann's; however not as good as Woodriff's or L'vov's. Much more severe matrix effects are observed with this furnace than with any of the other types mentioned.

The four major graphite atomizers which have been briefly described can be divided into two main categories: "constant temperatures furnaces" (L'vov and Woodriff), in which the heater tube is heated to the desired atomization temperature before sample introduction; and the "pulse type atomizers" (Massmann, and Amos and Matousek), in which the sample is introduced into the cold tube, which is then heated to the desired atomization temperature via three steps, with a rapid temperature change during the final step. It is noted that the constant temperature furnaces have higher sensitivity and fewer matrix effects than the pulse type atomizers. The pulse type atomizers, however, have gained widespread use and the constant temperature furnaces have not. The pulse type atomizers have the advantages of being small, such that they can be used on the same instruments as the already present burner heads for flame atomic absorption, with little effort to change over. They are also simpler and more easily repaired than the constant temperature furnaces. An attempt[22] has been made to approximate constant temperature conditions with a pulse type atomizer

with fair success.

L'vov's graphite cuvette has not gained widespread use due to its complexity and the time required for analysis of a few samples. If L'vov could introduce samples directly from the atmosphere into his furnace it would gain more widespread use; however, this is virtually impossible because operation is usually at a pressure greater than one atmosphere.

Woodriff's furnace has the drawback of being large and complex, requiring a complete atomic absorption set-up for the furnace. If a Woodriff furnace could be made small enough so that it could fit on commercial instruments already present and could be exchanged for the burner head when greater sensitivity is required, it should gain greater use. Such a smaller Woodriff furnace has been constructed. The main thrust of this thesis deals with characterizing and improving this furnace. It is compared with the large model Woodriff furnaces in terms of sensitivity, resistance to matrix effects, power consumption, and operational characteristics.

GENERAL CONSIDERATIONS

Several important questions arise upon consideration of a smaller Woodriff furnace: 1) Will the sensitivity be decreased? 2) Will it have the resistance to matrix effects for which the large furnaces are well known? 3) Will power consumption be increased? 4) Will it work in a commercial instrument? 5) Will operating conditions be drastically different? and 6) Will it be simpler to repair? These questions and others will be answered, first from a theoretical viewpoint and then experimentally.

As explained by L'vov[4], the absolute sensitivity is a function of the cross-sectional area, but independent of the path length. The sensitivity, then, of this smaller furnace is expected to be the same as that of the larger furnaces, when both use heater tubes of the same cross-sectional area. The shorter path length of this smaller furnace gives it the capability to use a heater tube with a smaller cross-sectional area than can be used in the larger furnaces, thus giving the possibility of higher sensitivity than in the larger furnaces. This smaller cross-sectional area is possible, because the loss of signal is proportional to path length.

The resistance to matrix effects in the large Woodriff furnace should be present here. The major cause of matrix effects is removal of the element from the optical path before it reaches the atomization temperature. In pulse-type atomizers this can easily be

due to a short path length and a rapidly changing temperature. In this small constant temperature furnace the element should not be able to escape before reaching the atomization temperature, for several reasons: 1) The heater tube is held at the atomization temperature during sample introduction, thus avoiding matrix atomization before sample atomization; 2) The sample is introduced perpendicular to the length of the tube; the sample must then make contact with the hot tube walls before escaping from the optical path, ensuring complete atomization; and 3) a fairly long path length.

The power consumption of the smaller furnace should be almost the same as that of the larger furnaces if the only difference is in the length of the heater tube. The resistance of the heater tube is small compared to the total resistance of the system. If any effect is observed, it should be a slight increase in power consumption, due to the cooling of the tube by the graphite heater tube holders that are closer to the center of the tube than in the larger models.

This small furnace should work in a commercial instrument, because it was physically constructed to fit. No problems should exist with the electronics as the signal processing is the same for this furnace as for other methods of atomic absorption.

The operating conditions, such as the argon flow, coolant flow, optimum temperature, etc. are expected to remain the same with perhaps increased coolant flow to keep the stainless steel cooling jacket cool, due to the closeness to the graphite tube with less insulation. The

argon flow should remain the same although the amount needed should be slightly less because of the smaller volume to flush after repairs. The optimum temperature should be the same, as it is characteristic of the element and not of the atomizer.

The graphite parts should be slightly simpler to replace because of their design and size. The heater tube will be cooled more rapidly because of the smaller amount of insulation between it and the cooling jacket; thus it can be replaced sooner after failure. The smaller volume of the furnace will allow for a shorter flush time with argon making the down time considerably less.

These answers are only theoretical. They make the small furnace look very feasible; however, experimental data need to be used to determine the real characteristics of the furnace.

EXPERIMENTAL

The outer shell of the furnace is a double-walled stainless steel cooling jacket, 10.16 cm in diameter and 15.56 cm long with ends of curved, double-walled, stainless steel having a short piece of pipe attached in the center on which the lenses are attached. The total overall length of the furnace is 25.10 cm. At a point 7.78 cm from the end of the cooling jacket, a 1.0 cm hole was drilled and the metal around it machined to accept a vycor ground glass joint, to attach the entrance port. Also, in this piece of brass the argon inlet was made. In order to flush the air from the samples and to simultaneously minimize the air flow into the furnace, the inlet was made at an angle away from the center of the furnace. At a point 90^{o} along the diameter from the sample inlet, a cylindrical brass block, 2.22 cm in diameter was attached to allow the furnace to be attached in a burner mount. The power connections were made of a brass band 8.5 cm in diameter, 1.2 cm long and 0.2 cm thick. To the inside of this band a ring of tubing to be connected to water for cooling was attached, and a graphite disc 3.5 cm thick at the outside and 6.2 cm thick on the inside were attached. The disc had a 2.6 cm diameter hole in the center into which the heater tube holder was inserted. On inside of this band a rubber insulator was placed to insulate the cooling jacket from the high current applied to the furnace. Another insulator was placed between this ring and the end plate, too. These insulators also serve the purpose of sealing the furnace from the atmosphere. The heater tube holder was made of a

graphite cylinder 2.6 cm in diameter for the first 0.7 cm of length and 3.0 cm for the remaining 0.9 cm of length. A hole 0.95 cm in diameter was drilled through the center of this cylinder. Two circular grooves 0.2 cm wide and 0.6 cm deep were cut into the cylinder. One was at 0.67 cm from the center on the end with the smaller diameter and the other groove was cut 0.88 cm from the center on the opposite end. The grooves were cut into the heater tube holder to act as a heat sink, preventing the complete transfer of heat from the heater tube to the holder. This allows the heater tube to be very hot and the holder to be relatively cool. Without the grooves the power consumption would be greater and the temperature variation observed between the end and the center would also be greater.

The heater tube was made from a 0.95 cm diameter graphite rod drilled lengthwise to an inside diameter of 0.77 cm. Halfway along the length of the heater tube a small hole was drilled through the wall on one side. A center piece was attached to the heater tube at this point. The center piece was made from a graphite cylinder 2.9 cm in diameter and 2.6 cm long. The cylinder was drilled with a 0.95 cm drill across its diameter 0.6 cm from one end. It was then cut lengthwise at the center of this hole, so that it could be assembled around the heater tube. In the larger piece a hole 0.68 cm in diameter was drilled in the center. This hole was tapered from the end 0.8 cm. Two holes were drilled in the grooved end and threaded. On the other piece two holes were drilled large enough to allow graphite screws to be inserted to

fasten the two pieces together around the heater tube. The inside of the furnace was filled with graphite felt insulation 3.0 cm thick. The furnace was assembled as shown in figure 1. The furnace was connected to a power supply consisting of a Powerstat 7.8 KVA autotransformer connected to a G.E model 9T21B1037 G2 5KVA transformer powered by a 240 volt wall outlet. The ends of the furnace were fitted with quartz lenses of the correct focal length to maximize the amount of signal on the slit.

Significant variations in temperature along the length of the heater tube have been observed in all types of atomizers. These variations, both hot and cold, can have a significant effect upon the absorption signal observed, by altering the rate of analytic movement down the tube and the percent analyte atomization. In the flame the burner is altered and kept clean to obtain a uniform flame. For the graphite atomizers there has been little that could be done to alleviate this problem. The temperature of the whole tube could be increased until the coldest spot was at the temperature desired for operation, however the action would increase the hottest points to an even hotter temperature causing the heater tube to burn out prematurely. In the case of the larger Woodriff furnace a three phase power system has been developed, to partially alleviate this problem. The three phase system is much more complicated than the single phase system and is also more expensive. It does improve the situation; however it does not

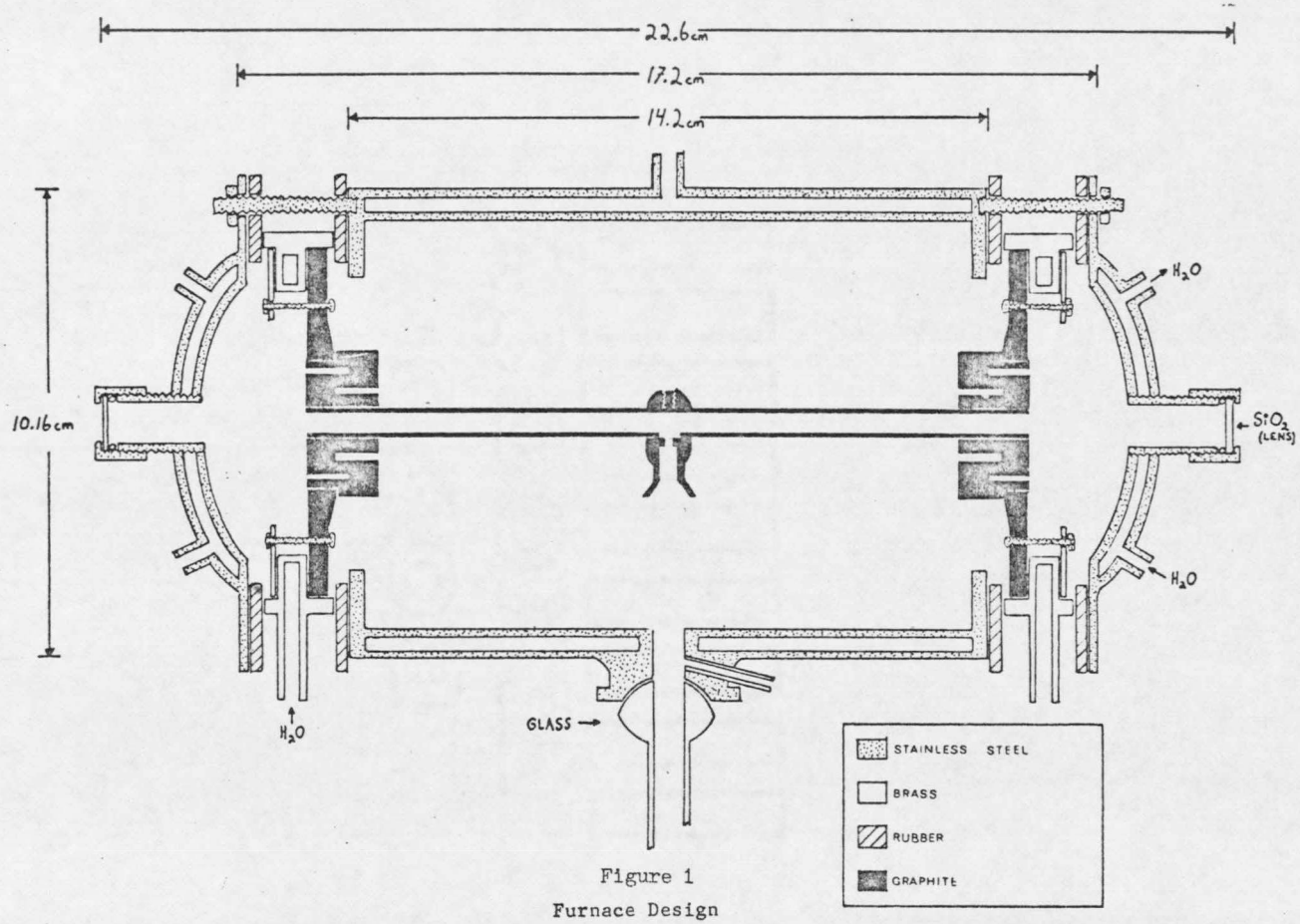


Figure 1
Furnace Design

completely eliminate this problem, but adds problems to the operation of the furnace, such as balance the current (temperature) on the three legs.

A temperature profile was made of the heater tube to determine the extent and location of the temperature variations. A graphite block 0.77 cm in diameter and 0.25 cm long was made with one end being concave and the other flat. This block was placed in the heater tube at one end, with the concave face away from the center of the furnace, while the furnace was cold. The furnace was heated to the desired center temperature, determined with an optical pyrometer by observation through the sample entrance port. The temperature of the concave end of the block is then measured from the end of the furnace, using an optical pyrometer. The window on the end of the furnace was removed, a graphite rod inserted to move the block 1 cm and then removed, the window replaced and the block allowed to reach equilibrium with the tube around it. The temperature of the block was again measured. This procedure was repeated until the block reached the other end of the furnace. The temperature was recorded at each position. A temperature vs. distance plot was made using this data (figure 2) and the data analyzed. A significant temperature variation is observed with a change of over $400^{\circ}C$ in 3 cm. This situation will cause the heater tube to burn out prematurely at the hot spots. Much of the difference in temperature appears to be due to the large mass of the center piece causing the center to be cooled.

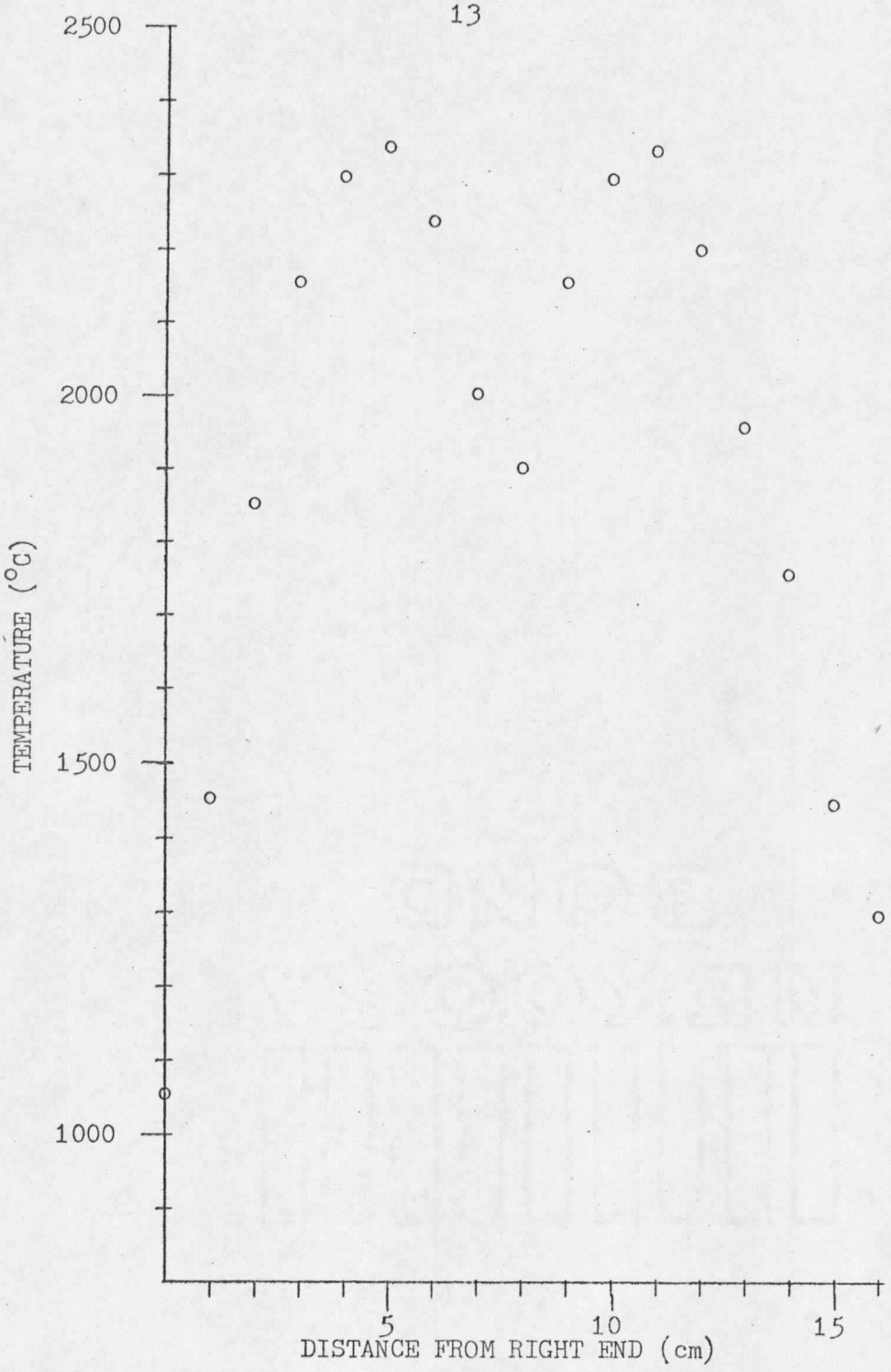


Figure 2
Temperature Profile of Heater Tube Using Large Center Piece

A new center piece was made using 1.27 cm graphite rod 2.54 cm long, with a hole drilled 0.95 cm in diameter at 0.67 cm from one end and a hole drilled 0.32 cm in diameter from that end toward the hole. Threads were cut into this hole and another piece of graphite was cut and threaded to fit the hole. From the other end a hole 0.68 cm diameter was drilled and a 0.5 cm deep taper was made from this hole to the outside of the piece. The previous center piece was replaced with this one and a temperature profile, shown in figure 3, shows a considerable improvement over the previous one in the uniformity of the temperature along the heater tube.

In an attempt to cool down the hot spots some graphite washers 2.5 cm in diameter and 0.3 cm thick were made with a hole 0.95 cm in diameter in the center enabling them to be placed on the heater tube. One of these washers was placed at each of the two hottest points along the heater tube. The furnace was heated, and the temperature in these regions was found to be more uniform than before. Some more washers, 1.25 cm diameter and 0.5 cm thick were made and placed on the heater tube next to the other washers. The effect of these large and small washers was determined and approximations were made for the locations necessary to obtain uniform temperature along the heater tube. Washers were placed at the approximated locations and found to do a fairly good job of producing a uniform temperature as determined by another temperature profile (figure 4) was taken of the heater tube. With these washers properly placed a uniform temperature was obtained along the

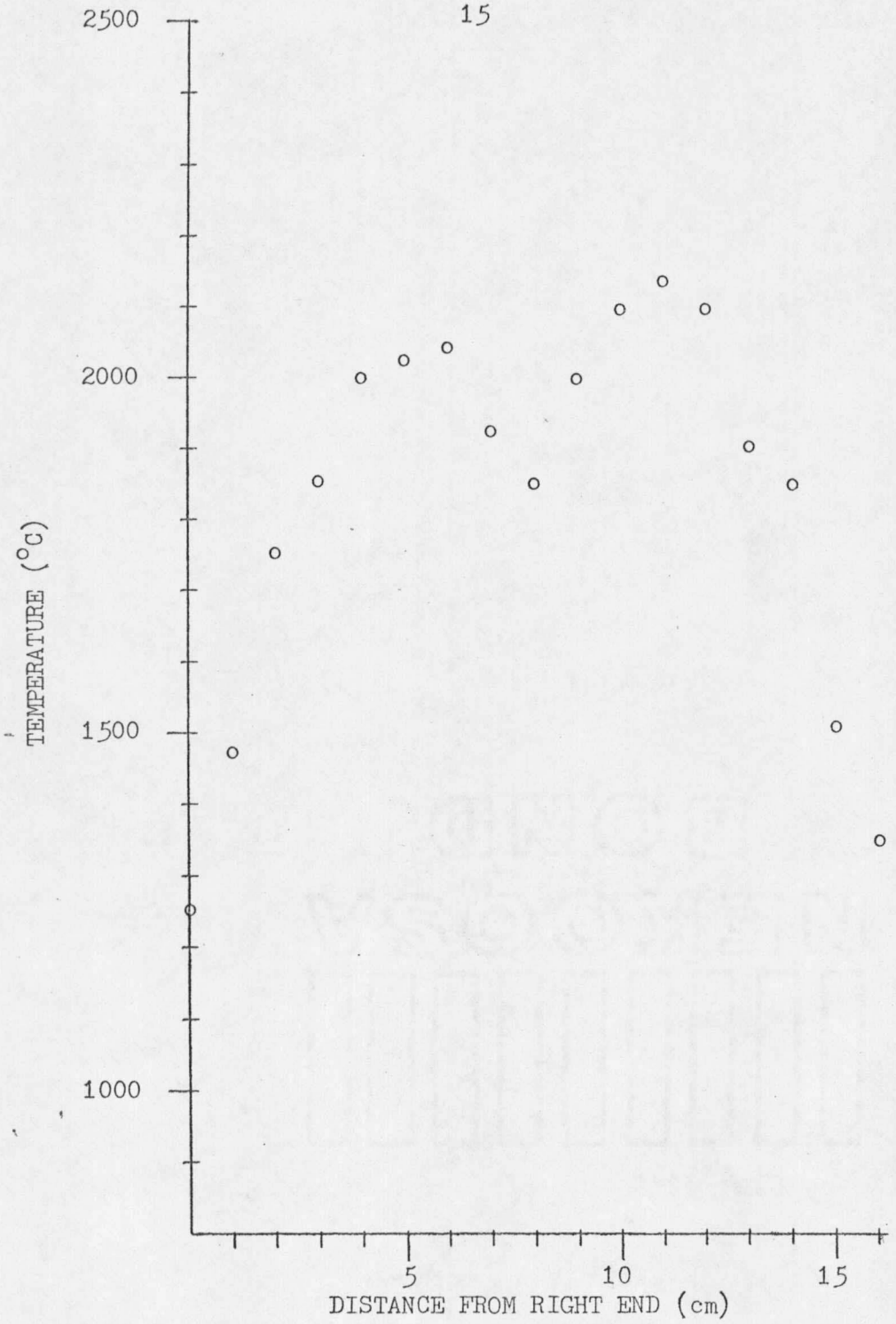


Figure 3
Temperature Profile of Heater Tube Using Small Center Piece

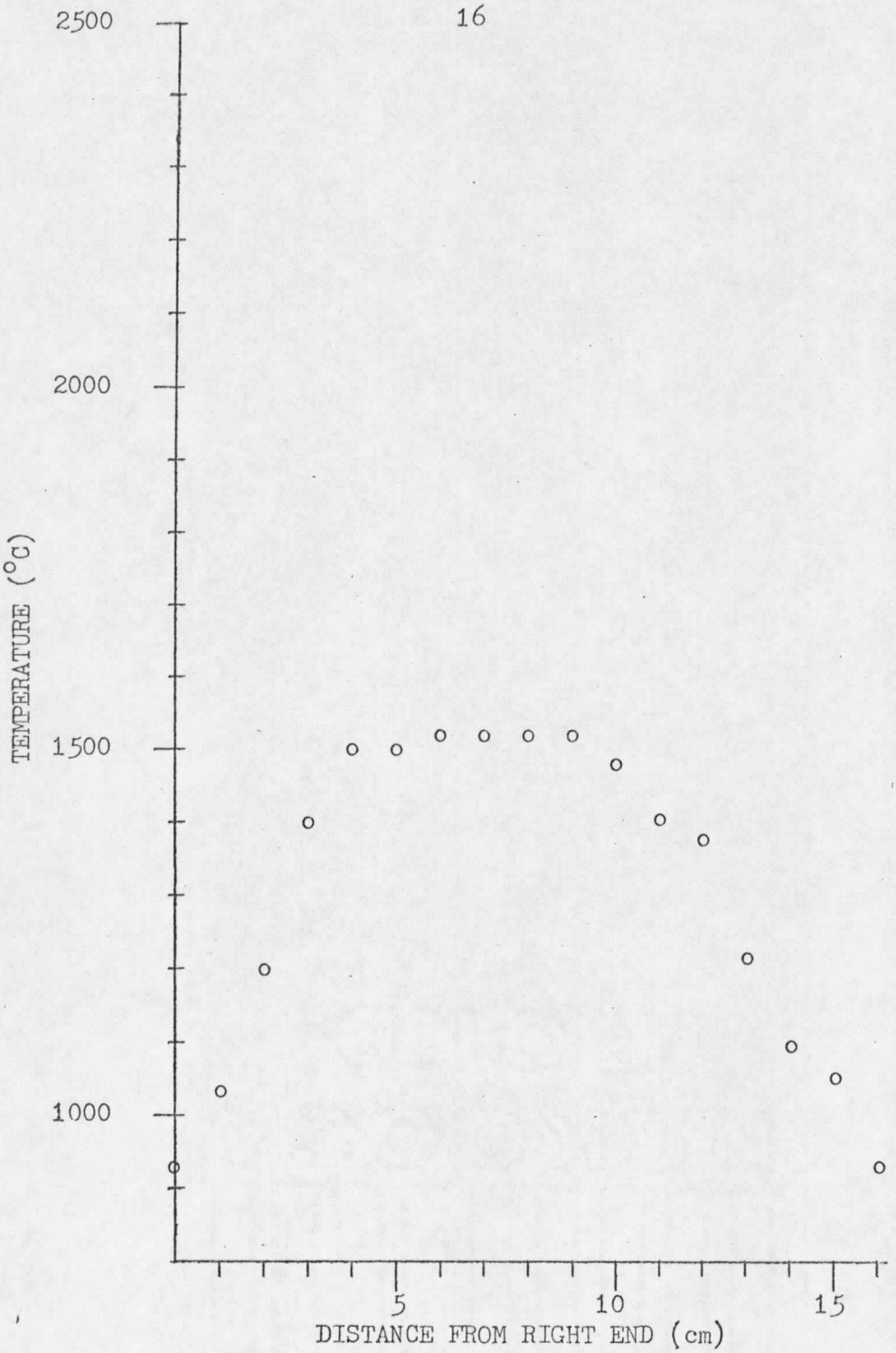


Figure 4
Temperature Profile of Heater Tube Using Small Center Piece and Washers

length of the heater tube except on the very ends which, as expected, were slightly cooler.

This method of obtaining a uniform temperature along the heater tube worked quite well on this little furnace causing a very slight increase in power consumption. The slight increase in power consumption caused by the addition of these washers on this small furnace will be more than offset by the gain in life of the heater tube and the consequent decrease in down time. The absence of signal alterations due to the varying temperature is an even more important justification for this increased power consumption . However, when this method was applied to a larger furnace, it was not found feasible. A considerable amount of graphite is necessary to cool this much larger area which causes a large increase in the power consumption of the furnace.

By using a few small washers a uniform temperature was obtained without going to the more costly three phase heating. With a little more research, this washer system could possibly be applied to other atomizers as well as this small furnace.

Most of the measurements made with this furnace were made using a system consisting of a Beckman DU quartz prism spectrometer equipped with a photomultiplier attachment. A Sola high voltage power supply was used to power the photomultiplier (IP28). The photomultiplier output was fed into a Princeton Applied Research model JB5 lock-in amplifier that was coupled with a Spectogram Corporation dual lamp power supply which powered the hollow cathodes. The output of the lock-in amplifier

was fed into a Heath Built Servo Recorder model EUW - 20A. This system is shown in figure 5.

Another system was briefly used consisting of a Varian Techitron model AA-5 spectrometer with an IM6 amplifier and a BC-6 background corrector. The furnace was mounted in the burner head mount. A minor problem was encountered with this mount due to the fact that this furnace is considerably heavier than a burner head or a carbon rod atomizer for which the mount was designed. For a short time the mount can be used without modification; however, for prolonged use the mount would need to be modified to stabilize the added weight. On this system the same type of power supply was used as before. The quartz lenses on the ends of the furnace were replaced by quartz windows and the lenses already on the optical rail for flame and carbon rod work were used. The reasoning for using this set up was two-fold: First simultaneous background correction is present, whereas, on the other system, background correction was accomplished by running each sample twice; once to get the sample plus background signal, and then once again to get the background signal. The background was manually subtracted from the signal plus background to get the analytical signal. Second, the AA-5 was used to check to see what problems would be encountered in using the small furnace on a commercial instrument.

For this small furnace, as with any sensitive method of analysis, many precautions are necessary to avoid contamination. A place of utmost concern in this system is the vycor side tube through which all

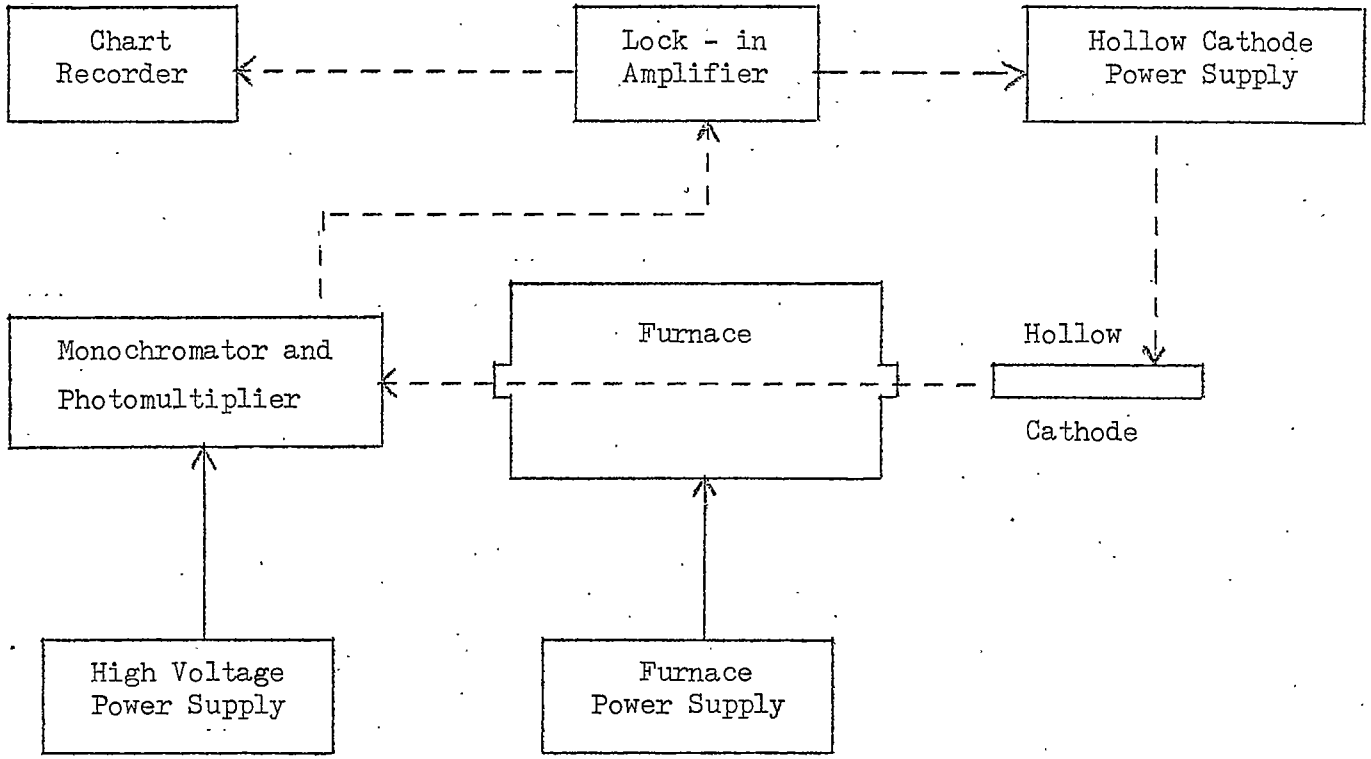


Figure 5

Sysyem Layout

samples are introduced. If any contamination is present here it is present with every sample. The vycor side tube used has a larger inside diameter than the outside diameter of the cups used for introducing the samples. A cylinder of graphite slightly smaller than the inside diameter of the vycor tube is put on the push rod, to which the cups are screwed on, approximately 5 cm from the point at which the cup attaches. The function of this cylinder is to prevent loss of argon and introduction of air while the sample is in the furnace, thus increasing the life of the heater tube. The other use of this cylinder is to help guide the cup into the center piece. This graphite cylinder can pick up and spread impurities along the vycor tube unless it and the tube are kept very clean. The vycor tube and graphite cylinder are regularly cleaned with nitric acid and rinsed with double-distilled water. Another source of contamination to be considered is the cups used for introduction of sample. The cups are cleaned before each use by heating in the furnace at a temperature higher than that to be used in the analysis and observing the absorption signal. The cups are repeatedly injected into the furnace until they are clean, as indicated by an absorbance of less than one percent on two or more consecutive injections. Anything which comes into contact with the cups can cause contamination, such as the glass plate or metal sheet on which they are placed and the forceps used to screw them on the push rod. When the cups are being cleaned they are treated exactly as if a sample is in them. Sources of contamination can be determined by the following procedure. When

removing a cup from the center piece after absorption has decreased to zero, pull the cup out of the center piece almost to the vycor tube, allow to cool and re-inject. If absorption occurs, then the cup is dirty; if not, it is due to something else. If the cup can be completely removed from the furnace and re-injected without touching anything and absorption occurs, but did not when only removed almost to the vycor tube, then the vycor tube is dirty and needs to be cleaned. If no absorption occurs after removing the cup from the furnace and re-injecting it without touching it with anything, then the cup and vycor tube are considered clean, and the contamination is either caused by the forceps or the glass plate and both should be cleaned. The vycor tube, glass plate, and forceps can all be cleaned by washing with dilute (1:1) nitric acid, rinsing several times with double-distilled water and drying under a heat lamp. Once the cups and other items contacted are clean the furnace is cooled down to optimum temperature for the element of interest and the samples are analyzed. This cleaning procedure does not need to be carried out between consecutive samples. It only needs to be done occasionally or whenever the cups are suspected of causing some spurious results.

Extreme care must be taken in assuring that all glassware and chemicals used in sample handling are very clean and will not cause contamination of the sample.

The first step in the development of procedures using this furnace for analysis of an element is to determine the optimum

temperature for that element in the furnace. The optimum temperature is defined as the temperature at which a given amount of sample gives the greatest absorbance. To determine the optimum temperature the approximate analytical range was determined and a series of standards covering this analytical range were made. The furnace was heated to the maximum operating temeprature of 2400^{o}C (the furnace is capable of higher temperatures than this; however, these temperatures are not recommended, due to two factors: high light emission from the entrance port and the large coolant flow necessary to keep the cooling jacket from getting hot). The cups were cleaned at this temperature and the series of standards was run several times. The temperature of the furnace was lowered by 50^{o}C and the cups were checked for cleanliness and the series of standards was repeated in 50^{o}C increments until a temperature of 1200^{o}C or a decrease in absorbance was noted for two or more consecutive temperatures. The data from each of these measurements was plotted with the absorbance of a given standard vs temperature. The graph is usually the form of a curve with a maximum. The temperature at which this maximum occurs is the optimum temperature, within 50^{o}C. Once the optimum temperature has been determined for an element it does not need to be determined again.

The optimum temperature was determined for silver, aluminum, gold, cadmium, and copper, using the above procedure. For aluminum and copper, a maximum was not found in the plot of absorbance vs temperature.

This is due to the formation of compounds which have a higher dissociation temperature than 2400°C. Carbide formation with the heater tube or oxides in the cup can be responsible for this. Mechanisms describing the effect of the oxides on the absorbance signal have been proposed by Agett and Sprott;[10] Campbell and Ottaway;[11] Fuller;[12] and several others.[13,14] For these elements 2350°C or 2400°C was chosen for analysis, depending upon the problems encountered with contamination. A plot of temperature vs absorbance for silver, aluminum, and gold is shown in figure 6.

From the optimum temperature plot one can not only get the optimum operating temperature, but also the change in temperature that can be tolerated without a significant decrease in absorbance. For most elements one can easily tolerate a change of ± 50°C with no significant problems. Exact temperature measurement with a pyrometer is not always necessary. A simple circuit can be made, using a photocell to detect the furnace light which is indicative of the temperature of the heater tube. There are two types of photocells that can be used. The first type is the one which generates a small current when bombarded by light. The leads from the photocell are connected to a milliameter, the photocell is permanently mounted in the path of the furnace light, yet out of the path of the hollow cathode signal. If the meter is of the correct range for the output of the photocell the system is ready to be calibrated. To calibrate the system the furnace is heated to the lowest reading of the meter. The temperature and meter reading are

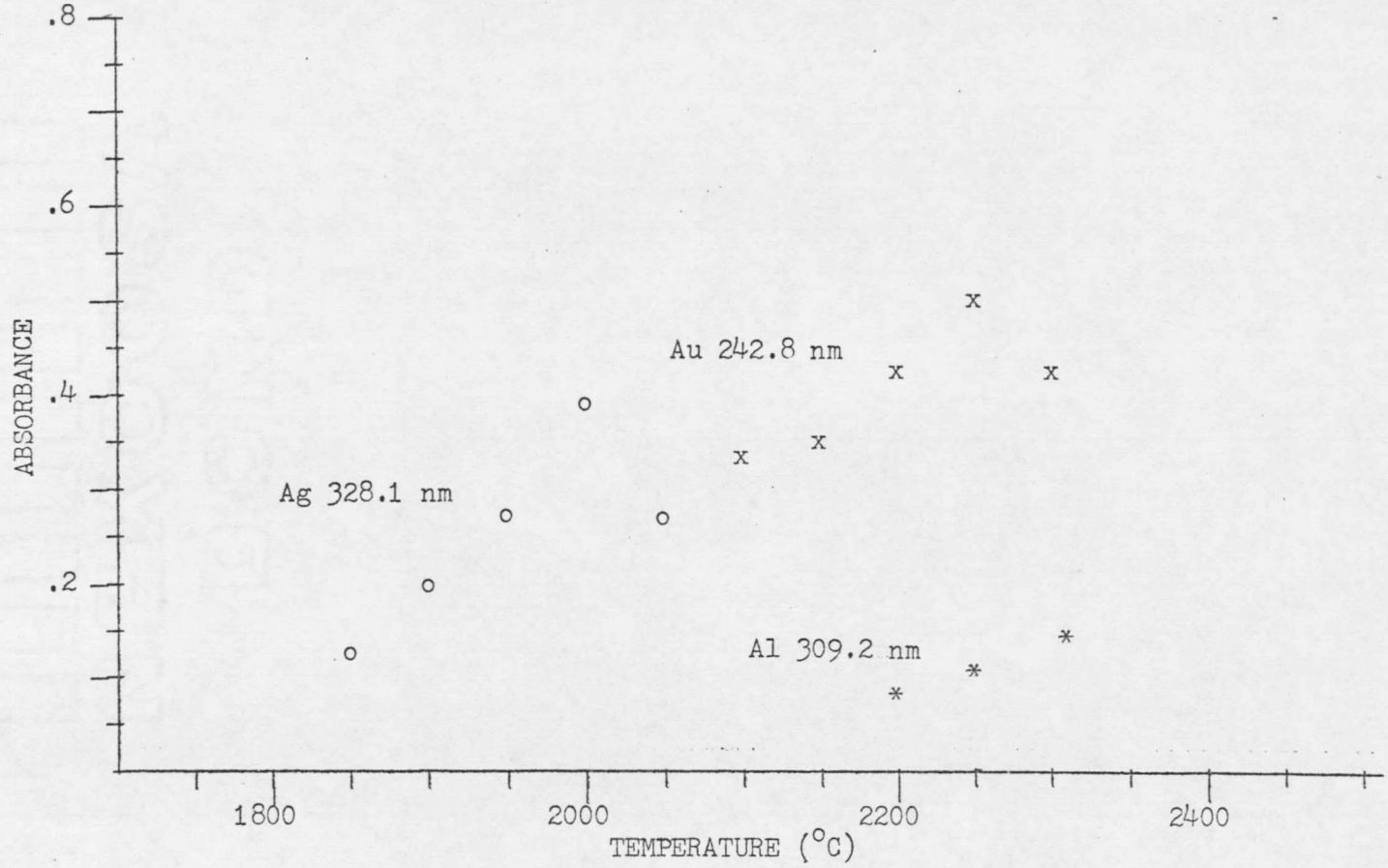


Figure 6
Optimum Temperature Curves for Au, Ag, and Al

recorded and the furnace is heated incrementally until the maximum temperature is reached, making sure that the furnace temperature is at equilibrium at each reading. This system needs only to be checked occasionally with a pyrometer to assure reliability. The other type of photocell that can be used is the type that is made of a semi-conducting material which changes resistance when light is shined on it. This system requires a battery as well as the photocell and milliammeter. The photocell is attached in the path of the furnace light as with the previous system. A battery is connected between one lead of the photocell and the meter, while the other lead is a direct connection. This system is then calibrated by the same procedure as the other system. Stability of the system is a little better than the conductive system and the relationship between current and light is more nearly linear. An elaborate way of mounting the photocell, of either type, is to install a slotted mirror in front of the monochromator slit such that it reflects the furnace light at a right angle and lets the analytical signal pass through. The photocell is then attached such that this reflected light is reflected onto it. This is enclosed in a black box so that the furnace light is the only light entering it. Both systems are shown in figure 7, along with a sketch of this method of mounting the photocell.

For the five elements mentioned previously, at the wavelengths corresponding to their major intensities, the absolute sensitivities were determined. The absolute sensitivity is defined as the amount of

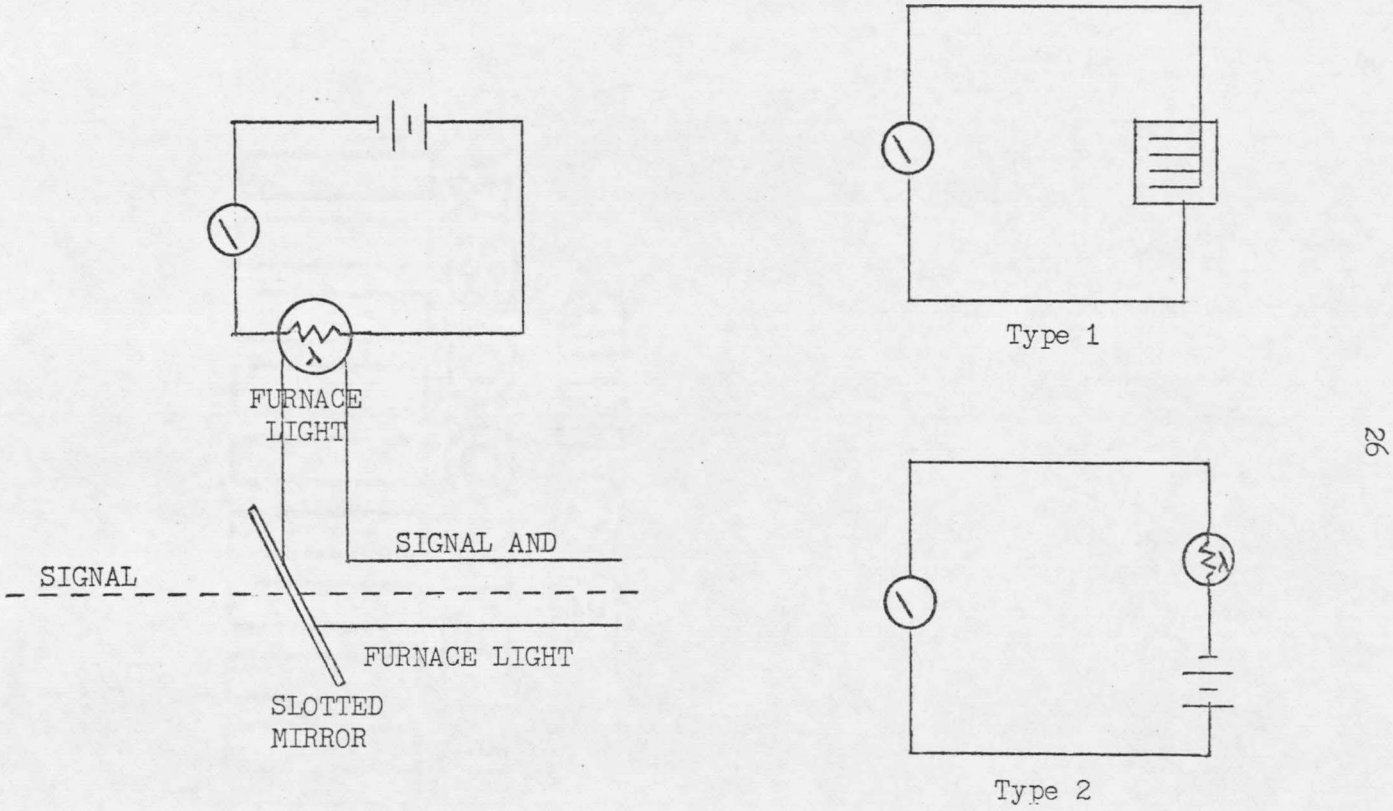


Figure 7

Temperature Measuring System

pure metal which gives an absorbance of one percent. To determine the sensitivity of each element, the monochromator was set to the corresponding wavelength, the furnace was heated to the previously determined optimum temperature, a series of standards was run, and a standard curve was made. From this standard curve a relationship between absorbance and grams of pure metal was determined and the amount needed to give a one percent absorbance was calculated. The assumption that all of the sample is in the heater tube at a given moment is necessary for this type of sensitivity determination. If this assumption is not valid, absolute sensitivity will be greater than that determined by this method. However, even if the assumption is not valid, the value determined by this method is useful. This method gives the amount of pure metal in grams that will make a change in absorbance of one percent in the linear range of the standard curve for the element. The results of this are shown in Table 1.

These results were compared with the values reported by Stone[15] on the large Woodriff furnace (Table 2). All were found to be lower for this furnace. This decrease is not necessarily due to the smaller furnace size, as variations in sensitivity greater than this have been observed among the larger furnaces. The same furnace may show differing sensitivity when the heater tube is replaced. Each Woodriff furnace that has been built has been of a slightly different design from the previous models, with each design having slightly different characteristics. If there was a large furnace of the same design as this furnace

Table 1

Sensitivity Data with 7.7mm I.D. Heater Tube

Element	Wavelength (nm)	Temperature (^{o}C)	Sensitivity (g)
Ag	328.1	2000	2.2×10^{-12}
	338.1	2000	3.5×10^{-12}
Al	309.2	2300	6.2×10^{-11}
Au	242.8	2200	1.2×10^{-11}
Cd	326.1	1750	2.0×10^{-10}
Cu	324.8	2300	2.5×10^{-10}

Table 2

Sensitivity Data for Large Woodriff Furnace

Element	Wavelength (nm)	Temperature (^{o}C)	Sensitivity (g)
Ag	328.1	1750	1.0×10^{-12}
	338.3	1750	1.5×10^{-12}
Al	309.2	2200	5.0×10^{-11}
Au	242.8	2200	5.1×10^{-12}
Cd	228.8	1500	1.0×10^{-13}
	326.1	1500	1.0×10^{-10}
Cr	359.4	2300	1.5×10^{-11}
Cu	324.8	2200	2.5×10^{-11}
	327.4	2200	5.2×10^{-11}
Fe	248.4	2400	5.0×10^{-11}
Mn	279.4	2200	6.0×10^{-13}
	270.1	2200	2.0×10^{-12}
	403.1	2200	3.0×10^{-11}
Ni	232.0	2350	5.0×10^{-10}
Pb	217.0	1750	2.0×10^{-12}
	283.3	1750	4.3×10^{-12}
Zn	213.9	1500	8.0×10^{-14}
	307.6	1500	1.0×10^{-9}

Table 3

Sensitivity Data with 3.9mm I.D. Heater Tube

Element	Wavelength (nm)	Temperature (°C)	Sensitivity(g)
Ag	328.1	2000	9.4×10^{-13}
	338.1	2000	1.7×10^{-12}
Al	309.2	2300	2.7×10^{-11}
Au	242.8	2200	6.3×10^{-12}
Cd	326.1	1750	9.8×10^{-11}
Cr	359.4	2300	7.1×10^{-9}
Cu	324.8	2300	4.0×10^{-11}
Fe	248.4	2300	8.5×10^{-10}
Mn	280.1	2300	3.1×10^{-12}
	403.1	2300	3.1×10^{-11}
Ni	232.0	2300	2.6×10^{-10}
Pb	217.6	1750	9.9×10^{-13}
	283.3	1750	7.6×10^{-12}
Zn	307.6	1850	1.5×10^{-9}

a comparison could be made fairly easily, with a minimum of variables. Since there isn't such a furnace available to make a direct comparison, one cannot attribute the loss of sensitivity to any given factor. According to theory[4], the length of the heater tube should have no effect upon sensitivity. In spite of this, its sensitivity is different and needs to be improved to get results comparable to those of Stone.[15]

In order to overcome the lower sensitivity observed, a smaller diameter heater tube was made for this furnace. The new heater tube was made from a graphite rod 0.64 cm in diameter and drilled out to an inside diameter of 0.39 cm, making the cross-sectional area considerably smaller. According to theory,[4] a decrease in cross-sectional area should give an increase in sensitivity. This smaller diameter heater tube is able to work in this furnace, but not in the larger ones. In the larger furnaces the light emitted by the hollow cathode cannot travel the length of the narrow tube without decrease in intensity due to furnace light. In this furnace the path length is only one half that in the larger furnaces and thus a greater percentage of the light passes through. Use of a smaller diameter heater tube necessitated making a new center piece and modification of the heater tube holder to hold this smaller heater tube. A smaller center piece was needed to keep from significantly cooling the center of the tube. The new center piece was made of 0.95 cm diameter graphite 2.6 cm long with a hole drilled 0.32 cm diameter and a taper on the outer end. A hole 0.65 cm in diameter was machined near the other end to fit the heater tube. Smaller cups were

made from 0.318 cm diameter graphite rod to fit into this center piece. If the center piece had been made compatible with the old cups, the mass of the center of the heater tube would have changed considerably when the sample was introduced. The smaller cups hold thirty microliters as opposed to one-hundred and ten microliters for the larger ones. Reducing the volume could, in certain cases, make a difference in the ability to analyze a low concentration sample directly. In the old cups a larger sample can be used, allowing a sample of lower concentration to be measured. Also more care must be taken when drying the samples as air can be entrapped in the smaller cup, which might force the sample out when heated. The heater tube holders were modified by taking a piece of graphite rod 0.95 cm diameter and 1.6 cm long and rilled out to an inside diameter of 0.64 cm. These cylinders were then placed inside the present heater tube holders and the heater tube fitted into them. The uniformity of the heater tube temperature was checked and two graphite washers were placed on it as in the previous heater tube to obtain a fairly uniform temperature.

The optimum temperature study was repeated, using this heater tube, and the optimum temperatures were found to be essentially the same as with the larger heater tube. Standard curves were made and the sensitivity of each of the aforementioned elements was measured. They were found to be considerably better and quite comparable with those found by Stone.[15] The number of elements under consideration was increased to include chromium, iron, manganese, nickel, lead and zinc. For each

of these elements the optimum temperature and sensitivity were determined. The results for all elements considered with this heater tube are shown in table 3.

This change in size of heater tube cross-section has made a significant improvement to the sensitivity as predicted; however, the effect that this change has on the power consumption of the furnace should be considered. The power consumption of this furnace was measured for both large and small heater tubes (Table 4) and found to be comparable at high temperatures. At lower temperatures the smaller one has a lower power consumption. The power consumption of these two different sized heater tubes was then compared to the power consumption data compiled by Stone[15] on the large Woodriff furnace (Table 4). Here the power consumption was found to be dependent upon the size of heater tube used in the large furnace. Using a thin-walled heater tube, the large furnace had higher power consumption. Generally speaking, if both furnaces had heater tubes of the same diameter the large furnace would have a little lower power consumption.

This furnace, when equipped with a 0.64 cm diameter heater tube with small cups, appears to equal the large furnace in sensitivity, with power consumption depending upon the thickness of the heater tube used.

Perhaps the greatest advantage of the Woodriff furnace over the pulse-type atomizers is its resistance to matrix effects. The explanation commonly given for this phenomenon is that the heater tube is kept

Table 4

Approximate Power Consumption Data
for both Large and Small Furnaces

	Small Furnace					
	9.3mm O.D. x 7.7mm I.D.			6.4mm O.D. x 3.9mm I.D.		
T°C	Volts	Amps	Power (watts)	Volts	Amps	Power (watts)
1500	9.4	174	1650	10.8	110	1200
1600	9.8	182	1800	12.0	122	1450
1700	10.4	195	2100	15.0	130	1950
1800	11.1	214	2400	15.8	140	2200
1900	11.6	225	2600	16.4	150	2500
2000	12.0	240	2900	17.6	164	2900
2100	12.5	248	3100	18.4	170	3100
2200	13.0	270	3500	19.0	178	3400
2300	13.5	285	3850	20.5	190	3900

Large Furnace

	7.3mm I.D.	5.9mm I.D.
T°C	Power (watts)	Power (watts)
1800	1080	2520
2200	2400	4800

at a constant temperature during the measurement, whereas in the pulse-type atomizers the temperature is rapidly changing. If this is indeed the case, then this furnace should also have this same resistance to matrix effects. A check was made for some well known interferences, to find the ability of this furnace to cope with them.

Several researchers[15,16,17,18] have observed significant interferences due to the presence of chlorides. Chloride solutions were made up as sodium chloride, calcium chloride, and as magnesium chloride. The effect of each of these on nickel at 232.0 mm was measured at a furnace temperature of 2300°C. Several different concentrations of chloride were used. Each sample was run several times recording the absorbance of the nickel hollow cathode and then several more times recording the background absorbance of the hydrogen lamp. The peak area must be measured in both cases as the chloride comes off first as a sharp spike and then the nickel peak comes off as a shoulder. If only the peak height method was used the appearance would be the nickel signal was totally eliminated by the chloride at high chloride concentrations. When the peak area method is employed the absorbance of the nickel is essentially the same with or without chloride. Data is shown in table 5.

This procedure was applied to manganese and as in the case of nickel no interference was observed. When this procedure was applied to cadmium a slight negative interference was found. The chloride

Table 5

Interference Measurement Data

g. Ni	g. NaCl	g. $CaCl_2$	Ni hollow cathode Abs	H_2 Abs	Corrected Abs
4×10^{-9}	---	---	0.097	---	0.097
4×10^{-9}	1×10^{-6}	---	0.089	---	0.089
4×10^{-9}	1×10^{-5}	---	0.108	.013	0.095
4×10^{-9}	2×10^{-5}	---	0.162	0.057	0.105
4×10^{-9}	---	1×10^{-6}	0.086	---	0.086
4×10^{-9}	---	3×10^{-5}	0.086	---	0.086
4×10^{-9}	---	2×10^{-5}	0.108	0.010	0.098

g. Mn	g. NaCl	g. $CaCl_2$	g. $MgCl_2$	Mn hollow cathode Abs	H_2 Abs	Corrected Abs
1.7×10^{-10}	---	---	---	0.196	---	0.196
1.7×10^{-10}	8.3×10^{-7}	---	---	0.196	---	0.196
1.7×10^{-10}	1.5×10^{-6}	---	---	0.229	0.022	0.207
1.7×10^{-10}	---	1.75×10^{-7}	---	0.261	0.044	0.217
1.7×10^{-10}	---	---	1.5×10^{-6}	0.240	0.444	0.196

g. Cd	g. $Cd+H^+$	g. NaCl	g. $NaCl+H^+$	g. $CaCl_2$	g. $CaCl_2+H^+$	Cd hollow cathode	H_2Abs	Cor. Abs
5×10^{-9}	---	---	---	---	---	0.278	---	0.278
5×10^{-9}	---	5×10^{-6}	---	---	---	0.167	---	0.167
5×10^{-9}	---	---	---	8.5×10^{-6}	---	0.138	---	0.138
---	5×10^{-9}	---	---	---	---	0.278	---	0.278
---	5×10^{-9}	---	5×10^{-6}	---	---	0.278	---	0.278
---	5×10^{-9}	---	---	---	8.5×10^{-6}	0.278	---	0.278

concentration was 8500 ng to 5 ng Cd. The addition of nitric or sulfuric acid to the solution removed the interference. The addition of acid to remove the interference has been observed by others[19], and is easily explained by the several mechanisms proposed for interferences.[10,11,12,13,14,20] The chloride combines with the acid to form HCL, which has a very low boiling point and is either removed in the drying process or in the very early stages in the furnace.

Another check for matrix effects was made using real samples. The real samples were fish muscle tissue which had been digested in distilled concentrated nitric acid, using a microwave oven. After digestion the samples were made up to a final concentration of approximately 50 percent nitric acid. These samples were then analyzed using either an air-acetylene flame or a carbon-rod atomizer, depending upon the concentration of the element in the sample. The results of these methods are shown in table 6, along with the results obtained using this furnace. In order to run lead on the carbon-rod atomizer, the standard addition method had to be applied, due to the interferences present. A comparison was made of results with this furnace, obtained by running the samples as is and by running them by standard addition, and the results showed that there was no significant difference in the results. Another observation on the analysis of nickel on the carbon rod atomizer was that the acid in the sample ate away the pyrolytic coating on the tube. As the pyrolytic coating is eaten away, the sensitivity of the nickel decreases. With constantly changing sensitivity it is harder to

Table 6

Comparison of Methods of Analysis
for Fish Tissue

Sample No.	Zn		Pb		Ni	
	Flame	Furnace	Carbon Rod*	Furnace	Carbon Rod**	Furnace
1	4.0	4.2	0.02	.02	0.98	0.94
2	3.6	3.7	0.09	.03	0.69	1.58
3	4.3	4.5	0.05	.04	1.90	0.89
4	3.3	3.2	0.06	.04	18.95	3.13
5	4.0	3.9	0.12	.11	1.92	3.80
6	4.1	4.6	0.01	.01	1.88	1.20
7	3.3	6.4	0.09	.04	2.68	1.70
8	4.6	4.9	0.05	.04	20.39	25.23
9	3.9	4.1	0.03	.04	1.29	1.99
10	3.7	5.8	0.07	.04	2.21	3.92

*Standard addition method used

**Ternary digest

All solutions were from a nitric acid digest unless otherwise noted.

All results are in ppm.

calculate results than with constant sensitivity. With this furnace the sample was dried before it got near the heater tube and no pyrolytic coating was on the heater tube for the acid to eat away. Thus the sensitivity was constant.

Another area in which the constant temperature furnaces have an advantage over pulse type atomizers is in the direct analysis of solid samples. The pulse type atomizers is in the direct analysis of solid samples. The pulse type atomizers are limited by the size of sample which they can handle. With the small sample size which they can handle, considerable error may be introduced. To obtain a uniform sample one needs to use a fairly large sample or digest a large sample and make a solution to be subsequently analyzed. The constant temperature Woodriff furnaces, including the smaller model (using the larger diameter heater tube), can handle a fairly large solid sample, thus making the analysis of solid samples a reality.

One problem encountered in the analysis of solid samples is that of silicates sticking to the walls of the sample cup. This has been handled in one of two ways: the first is to ignore the silicates and the second is to mix powdered graphite with the sample. In the first case one is assuming that there is no effect upon subsequent analysis by the silicates. This may or may not be the case. The second requires totally uniform mixing of the graphite with the sample to get an accurate weighing of the sample. Also a better background correction system is necessary for this to compensate for the silicates leaving via

the optical path. A new method[21] has been developed in conjunction with this thesis. For this method, a cone of powdered graphite is made in the bottom of the graphite sample cup before the addition of the sample. After atomization the silicates are poured from the cup and the cup is ready for the next sample.

Generally speaking, the needs of this small furnace are similar to those of the large Woodriff furnaces. The amount of argon necessary to operate the furnace is less with a shorter flush time and a lower flow rate during operation. At high temperatures, a slightly higher flow is needed to keep the cooling jacket cool. This small furnace has a much faster cool-down rate than the large furnaces, enabling repairs to be made sooner after operating the furnace, without fear of damaging still usable graphite parts by exposing them to air while still hot. The rapid cool-down along with the shorter flush time allows for a considerably shorter down time for the replacement of a burned out heater tube. In one instance, the heater tube of this furnace burned out at 2300^{o}C and within 45 minutes the heater tube was removed, a new one made, the furnace was flushed with argon, and started heating up. With the larger furnaces the heater tube would still be too hot to handle! The down time for the large furnaces has been greatly reduced in the suitcase models over the previous models; however, they still cannot compete with this short a down time. Less graphite is needed to construct this furnace than the large furnaces and thus parts are less expensive.

CONCLUSION

The four major graphite atomizers were briefly discussed and each has been classified as either a constant temperature furnace or a pulse type atomizer. The constant temperature furnaces have several advantages over the pulse type atomizers; however, they have the disadvantages of being large and complex.

A small constant temperature furnace, modeled after a Woodriff furnace has been built, tested, refined, and found to have the same good sensitivity and resistance to matrix effects observed with the Woodriff furnace without drastically increasing the power consumption. This small furnace can be mounted in commercially available instruments with very few modifications necessary. This furnace has advantages over the larger Woodriff furnace in terms of size, ease of replacement of parts, reduced amount of down time, and reduced amount of argon necessary. The large Woodriff furnace has advantages in terms of decreased amount of water necessary for cooling, decreased power necessary for operation (in some cases), and in the amount of use and research which has gone into its present state.

It is hoped that this work will lead the instrument manufacturers to take a long serious look at the constant temperature furnaces and begin production so that the constant temperature furnaces are also commercially available to the chemists of the world to use.

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