



Design, operation and optimization of an atomic absorption spectrometer with a constant temperature furnace

by Frederic Garland Dewalt

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry

Montana State University

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Abstract:

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Changing internal graphite part dimensions inside electrothermal atomizers results in changing the temperature profile of the absorption tubes which may alter sample signals. Effects of changing these parts in a constant temperature furnace is discussed. Effects of changing some other operational parameters such as argon flow and sample insertion rate are also discussed.

A temperature controlled annealing oven for glasswork is presented as an aid for preparation of analytical glassware.

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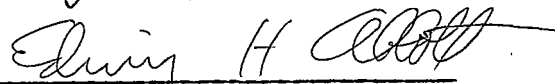
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ABSTRACT

An examination has been made of problems associated with early constant temperature designs. This information is applied to producing continually better constant temperature furnaces.

A simple electronic system which corrects for both broad band absorption and broad band emission is presented.

Changing internal graphite part dimensions inside electrothermal atomizers results in changing the temperature profile of the absorption tubes which may alter sample signals. Effects of changing these parts in a constant temperature furnace is discussed. Effects of changing some other operational parameters such as argon flow and sample insertion rate are also discussed.

A temperature controlled annealing oven for glasswork is presented as an aid for preparation of analytical glassware.

CHAPTER 1

General Atomic Absorption

1.1 Brief Introduction

Atomic absorption spectroscopy has come a long way since Kirchhoff and Bunsen first established this type of light absorption in a series of papers published in the 1860's (1-4). Advantages of atomic absorption for chemical analysis were not fully recognized until the independent publications of Walsh (5) and of Alkemade and Milatz (6,7) appeared in 1955. Some of the first reported applications of this technique by Allan (8) and David (9) used an air-acetylene flame to determine magnesium and zinc in plants. After introduction of the nitrous oxide-acetylene flame by Willis (10) in 1965, rapid growth in atomic absorption methods occurred which replaced many classical chemical methods of analysis. Likewise, rapid growth in the development of atomic absorption spectrometer systems has occurred. Today atomic absorption spectrometers are fast and relatively inexpensive making atomic absorption analysis commonplace in many laboratories.

1.2 Fundamental Principles of Atomic Absorption Spectroscopy

All atomic absorption spectrometers contain four basic components used to measure the absorption of an atom cloud at a specific wavelength, i.e., a light source, an atomizer, a dispersion device

(monochromator) and a detector with some type of readout system. The spectrum of the element under study is emitted by the light source. The atom cloud, produced from a sample placed in the atomizer, absorbs a portion of the radiation coming from the light source. The portion of the radiation observed is selected by use of the dispersion device which allows a narrow band width of the spectrum to strike the detector. The detector "sees" an attenuation of the light coming from the light source when an absorbing sample is in the optical path, i.e., in the atomizer. This attenuation of light is governed by Lambert-Beers law

$$A = \log \frac{I_0}{I} = abc$$

where there exists a linear relationship between the absorbance (A) and the concentration (c) of the element. Both the absorptivity (a) and the absorption path length (b) are constants.

1.3 General Spectrometer Design

1.3.1 Light Sources

Most atomic absorption spectrometers employ hollow cathode lamps (HCLs) for light sources. The cathode is a hollowed out cylinder constructed entirely or in part of the metal whose spectrum is to be produced. The anode and cathode are sealed in a glass envelope filled with either neon or argon. When an electrical potential is applied across the anode and cathode, a sputtering process occurs. The

spectrum of the cathode material is thus produced. Some of the more volatile elements make poor hollow cathode lamps. Electrodeless discharge lamps (EDLs) are sometimes used for these elements. EDLs are made by sealing a small amount of the element or salt of the element inside a quartz bulb with an inert gas. Excitation of the element is accomplished by ionization of the inert gas with an external RF field. Both HCLs and EDLs usually have quartz end windows to emit radiation in the ultra violet region of the spectrum.

1.3.2 Monochrometers

Many types of monochromators have been designed and used utilizing prisms or gratings as dispersion devices. Great advances in grating manufacture in recent years have produced extremely good monochromators with no coma and no astigmatism capable of very narrow band widths. However, too narrow a band width can result in inaccurate background correction using continuum lamp type correction as will be discussed in Chapter 3.

Atomic absorption light sources have simple spectra, unlike atomic emission where spectral emission lines are numerous, thus in most cases average quality monochromators can be used equally as well as the more expensive high resolution types.

1.3.3 Detectors

Photomultiplier tubes are the most often used detectors for atomic

absorption. Photodiode arrays have been used in multichannel detector systems (11), but these are less sensitive than photomultipliers in the UV region and have limited response linearity. Readouts for the photomultiplier signals have greatly advanced along with the recent advances made in the field of electronics. Early readouts consisted of simple transmittance and absorbance calibrated meters. Today's modern instruments store and process detector information with various data handling schemes, some using microprocessor control. These recent major advances in electronics have helped reduce errors associated with data handling far below errors originating in other areas of the spectrometer.

1.3.4 Atomizers

1.3.4.1 Brief Introduction

Most errors involved with analysis by atomic absorption originate in the atomizer. Many of these errors are chemical in nature and atomizer design can greatly affect the analysis of real samples by altering the chemical reactions taking place inside the atomizer. There are two major classes of atomizers commonly used in atomic absorption analysis; flames and electrothermal atomizers.

1.3.4.2 Flames

Atomization by flames is the most commonly used technique for producing an atom cloud. The great appeal of this type of atomizer

stems from its simple and inexpensive design. Flame type atomizers can be operated by personnel with minimal training making it the choice for routine trace metal analysis by most laboratories. However, flames have a great many disadvantages. The disadvantages have been well documented (12-17) and have been discussed by Stone (18) and Lundberg (19). Even with all its disadvantages, flames will continue to be popular since many samples can successfully and inexpensively be analyzed with this method.

1.3.4.3 Electrothermal Atomizers

Most commercially available electrothermal atomizers are of the pulsed-heated type. These atomizers produce greater absolute sensitivities and correspondingly lower limits of detection than flame atomization. This is due to confining the atoms in a small volume within the optical path. These pulsed-heated type atomizers are very popular and are used in many laboratories for trace metal analysis. However, most of these atomizers suffer from various matrix interferences mainly due to the sample experiencing rapidly changing temperatures during atomization. An excellent review of the problems associated with these types of atomizers is given by Lawson (20). Success at eliminating matrix interferences from lead determinations in steel using a pulsed-heated type carbon rod atomizer was achieved by Lundberg and Frech (21). They eliminated matrix interferences by

introducing the samples after the atomizer reached its final temperature. Operation of an atomizer under isothermal conditions thus can greatly improve analysis. Although major manufacturers of commercial atomizers have yet to build and sell such an isothermal device for routine analyses, Woodriff has been using homemade constant temperature furnaces for about 15 years.

Woodriff's atomizer is relatively free from matrix interferences which plague many of the commercially available pulsed-heated electrothermal atomizers (22,23). This atomizer has several other important advantages which will be discussed in the following chapter. The main disadvantages stem from its complexity and expense. Advances in the design and understanding of the constant temperature furnace, as will be discussed in the following chapters, have helped to make it a more easily manipulated atomic absorption instrument for routine analysis. Hope remains, from work presented in this thesis, that commercial manufacturers of pulsed-heated electrothermal atomizers will take the initiative to develop and sell constant temperature atomizers for accurate direct analysis of samples with difficult matrices.

CHAPTER 2

Designs and Operation of Constant Temperature Furnaces

2.1 Introduction

Two different constant temperature furnaces were developed independently for use in Atomic Absorption. One type was developed by L'vov (17,24,25) in Russia. In L'vov's system, the atomizer and five or six samples on the end of carbon rods are placed in an evacuated chamber. Argon is introduced until the desired pressure (up to 8 or 9 atm.) is reached. Next, the atomization tube is heated to constant temperature. The carbon rod containing the dried sample is next inserted into a hole in the bottom side of the atomizer tube and is heated by auxiliary power atomizing the sample.

Woodriff (26) first reported his constant temperature furnace in 1966. The Woodriff furnace atomizer, with a much longer heater tube than L'vov's, operates at atmospheric pressure. The longer tube compensates for shorter analyte residence times at atmospheric pressure compared to L'vov's higher operating pressures. Operating the atomizer at atmospheric pressure allows direct introduction of samples from the outside without power interruption, depressurizing or re-loading sample rods as required by L'vov's design

once the limited number of samples contained inside the chamber have been atomized.

2.2 History of Woodriff Furnace Design

2.2.1 Introduction

The furnace design was constantly improved following its introduction in 1966 (26) through a total of ten different models. Each successive model provided new insights or improvements. With only a few exceptions (27), the internal resistive heating elements of the Woodriff furnace are made from graphite. The best graphite our research group uses for this purpose is Poco graphite (28) grade AFX-50. This is a very hard, easily machined graphite with low porosity. Insulation for these furnaces is generally made using 6 mm thick graphite felt from Union Carbide Corporation (29).

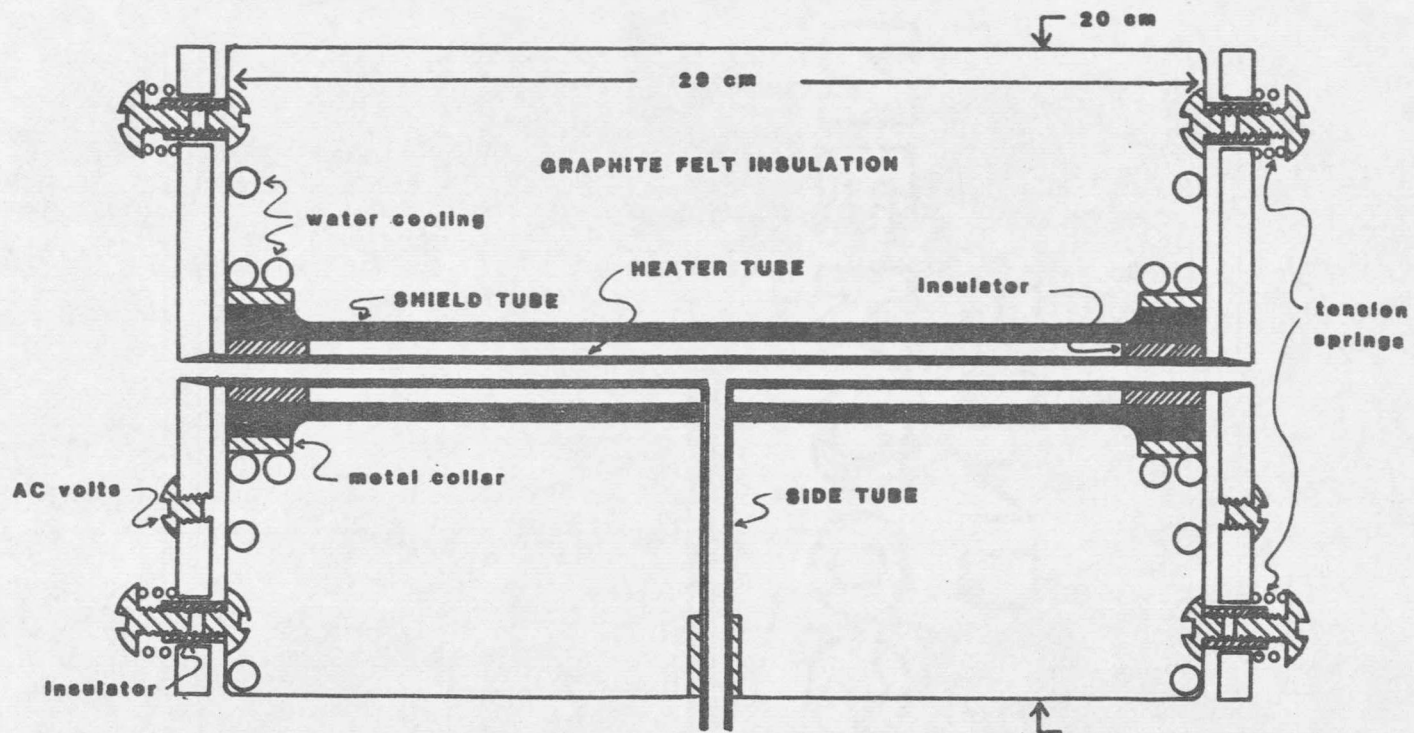
2.2.2 Single Phase Furnaces

The first furnace model (26,30) used a central graphite tube, 8 mm O.D. by 6 mm I.D., for the resistive heating element. This tube was surrounded by other concentric graphite tubes and graphite felt insulation, all housed inside a steel cylinder. Argon enters the furnace at a side tube connecting the center of the heater tube with the outside of the furnace. Samples are inserted and atomized on low conductivity rods pushed through the side tube until contact is made with the "hot" heater tube. Although good preliminary data was

gathered with this model, it had drawbacks. The heater tube was open to the air on the ends causing rapid deterioration. Inefficient cooling caused this model to become excessively hot, making handling difficult. Its rigid design did not allow for heater tube expansion causing frequent tube breakage.

The second model (Figure 1), first introduced by Woodruff and Ramelow in 1968 (31), solved the problem of tube breakage. Graphite plates mounted on spring loaded bolts held heater tube ends allowing for expansion as well as providing good electrical contact at high temperatures. Improved cooling was achieved by forcing water through copper tubing brazed to the housing of the furnace. Rapid deterioration of heater tube ends continued to plague this model due to back diffusion of oxygen into the atomizer.

Woodruff, et. al. (32,33) designed another model, which provided even more efficient cooling for easier handling. This third model used a metal, water cooled, spring loaded, electrical connector to hold the heater tube ends. This model also contained a massive "tee" connector connecting the side tube to the heater tube. The massive "tee" connector increased the heat capacity of the central part of the heater tube decreasing sample atomization time. These design changes, although they improved the operation of the furnace, also caused some



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Figure 1. Cross-sectional view of constant temperature furnace, Model 2.

detrimental effects. More efficient cooling of the heater tube end connectors caused excessive cooling of the tube ends. Deposition of sample vapor on to the tube ends thus became a problem. A massive tee connector in the center gave a similar effect. A larger center has less resistance and thus a lower voltage drop than adjacent furnace parts. This including the larger surface area allowing increased radiative heat loss, results in a lower temperature. The side tube also contributes by conducting heat away from the center to the furnace housing. Thus a cold spot is produced at the point of sample introduction. Variation in heater tube temperature profile as a sample vapor travels down the tube might possibly lead to some matrix interferences. Analyte residence times can change if temperature gradients are large enough. The ultimate goal is to design a system with a uniform temperature profile down the heater tube. Such a system is extremely difficult to build while still providing proper cooling of the electrical connections as well as keeping the furnace itself cool enough for an operator to handle.

The fourth model (34,35) was the first design allowing the heater tube ends to be sealed inside the water cooled steel shell (see Figure 2). The tube ends were held with a spiral heater tube contact. This contact was constructed by coiling up copper tubing in a flat coil spiralling into the center to a graphite disk drilled to fit the heater

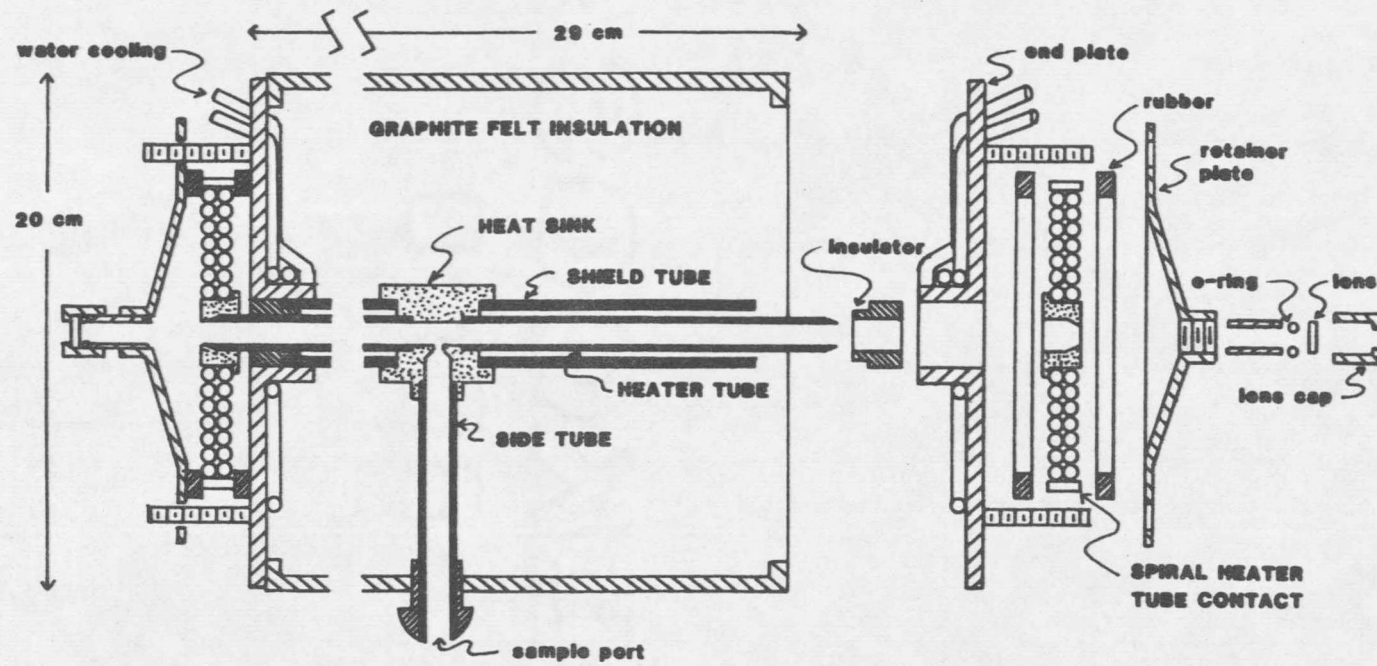


Figure 2. Cross-sectional view of constant temperature furnace, Model 4.

tube end. The copper tubing is then spiraled back out to the outside of the coil. This contact allowed for water cooling, electrical connection and was also springy enough to allow for graphite expansion. Its flat design allowed it to be squeezed between two plates and thus sealed on to a cylinder to form an airtight housing for the heater tube. Argon was introduced just inside the sample port at the end of the side tube. When the sample port is opened to insert a sample, argon flows out of the port washing oxygen off the sample. When the sample port is closed, argon flushes through the furnace and exits through a port made in each spiral heater tube contact. Both heater tube and shield tube in this model were made in two halves in order to simplify construction (shorter tubes are easier to drill from rod stock).

A number of studies (36-40) used the fifth model partially diagramed in Figure 3. It had two distinct differences from the previous design. The side tube wall, next to its connection with the shield tube, was made very thin, reducing heat conduction away from the center of the heater tube. Water cooling of the furnace housing was greatly improved by constructing it from a double jacketed stainless steel shell.

A single simple design change of the fifth model produced a new design with significant improvements over previous models. The sixth

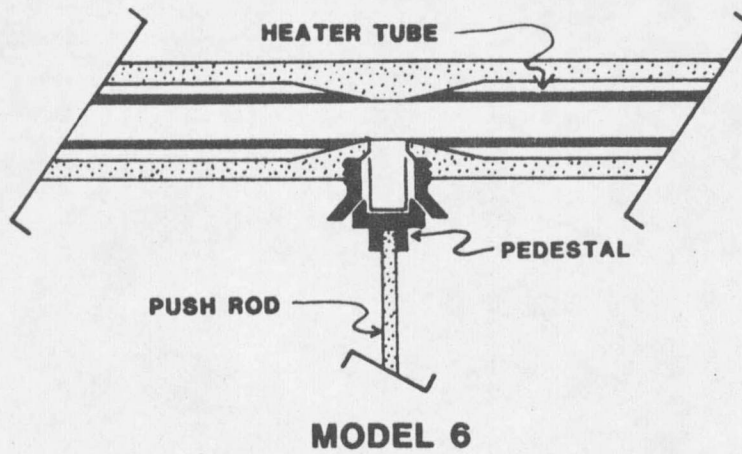
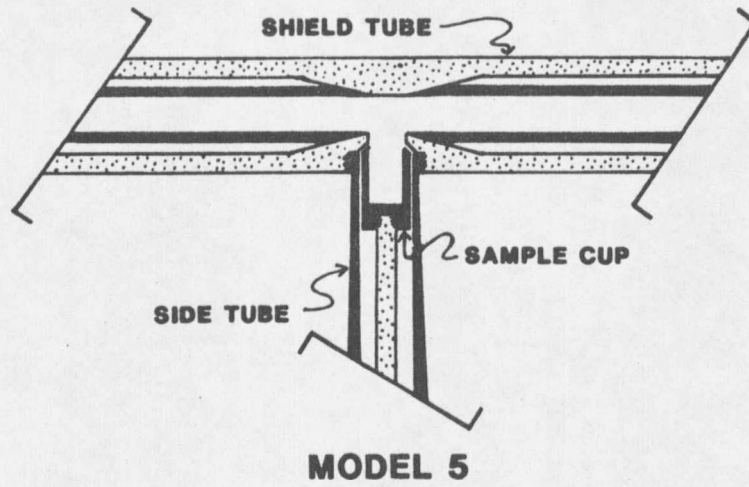


Figure 3. Cross-sectional view of center sections of constant temperature furnace, Models 5 and 6.

model was made by substituting a very small bell shaped entrance port for the side tube as indicated in Figure 3 (41). Existence of a side tube not only conducts heat away from the center of the heater tube, but can also cause contamination problems. As sample cups are inserted into the side tube, some of the sample material can transfer onto the side tube to be later re-transferred onto different sample cups. The result is sample loss in some cases and sample contamination in others. Removal of the side tube eliminated this problem (18). Unfortunately, however, removal of the side tube also eliminated the ability to direct nebulized samples into the heater tube (18,30,31,33-35). Previous to this model, sample introduction was accomplished by either nebulization or by sample placement in a graphite crucible. These graphite crucibles were manufactured with a threaded bottom for attachment to a thin graphite push rod. Upon insertion through the side tube, the rim of the crucible made a seal with a constriction at the top of the side tube. When using this technique with uncoated crucibles, it was found that individual crucibles consistently gave slightly higher or lower sensitivity, depending on the seal they make with the atomization chamber and on the rate of diffusion through their walls (42). This problem was solved by placing the crucible on a pedestal which makes the seal rather than the crucible rim. This method was subsequently used in all future designs. A number of successful studies were done

utilizing this sixth model (23,41-44). A smaller version of this model was also designed and used for easy placement into commercial spectrophotometers (45).

This stage of advancement in design of these furnaces marks the end of development of the single phase furnaces. The term single phase represents the type of electrical powering used to heat the heater (or absorption) tube. Single phase furnaces are typically heated by utilizing single phase 220 volt AC power. This voltage is first dropped across an autotransformer for power control, then run through a ten to one step down transformer before attachment to the heater tube ends (Figure 4).

Single phase furnaces all have the disadvantage of possessing an uneven heater tube temperature profile. The necessity of sample placement at the center of the heater tube causes a cooler temperature at that point which cannot be overcome by single phase heating. For example, in the sixth model the center temperature is typically 60-100°C lower than adjacent parts while heater tube end temperatures can be 600 to 1000°C lower (see Figure 5). The tube end temperatures can be raised considerably by suspending them on posts, but raising the cooler center temperature was solved only by switching to three phase type heating.

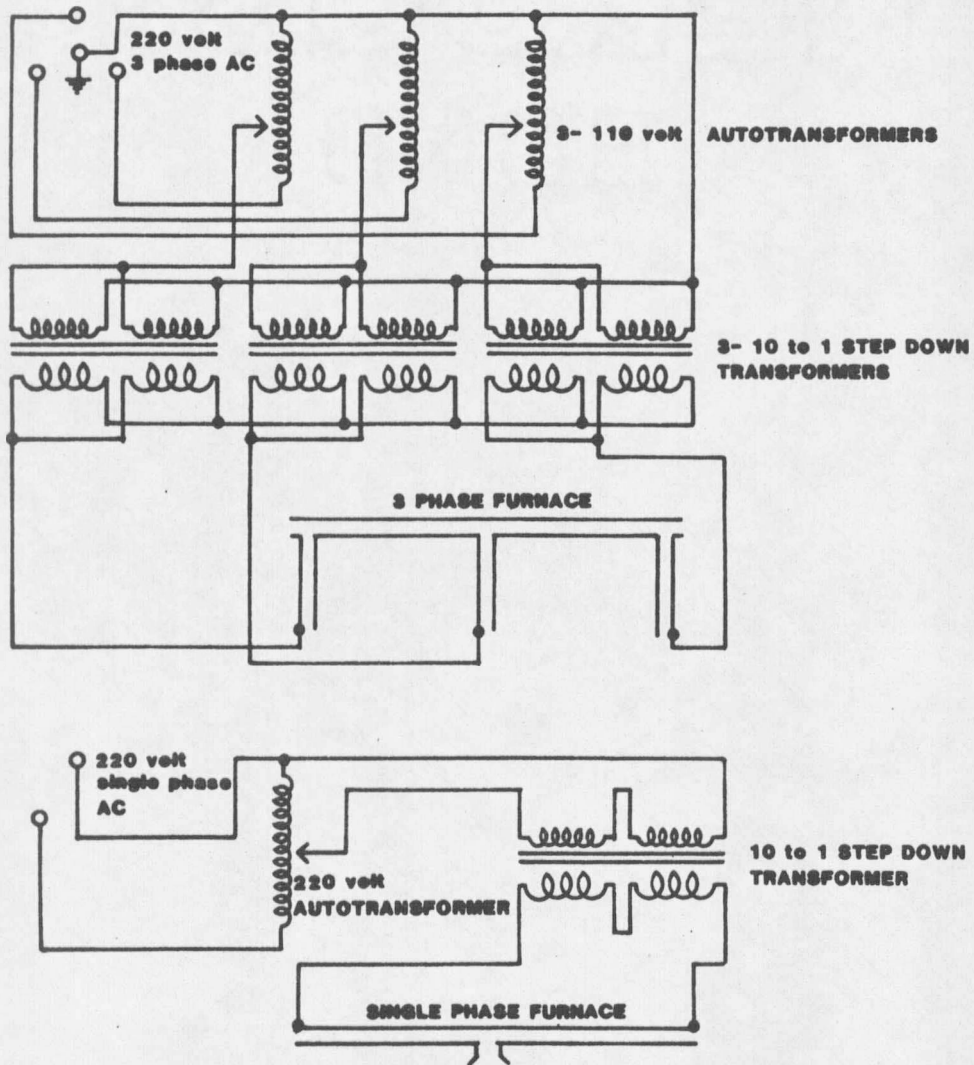


Figure 4. Wiring diagram for single phase and 3 phase furnaces.

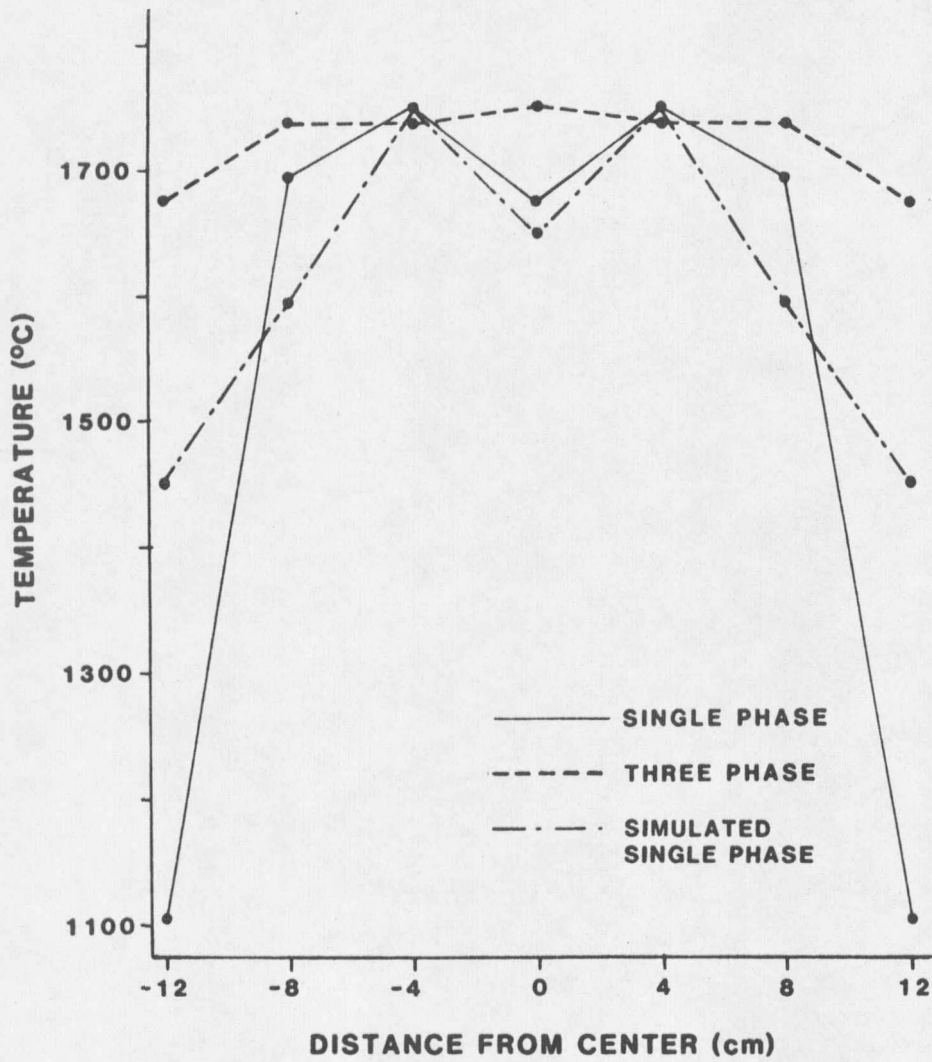


Figure 5. Temperature profiles of a single phase furnace (end held, Model 6), a three phase furnace (post held) and a simulated single phase profile inside a three phase furnace as discussed in Chapter 4.

2.2.3. Three phase furnaces

Three phase heating was first introduced by Woodriff (46) in 1976 and is subsequently used for powering all newer models (22, 47-53). Electrical hookup is accomplished by connecting each leg of the furnace (each side of the heater tube plus the side tube) to different phases of a 220 volt three phase AC power source by way of an autotransformer and step down transformer (Figure 4). The effect of such an arrangement can be easily understood by use of the simplified current flow diagram shown in Figure 6. When the left side of the heater tube (point 1) is at its most positive potential, the main current flow is from point 1 to both the right side of the heater tube (point 2) and the side tube (point 3). Likewise, later in time when the right side of the heater tube is at its most positive potential, the main current flow is to points 1 and 3. A similar situation occurs when the side tube is at its most positive potential. Considering only these three points in the complete three phase cycle, only four lines of current flow travel through each leg while six lines of current flow travel through the center "tee" connection. The result is that more current passes through the center than either of the three legs alone, causing the center to be the hottest part of the furnace. Marinkovic and Woodriff (49) showed that in order to minimize temperature decreases upon sample insertion, the tube connection should be made as massive as

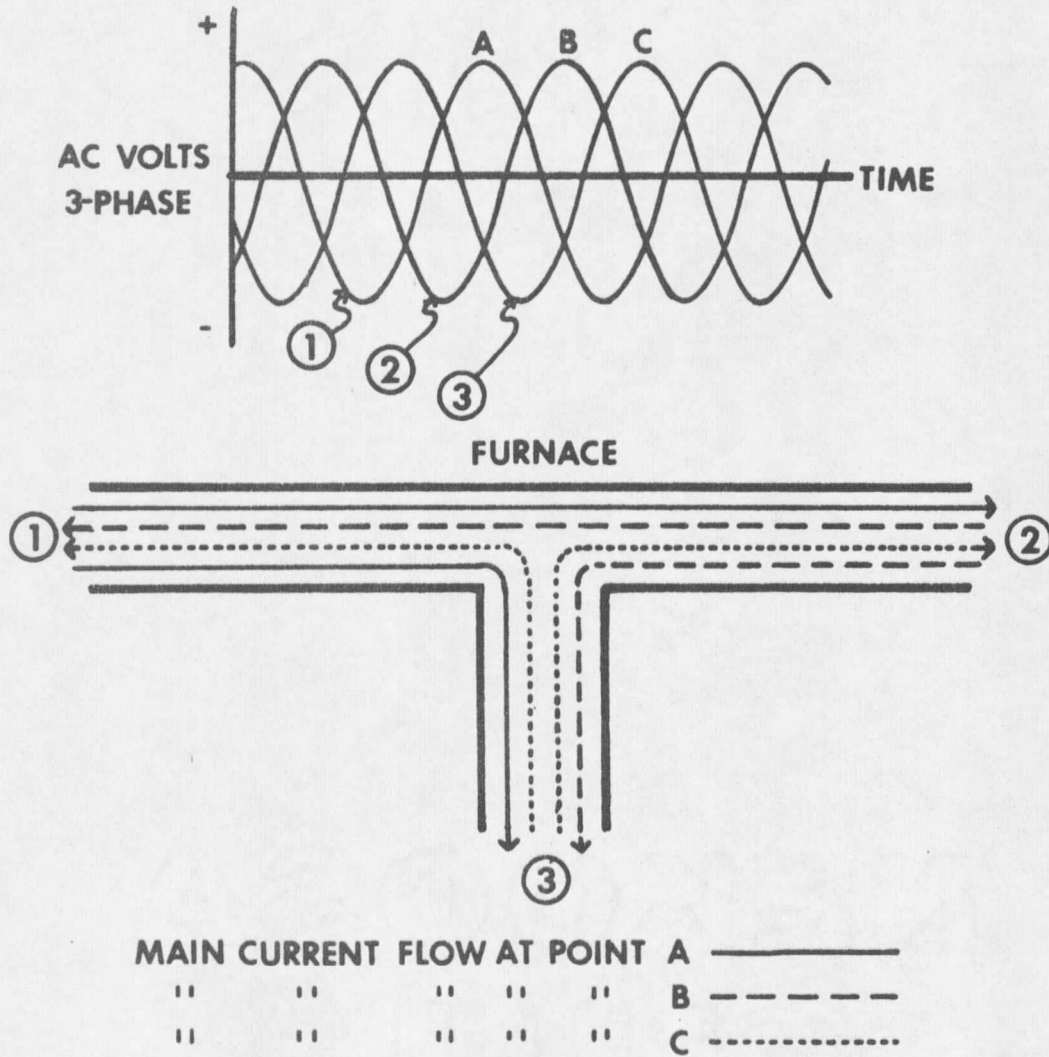


Figure 6. Simplified current flow diagram for 3 phase type heating in a constant temperature furnace.

possible. Since massive tube connections have less resistance than adjacent parts, more current flow through this connection is necessary to keep it from having a lower temperature than other parts of the tube. The much cooler heater tube end temperatures were raised in the newer three phase models by suspending the heater tube ends on graphite posts (50,53).

Near uniform temperatures can be achieved by utilizing the independent power control on each leg of a three phase furnace as shown in Figure 5.

An advanced three phase furnace is shown in Figure 7. Examination of its design will show some additional improvements over single phase models. All early single phase models possessed a guard or shield tube which surrounded the heater tube. The original purpose for this piece was to maintain optical stability, help insulate the heater tube, and keep graphite felt from contacting and thus shorting out the heater tube. This part was later found to be unnecessary. Good graphite felt insulation alone provided adequate insulating ability. This insulation can be easily cut and placed so that minimal contact with internal parts are made. If slippage of felt causing some heater tube contact does occur, the felt quickly burns back. This is probably due to its inability to maintain the high currents used to power the furnace. Optical stability of the heater tubes is maintained due to the side

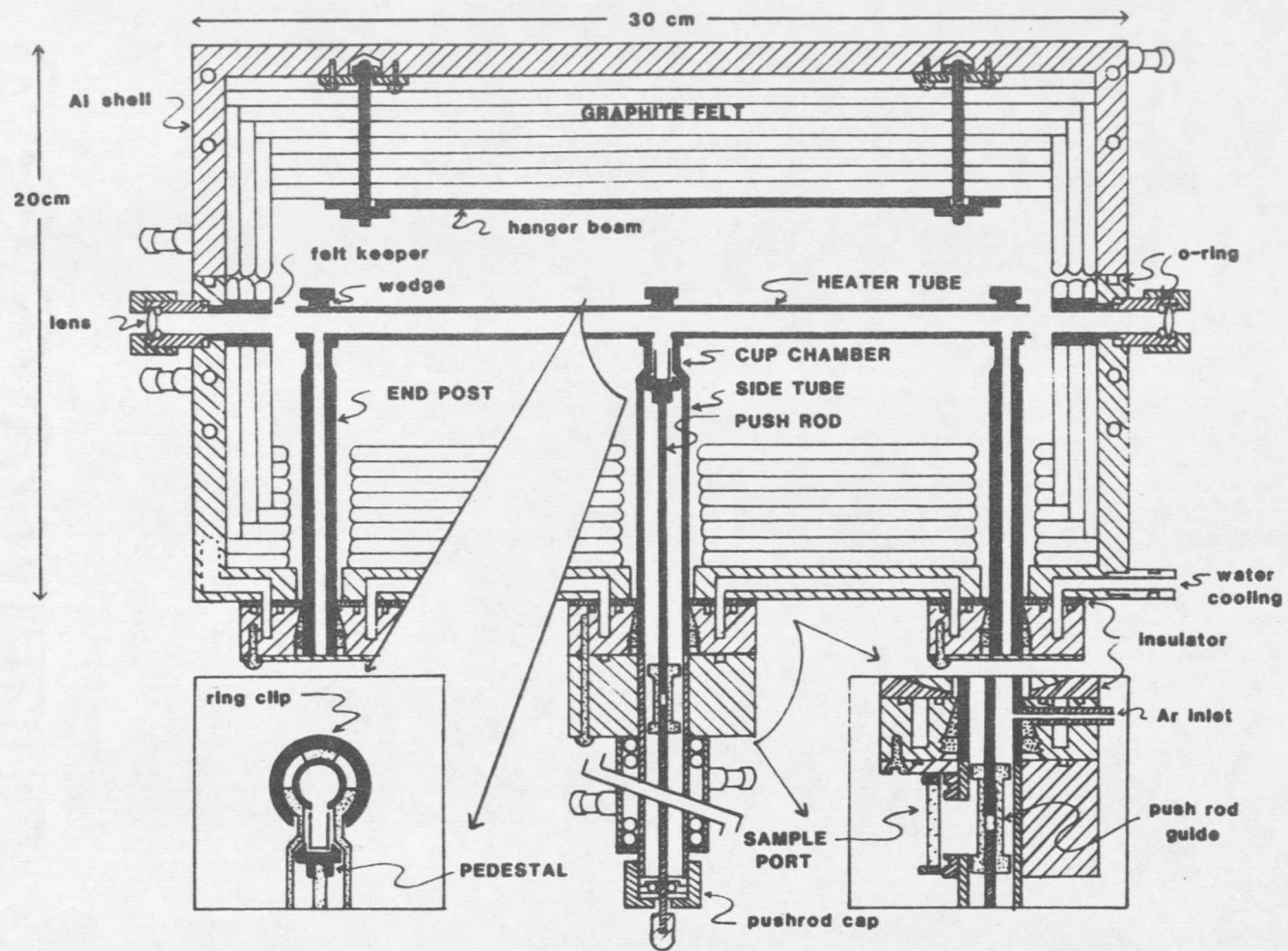


Figure 7. Cross-sectional view of a modern 3 phase constant temperature furnace.

tube being held rigidly against the pressure of the pedestal while samples are inserted. The housing surrounding the furnace was changed from a double-walled stainless steel construction to a 13 mm thick aluminum shell. This aluminum shell is drilled in such a way as to allow water to circulate throughout its interior (50). The superior conductivity of aluminum helps keep this shell cool to the touch even at internal temperatures exceeding 2500°C. The shell is cut horizontally, producing a suitcase type opening furnace for easy access to the interior parts. Previous models had end plates which had to be removed, disturbing the optical alignment, for access to the interior (46).

Three phase powering introduced new problems. At temperatures exceeding 2100°C, vertical expansion of the graphite posts becomes significant. This necessitates the alignment of the cold furnace in such a way as to compensate for thermal expansion. O-rings used to seal lenses in the furnace burned away due to the increased radiation caused by increasing the temperature on heater tube ends of post held furnaces. This problem is generally compensated for by a combination of shielding and water cooling the lens caps. Three phase powering requires addition of the side tube which re-establishes the problem of side tube contamination. However, recent studies indicate that if the side tube is made large enough to eliminate pedestal contact as samples

are inserted, this contamination problem does not occur. Physically connecting the heater tube to the two graphite end posts and side tube is difficult with post type furnaces. Heater tube contact with the end posts must be tight or arcing will occur. Connection to the side tube is more difficult than end posts because it must be manufactured tight enough to hold in sample vapor as it diffuses into the heater tube. Some of the connectors used for heater tube connection are shown in Figure 8. The one on the far right, the most recent, is easy to build but suffers from expansion effects. It holds the heater tube down on well fitting surfaces machined in the posts by pushing in a wedge which distorts the clip, putting pressure on the heater tube. As the heater tube is powered, expansion of all parts including this clip occurs. After 2100°C expansion of this clip tends to become permanent. After the heater tube is cooled the clip stays expanded, causing it to become loose and arcing may occur. Larger and larger wedges must be fitted each time the furnace is heated over 2100°C. The problem was partially remedied by making these clips more massive. Increasing the mass of these clips by three times results in only a 40°C decrease in temperature at those points where they are attached to the heater tube. These increases in mass allow the clips to be reused about three or four times above 2100°C before larger wedges are required. Other connectors using a screw type tightener also tend to suffer from

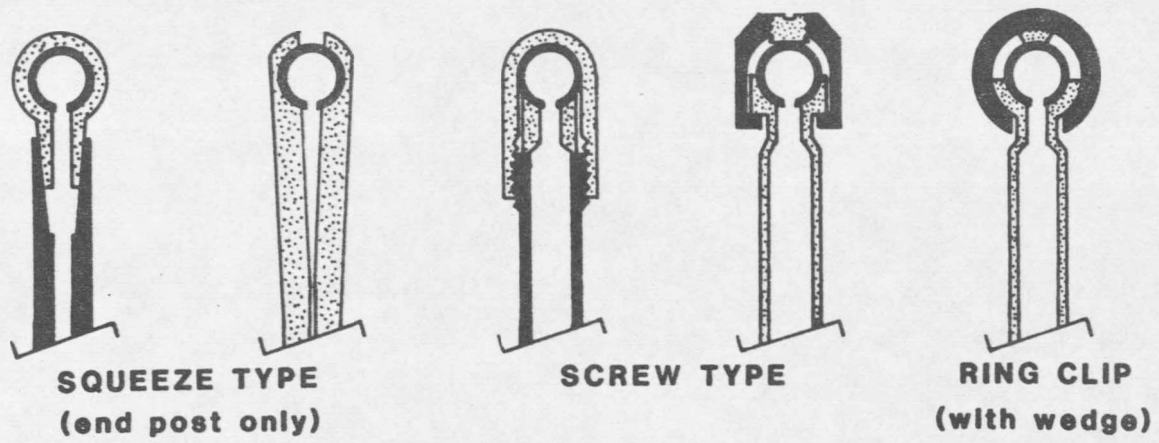


Figure 8. Cross-sectional view of graphite heater tube connectors used to hold heater tube on post type furnaces.

hysteresis. Repeated tightening of the graphite screw is a necessary operation. The end post connector shown on the far left does not suffer from expansion problems. Design of heater tube attachment is continuing.

2.2.4. Sample introduction systems

Sample introduction to these constant temperature furnaces is difficult. For a three phase powered system, the sample introduction system must: be electrically insulated from the shell, make a tight rigid contact with the side tube, keep oxygen out, stay cool to the touch, keep sample contamination at a minimum, and be easy to manipulate. The sample introduction system shown with the three phase furnace in Figure 7 is the most advanced at the time of this writing. The largest problem is cooling. When a sample is atomized, the pedestal and crucible are at furnace temperature. Lowering the hot pedestal for sample removal transfers heat to the sample port. This heat must be removed to keep the sample port from becoming too hot to handle. The pedestal must be lowered slowly to prevent the sample port window from shattering. Higher atomizer temperatures require slower sample removal rates. This limits sample cup removal time from the atomizer to about 30 sec at 2400°C. Argon is introduced into the furnace slightly above the sample port. As in earlier furnace models, argon flows out the sample window, washing oxygen off the sample

crucible when the sample is inserted. The pedestal is kept from touching the inside of the side tube, thus eliminating contamination problems as previously discussed by restricting the horizontal movement of the pushrod with a pushrod guide as shown on Figure 7.

A completely new type of sample introduction system is presently being constructed using a circular insertion motion (Figure 9). Such a system easily lends itself to automation which would be difficult with previous sample introduction systems. Work is continuing.

2.3 Operating parameters

2.3.1. Atomizer temperature

Stone (18) reported that there was a minimum furnace temperature above which a maximum absorption was observed. Above that temperature the absorption remained relatively constant. Ramelow (30) reported that above the maximum temperature the absorbance gradually decreases. Neither of these reports appears entirely correct. Studies shown in Chapter 4 indicate a more complicated picture. From this data, peak height absorbances for the 283.3 nm Pb line do appear to approach a constant absorbance at increasing temperatures, but above the value reported by Stone. A detailed account of the effect of temperature on absorbance is given in Chapter 4.

Emission from the furnace can be large at higher atomizing temperatures (particularly at longer wavelengths). The resulting

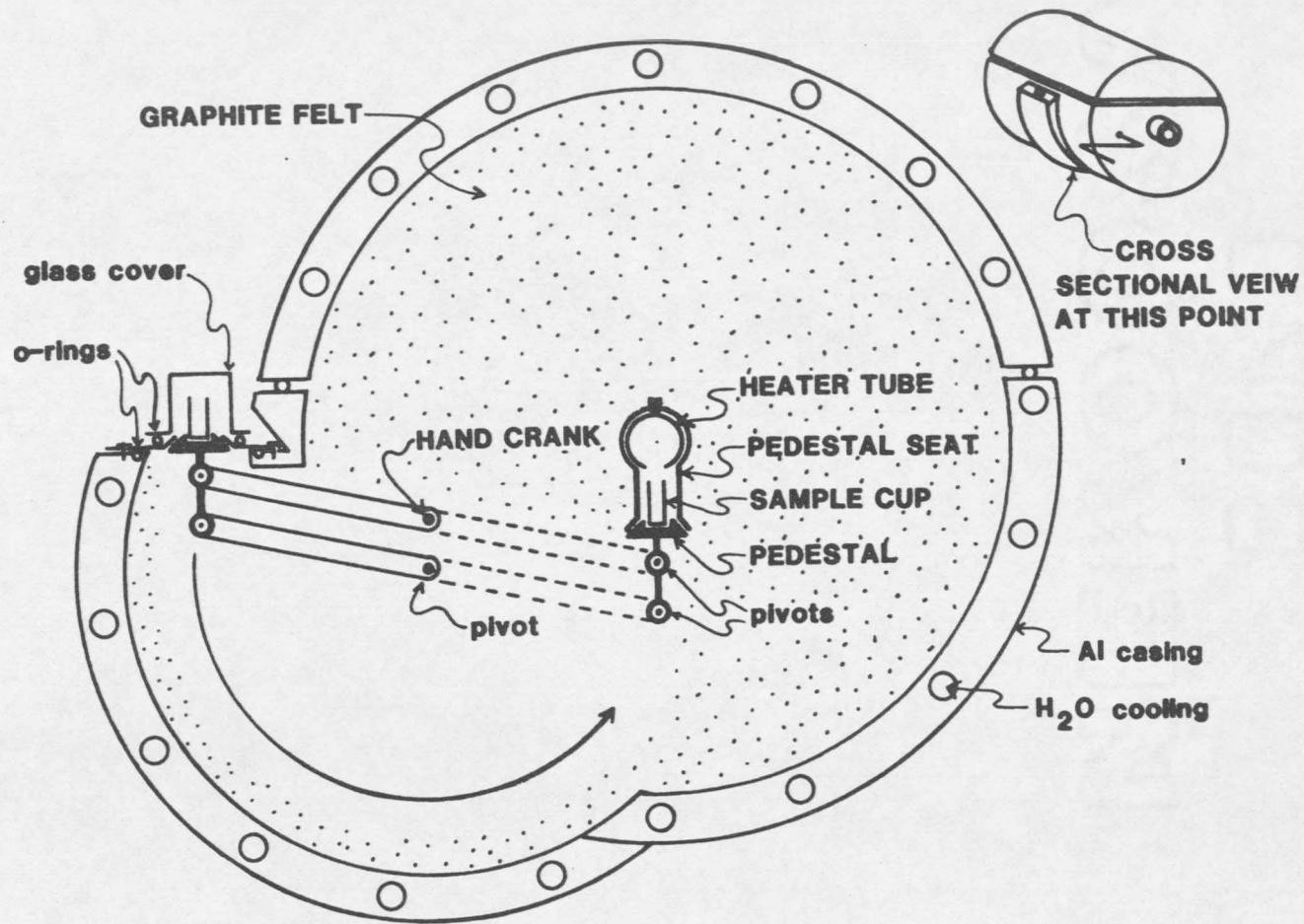


Figure 9. Cross-section view of a newly proposed furnace using a circular motion sample introduction system.

signal generated at the photomultiplier tube may create problems in absorbance computations (54,55). This furnace emission is reduced by shielding the monochromator slit with a cover plate containing a small hole. Moving the slit away from the furnace slightly greater than the focal length of the furnace lens, combined with the use of the cover plate, can bring furnace emission signals down to a manageable level (see Figure 10). The remainder of the furnace emission signal can be corrected for electronically (54,56).

2.3.2 Argon flow

The furnace is flushed with approximately three times its internal volume to assure oxygen concentrations low enough to minimize graphite part deterioration.

Early studies using peak height (18) showed that argon flow rates through the furnace had little effect on absorption signals. However, recent work using both peak height and peak area measurements show that argon flow rates do effect absorption signals. These effects are discussed in Chapter 4.

2.3.3. Sample preparation

Due to the lack of major matrix interferences in constant temperature furnaces, little sample preparation is necessary. Problems are encountered when the sample produces more background absorption than is correctable by typical background correction methods. When

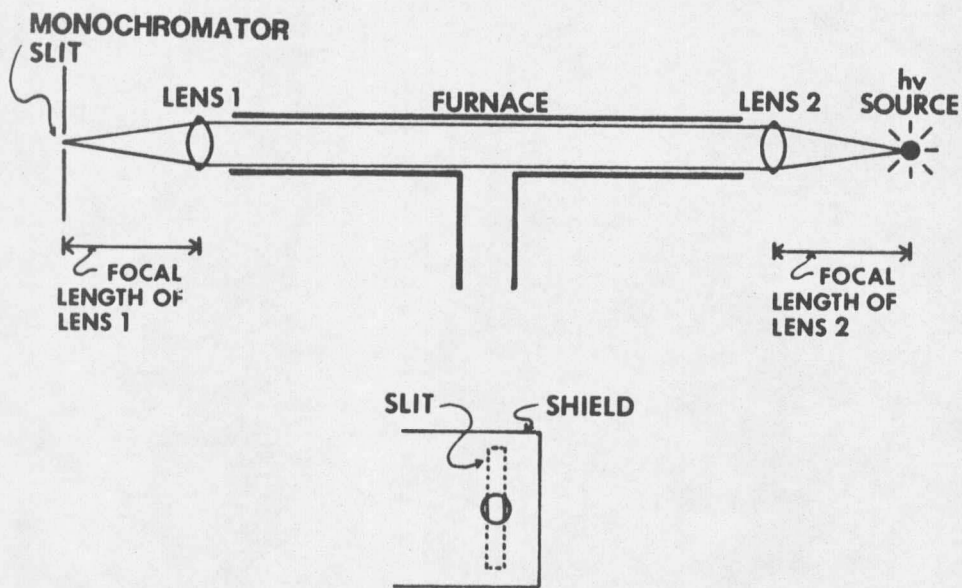


Figure 10. Diagram of the focusing system used on constant temperature furnaces. To minimize furnace emission entering the monochromator slit, the slit should be shielded as shown and the distance between lens 1 and the slit should be slightly larger than the focal length of lens 1 (too large a distance will result in decreased $h\nu$ from the light source).

this happens, acid digestion or ashing is useful. Many times this is done in the graphite crucibles themselves although it greatly reduces their useable life. Another method of background reduction is to place the sample in a closed cup (52).

The three types of crucibles used in these furnaces are shown in Figure 11. The open cup crucible is generally made from hard graphite. Some open cups made from soft porous graphite are used as filters for air particulates (38), liquids (53,57), as well as gold plated for use as filters for mercury analysis (39). The closed cup used for background reduction has a porous graphite cap. Closed cups with porous bottoms have been used unsuccessfully with liquid samples. Memory effects were found on clean cups placed in racks previously occupied by cups with porous graphite bottoms. This was caused by leakage through the cup's bottoms. Another closed cup made of molybdenum or platinum was used for high temperature vapor pressure studies (51). The tapered top on this vapor pressure cell makes the seal with the seat rather than the pedestal. This assures that only atoms escaping from the orifice in the top and not through the threads will enter the atomizer tube for correct vapor pressure determinations.

Solid samples are weighed into cups prior to insertion into the furnace. Liquid samples are pipetted into cups and dried under an infrared lamp before atomization. Many samples can be dried or ashed

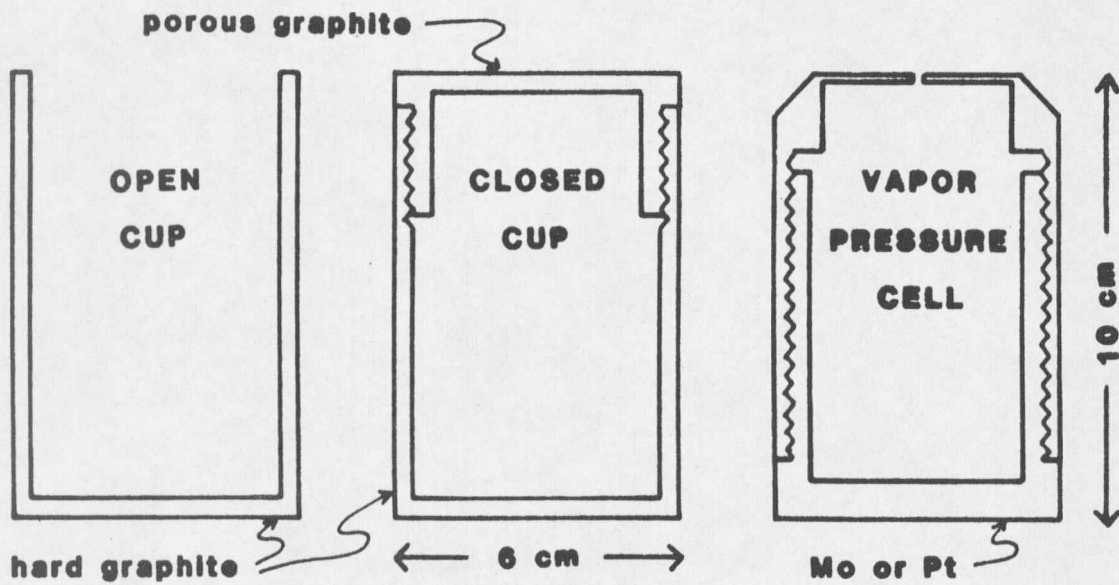


Figure 11. Types of sample crucibles used in constant temperature furnaces.

simultaneously without tying up the furnace for these routine operations.

Work described in Chapter 4 shows that differences in signals are obtained when samples are inserted into the furnace at different rates. If samples are inserted into the furnace too slowly, some atomization occurs before the pedestal mates with the seat. Samples should be inserted at a fast and steady rate to obtain the best results.

2.3.4. Sensitivity

Woodriff previously discussed absolute and relative sensitivity as it applies to tube-type atomizers (42). Absolute sensitivity, which varies inversely with the cross-sectional area of the atomizer tube, tells nothing about the sample capacity of the atomizer as a means of obtaining greater accuracy.

Chemists are often more interested in relative sensitivity: the grams of substance detectable per gram of sample. The applicability of relative sensitivity is limited because it depends on the nature of the matrix. However, it better expresses the usefulness of the device for real samples. The relative sensitivity of an atomizer, which is independent of the cross-sectional area of the tube, is directly proportional to the length of the tube. When using peak area instead of peak height (which can reduce some errors caused by matrix

materials), the relative sensitivity increases with the cube of the path length of the atomizer.

These constant temperature furnaces sometimes have greater and sometimes less absolute sensitivity than commercial pulsed atomizers depending on the element analyzed. However, their relative sensitivity is much greater due to the combination of increased path length and the ability to handle larger sample sizes. A typical graphite crucible can easily accommodate up to 200 μ l of liquid or 200 mg of solid sample. Larger crucibles capable of larger sample sizes are also applicable.

Absolute sensitivity data for some elements introduced as solid samples into these furnaces are shown in Table 1. Most of this data was taken on a single phase furnace by Stone (18). Although better temperature control and better atomizer design using three phase furnaces may slightly improve these reported values, in most cases these numbers have been found to be equally applicable to the newer three phase furnaces.

Table 1. Absolute Sensitivity Data for the Woodruff Furnace.

Element	Furnace Temp (C)	Wavelength (nm)	Sensitivity (1% Absorption) (gm)
Al	2200	309.2	5×10^{-11}
Ag	1750	328.1	1×10^{-12}
		338.3	1.5×10^{-12}
Au	2200	242.8	5.1×10^{-12}
As	2200	193.7	2.5×10^{-11}
B	2300	249.8	8×10^{-7}
Be	2350	234.9	1×10^{-12}
Ca	2300	422.7	1×10^{-12}
		228.8	9×10^{-15}
Cd	1500	326.1	1×10^{-10}
		240.7	2×10^{-11}
Co	2400	240.7	2×10^{-11}
Cr	2300	359.4	1.5×10^{-10}
Cu	2200	324.8	2.5×10^{-11}
		327.4	5.2×10^{-11}
Dy	2200	421.2	8×10^{-11}
Er	2200	400.8	7×10^{-11}
Fe	2400	248.4	5×10^{-11}
Hg	900	253.7	3.6×10^{-11}
Ho	2200	410.4	7×10^{-11}
		285.2	1×10^{-12}
Mg	2300	285.2	1×10^{-12}
		279.4	6×10^{-13}
Mn	2200	280.1	2×10^{-12}
		403.1	3×10^{-11}
Ni	2350	232.0	5×10^{-10}
		217.0	2×10^{-12}
Pb	1750	217.0	2×10^{-12}
		283.3	1×10^{-11}
Sb	2100	217.6	1×10^{-11}
Se	2100	196.0	6×10^{-11}
Zn	1500	213.9	8×10^{-14}
		307.6	1×10^{-9}

CHAPTER 3

Supporting Electronics for the Constant Temperature Furnace

3.1 Introduction

Earlier detailed studies of the constant temperature furnace was stifled by poor supporting electronics and electronic data handling. These earlier constant temperature furnace systems were often put together with mismatched and poorly maintained electronic equipment which added to atomic absorption measurement inaccuracies. Background correction was either non-existent or had to be hand calculated from simultaneous reference line tracings in a two channel monochromator system. A good stable electronic system was greatly needed for accurate studies using constant temperature furnaces. The following sections describe the design and operation of supporting electronics for constant temperature furnaces made from modern inexpensive integrated circuit chips.

3.2 A Stable Pulsed Hollow-Cathode Power Supply

3.2.1 Introduction

Optical choppers and rotating mirrors have traditionally been used to interrupt hollow-cathode light sources used in atomic absorption spectroscopy, and to switch between sample and reference light sources in background corrected systems. Commercial pulsed hollow-cathode

power supplies have been utilized for the same purpose. The power supply described in this section, however, is much less expensive and at least as stable as commercially available units (for example, the 0.0082% stability of this unit compares favorably with the 0.05% stability figure published for the Spectrogram corporation Model LPA-ID hollow-cathode power supply). This power supply consists of an unregulated 400 volt DC power supply and a programmable constant current regulator which drives a hollow-cathode or hydrogen lamp. The lamp is switched from a very low "idle" level to a high emission level by digital logic signals. Both "idle" and "on" levels for each channel are adjustable by front panel potentiometers. The power supply provides a high level of current regulation and emission stability ($\pm 0.0082\%$) with large changes (± 40 volts) in lamp supply voltage. The parts cost of the system is minimal - less than \$20.00 plus an unregulated 400 volt DC power supply. It may be used to replace the optical chopper or commercial pulsed hollow-cathode power supplies in conventional atomic absorption systems using lock-in amplifier data acquisition.

3.2.2 Circuit Description

The basic regulator circuit, sketched in Figure 12, may be understood by following its operation from the time the hollow-cathode lamp high voltage supply is turned on until the lamp current is

