



Development of a constant temperature, platinum, atomic absorption furnace and its use in potassium vapor pressure measurements for MHD
by Bruce Michael Watne

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:

Pyrolytically coated graphite, vitreous carbon, tantalum, tungsten and platinum were tried as heater tube materials in a long path-length, constant temperature, ambient pressure vaporization chamber for flameless atomic absorption. Used in trace elemental analysis, this instrument is commonly known as a Woodriff furnace. Difficulties encountered are described and suggestions for improvement made.

Results obtained with pyrolytically coated graphite, vitreous carbon, and platinum heater tubes are compared with those obtained with the graphite heater tubes in the conventional Woodriff furnace. Construction of the platinum furnace is outlined and suggestions for significant improvement are made. Analysis of cadmium standard solutions are shown as a typical analytical application. A study on the vaporization of potassium, important for the magnetohydrodynamics program, was done as a representative physical chemical application. Results of one sample of $K_2O \cdot 9Al_2O_3$ -alumina obtained as a standard from the National Bureau of Standards are shown to be history-dependent in that the sample must be heated to above $1000^\circ C$ before the $\gamma-Al_2O_3$ is converted to $\alpha-Al_2O_3$, a process which is necessary for the vapor pressures to be in agreement with those of the N.B.S. The enthalpies of vaporization of $K(g)$ and $O_2(g)$ from K_2O in β -alumina were obtained from the temperature dependence of the absorbance using the same sample and Knudsen cell in the platinum and graphite furnaces. The ΔH 's were found to be 36.1 kcal/mole in the graphite furnace and 102.6 kcal/mole in the platinum furnace. This compares with 98.2 kcal/mole obtained by the N.B.S. The large discrepancy between the result obtained in the graphite furnace and that from the N.B.S. indicates that another or a different process was occurring within the graphite furnace. In a study of the effects of oxidizing and reducing atmospheres on the potassium vapor pressure, no significant effects were found. It was found that water vapor has a large but reversible effect on the vapor pressure of potassium. It was concluded that the platinum furnace, limited only by its upper temperature limit and its cost, is a valuable supplement to the graphite furnace because it is usable in a wider variety of applications which include physical chemical as well as analytical studies.

DEVELOPMENT OF A CONSTANT TEMPERATURE, PLATINUM, ATOMIC
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VAPOR PRESSURE MEASUREMENTS FOR MHD

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BRUCE MICHAEL WATNE

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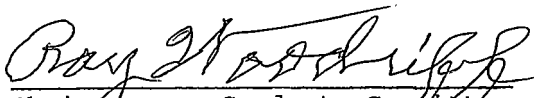
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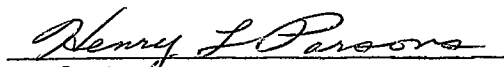
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ABSTRACT

Pyrolytically coated graphite, vitreous carbon, tantalum, tungsten and platinum were tried as heater tube materials in a long path-length, constant temperature, ambient pressure vaporization chamber for flameless atomic absorption. Used in trace elemental analysis, this instrument is commonly known as a Woodriff furnace. Difficulties encountered are described and suggestions for improvement made. Results obtained with pyrolytically coated graphite, vitreous carbon, and platinum heater tubes are compared with those obtained with the graphite heater tubes in the conventional Woodriff furnace. Construction of the platinum furnace is outlined and suggestions for significant improvement are made. Analysis of cadmium standard solutions are shown as a typical analytical application. A study on the vaporization of potassium, important for the magnetohydrodynamics program, was done as a representative physical chemical application. Results of one sample of $K_2O \cdot 9Al_2O_3$ -alumina obtained as a standard from the National Bureau of Standards are shown to be history-dependent in that the sample must be heated to above $1000^\circ C$ before the $\gamma-Al_2O_3$ is converted to $\alpha-Al_2O_3$, a process which is necessary for the vapor pressures to be in agreement with those of the N.B.S. The enthalpies of vaporization of $K(g)$ and $O_2(g)$ from K_2O in β -alumina were obtained from the temperature dependence of the absorbance using the same sample and Knudsen cell in the platinum and graphite furnaces. The ΔH 's were found to be 36.1 kcal/mole in the graphite furnace and 102.6 kcal/mole in the platinum furnace. This compares with 98.2 kcal/mole obtained by the N.B.S. The large discrepancy between the result obtained in the graphite furnace and that from the N.B.S. indicates that another or a different process was occurring within the graphite furnace. In a study of the effects of oxidizing and reducing atmospheres on the potassium vapor pressure, no significant effects were found. It was found that water vapor has a large but reversible effect on the vapor pressure of potassium. It was concluded that the platinum furnace, limited only by its upper temperature limit and its cost, is a valuable supplement to the graphite furnace because it is usable in a wider variety of applications which include physical chemical as well as analytical studies.

Chapter 1

INTRODUCTION

The Woodruff furnace is an ambient pressure, constant temperature, long pathlength sample vaporization chamber. It has been used primarily for trace elemental analysis by atomic absorption (AA) spectroscopy in place of a flame, and more recently for the high temperature equilibrium vapor pressure studies in association with the magnetohydrodynamics (MHD) project currently in progress in Montana State University.

The Woodruff furnace has a history dating from 1965 [1]. From 1965 to the present, more than 30 articles have been written and papers presented at scientific meetings detailing its construction, sensitivity and the wide variety of samples it is capable of analyzing [1-34]. Table 1 shows a comparison of sensitivities for selected elements by flame AA vs. AA in the Woodruff furnace.

All previous Woodruff furnaces have had their heater tubes and sample containers (called cups) made of graphite. Graphite is relatively inexpensive, fairly easy to machine, has good but not excellent electrical and thermal conductivity, excellent thermal shock resistance, and has an extremely high melting point (3367°C) [50], all of which make it an almost ideal material for this application. It does have a few limitations, however. One is rapid reaction at high temperatures with water, oxygen, and nitrogen, which eliminates the

Table 1. Furnace Method vs. Flame Method Sensitivities

Element	Furnace Temperature	Wave Length, Å	Nanograms for 1% Absorption	
			Furnace [6]	Flame*[47]
Ag	1265	3281	0.008	3.6
Al	1550	3092	0.2	76
Au	2150	2428	0.07	13
Ca	1200	4227	0.1	2.1
Cd	1200	2288	0.009	1.1
Co	2400	2407	0.11	6.6
Cr	2200	3579	0.08	5.5
Cu	1550	3247	0.09	4
Dy	2200	4212	0.1	74
Er	2200	4008	0.1	80
Fe	2200	2483	0.1	6.2
Hg	1050	2536	0.1	220
Ho	2200	4104	0.09	80
Li	1200	6708	0.01	1.7
Mg	1200	2852	0.08	0.3
Mn	1200	2795	0.08	2.4
Ni	2200	2320	0.2	6.6
Pb	1700	2833	0.01	2.3
Zn	1200	2138	0.007	0.9

* Assumes using 0.1 ml. Divide values by 100 to get µg/ml.

possibility of its use in an oxidizing atmosphere. A second limitation is the fact that it is porous to, and/or reacts with some of the elements to be analyzed.

It was the purpose of this thesis project to identify and evaluate other potential furnace materials, and to apply some of these alternate materials to problems not currently solvable with the present graphite Woodruff furnace.

Initial attempts to improve the furnace included pyrolytic coating of the graphite. It was found that pyrolytic coating reduces the porosity, increases the sensitivity and increases the lifetime of the heater tubes. Using vitreous carbon instead of graphite for the entire system should eliminate the porosity problem. It probably will not, however, eliminate the reactivity problem.

The use of platinum instead of graphite allows studies in oxidizing, neutral or reducing atmospheres, and measurement of the effect of water vapor on certain reactions, such as the $K + H_2O = KOH + 1/2H_2$ gas phase equilibrium.

Chapter 2

THE CONVENTIONAL WOODRIFF FURNACE

The Woodriff furnace in its most common form has a graphite atomizer (called the heater tube) which consists of an approximately 25 cm long graphite tube with a 6-8 mm inner diameter and a 1 mm wall thickness (see Figure 1). At the midpoint of this tube and perpendicular to it is another tube about 10 cm long with other dimensions the same. Together they form a "T". This perpendicular tube is called a "side tube." The sample, usually contained in a graphite cup on the end of a graphite rod, is introduced through the side tube. The cup is about 1.2 cm high with an outer diameter of 0.6 cm; it will hold approximately 100 microliters. The bottom of the cup may be threaded for a graphite rod, in which case the lip of the cup makes a seal such that the heater tube and the inside of the cup are one chamber, or the cup may sit on a "pedestal," in which case the entire cup is within the chamber (see Figure 2). The interior of the long tube is the absorption volume. Light from a hollow cathode lamp of the element to be analyzed passes down its length and is focused by one or more quartz lenses onto the entrance slit of a monochromator, which disperses the light into its component wavelengths. These are sensed by a photomultiplier tube, processed electronically and recorded on a strip chart recorder (see Figure 3). The heater tubes are surrounded by

Figure 1. Typical Woodruff Furnace with Graphite Heater Tubes

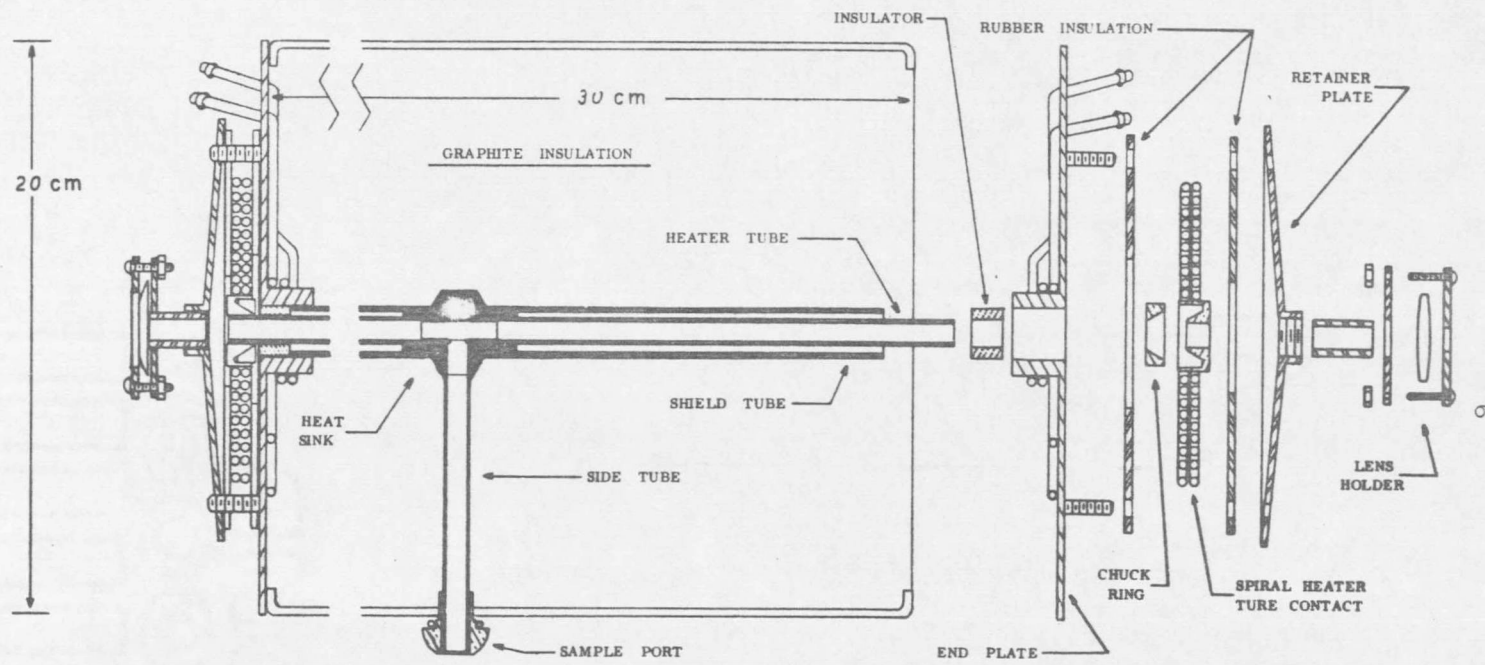


Figure 1 Furnace Model 2.

Figure 2. Side Loading with a Threaded Cup vs. Bottom Loading with a Pedestal

With the threaded cup, the lip of the cup makes a seal and only the inside of the cup is part of the absorption chamber. With the pedestal the diagonal side of the pedestal makes the seal hence the entire cup is within the absorption chamber. Powdered solids are conveniently loaded only from the bottom to avoid spilling the contents of the cup. Solutions are dried in either type of cup outside the furnace and can be loaded either way. Normally, a number of cups are prepared at one time and processed together. They are then run sequentially in the furnace. Each sample requires an average of about two minutes in the furnace. The pedestal using the bottom loading system is a little more awkward but a little more versatile. The simpler design of the cups for use with the pedestal reduces the cost and increases the availability of cups made from exotic materials such as iridium or vitreous carbon.

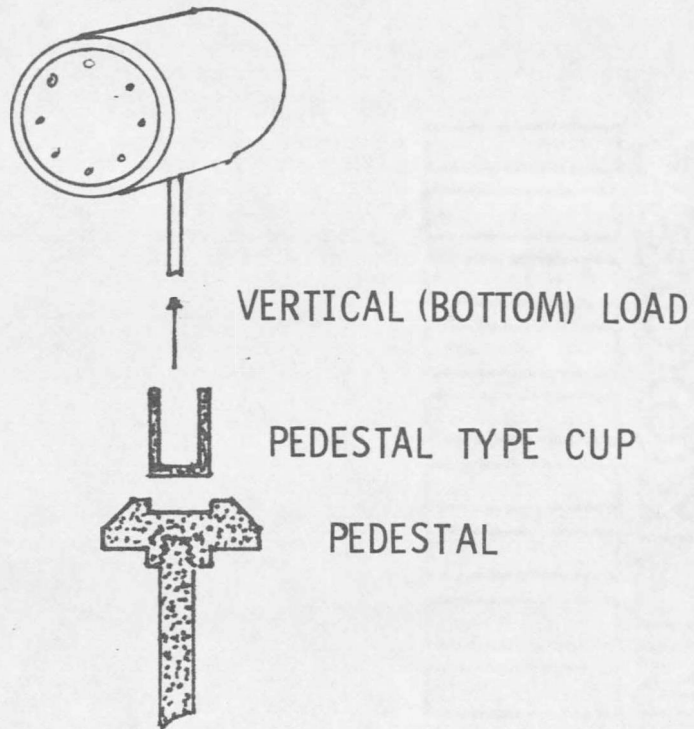
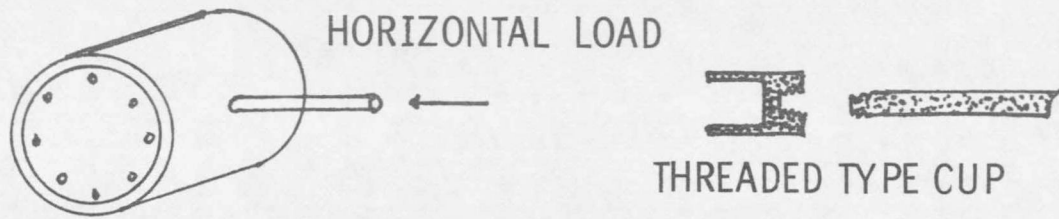
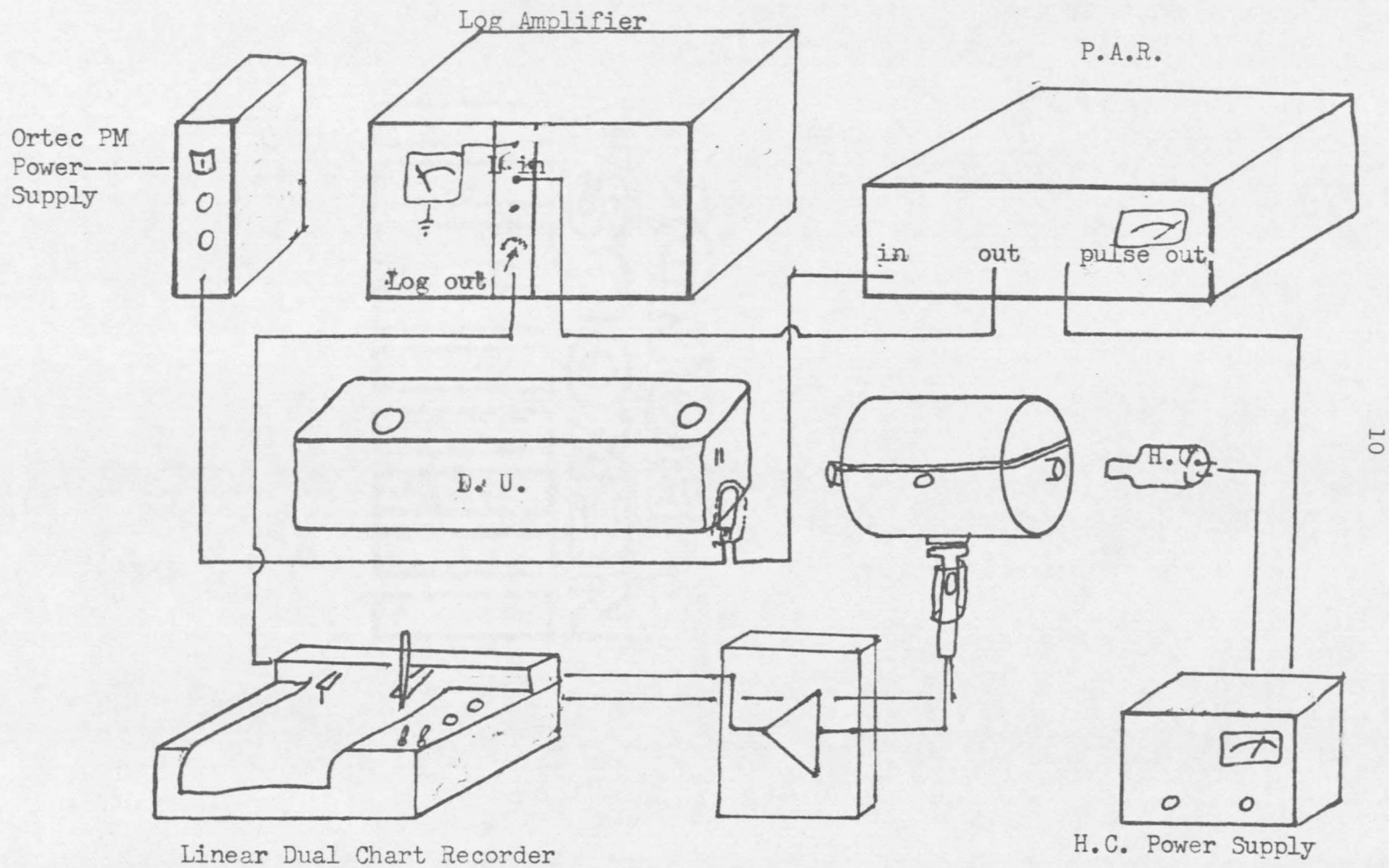


Figure 3. Sketch of the Entire System

Light from the hollow cathode (HC) goes through the furnace and is focused by lenses at both ends of the furnace onto the entrance slit of a Beckman DU monochromator onto an R955 photomultiplier (PM) tube. The PM tube is powered by an Ortec model 456 high voltage power supply running at -700 volts. The signal from the PM tube goes through the Princeton Applied Research (PAR) lock-in amplifier model JB-5. The d.c. output of the PAR amplifier is applied to the voltage (E) input of a logarithmic amplifier (see Figure 8). The output of the log amplifier is proportional to the absorbance and is recorded on the model 232 dual channel recorder. The PAR amplifier also pulses (at about 21 hz.) the Spectrogram dual lamp hollow cathode supply. The temperature is monitored independently with an optical pyrometer and with the potential of a platinum-10% rhodium vs. platinum-30% rhodium thermocouple. The thermocouple signal is amplified about ten times with a 741 operational amplifier and recorded on the lower channel of the chart recorder.



graphite felt insulation and encased in a water-cooled metal jacket with appropriate power lead-ins.

Each leg of the furnace (the side tube and each end of the heater tube is considered a leg) is heated via the two paralleled secondaries of one of three separate 10:1 step-down transformers. The sides of the secondaries not going to a leg of the furnace are connected together (in a star configuration, point S of Figure 4). Each transformer has two primaries and two secondaries on the same core. The primaries are connected in series and the secondaries are connected in parallel. Each set of primaries are connected to a separate Variac. The three Variacs are connected in a delta configuration. One leg of the three phase 220 volts alternating current (VAC) is connected to each apex of the delta.

The current in each leg is monitored by using the lead-in cable to that leg as the primary of a step-up transformer. The voltage of the secondary of this step-up transformer is read on an AC volt meter in series with a variable resistor for calibration (see Figure 5).

SOME PROBLEMS WITH THE GRAPHITE ATOMIZER IN THE WOODRIFF FURNACE

Graphite has certain characteristics which make it less than ideal for the construction of heater tubes. The graphite itself is porous to some materials [35], and with other elements such as

Figure 4. Electrical Power Circuit Diagram

220 volts a.c. three phase goes through three switches and then to the primaries of two Adjust-A-Volt type 1520B 230 volt input 2.4 KVA (9 amp), A, and one Staco type 5020-CT 240 volt 7.8 KVA (28 amp), C, auto transformer connected in a delta configuration. One 220 volt input and the slider from each autotransformer is connected to the primaries, B, of one of three General Electric 5 KVA buck/boost stepdown transformers type 9T21B1037 G2 which have two separate sets of 10:1 windings on the same core. The primaries of each transformer are connected in series, B, and the secondaries, G, are connected in parallel. One side of the secondary from each of the three G.E. transformers is connected to a common point, S, forming a star configuration. The other sides of the secondaries each go to one leg of the Woodriff furnace, W. Note that the heavier duty autotransformer goes to the side tube of the furnace since more current is needed at this point due to its shorter length, hence lower resistance.

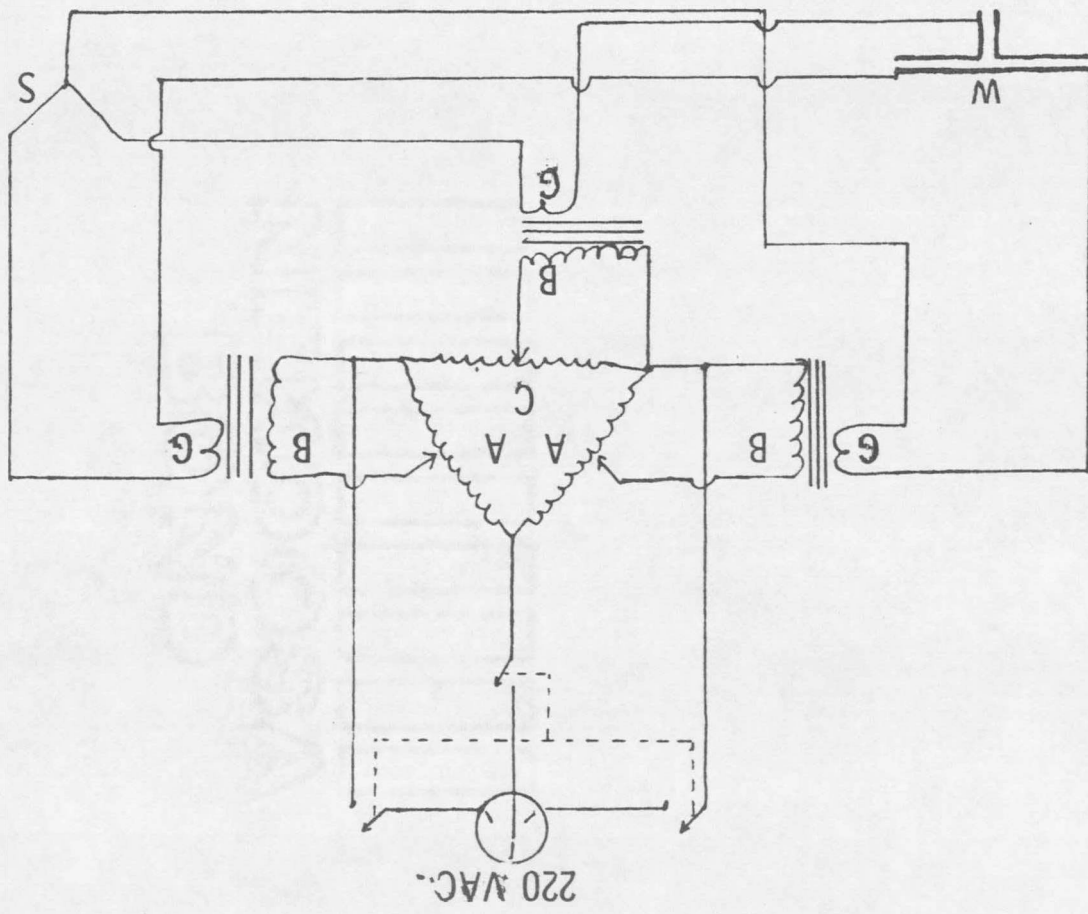
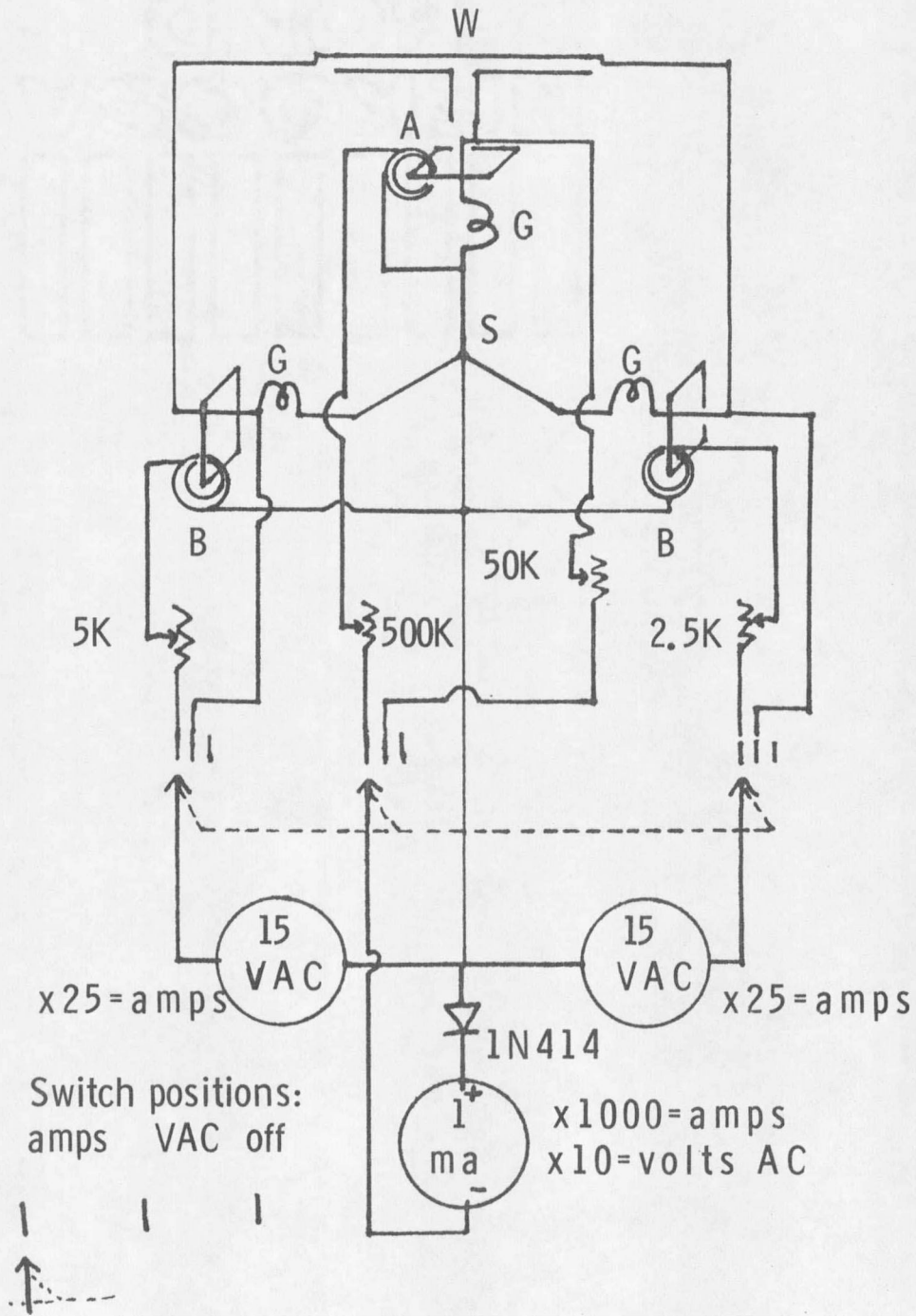


Figure 5. Current and Voltage Monitoring System

A and B are current-to-voltage transducers. They are made from a 110 to 6.3 volt filament transformer. The center laminated section of the transformer is cut out and the primary coil moved to an outside section of the laminations. The power cable to each leg of the furnace, W, is passed through the center of the laminations. The primary is connected in series with a variable resistance for purposes of calibration against a known current meter. Each variable resistor is in series with a switch which allows the selection of current monitoring or direct voltage monitoring. G in the figure represents the secondaries of the 10:1 stepdown transformers (see Figure 4). For the temperature to be uniform, the side-tube leg must have more current passing through it since it is shorter and hence its resistance is lower.



potassium and possibly copper it appears to react [31]. The graphite furnace is more than ten times less sensitive for copper than for silver, for no apparent reason (see Table 2). The sensitivity should be proportional to the oscillator strength.

Graphite can be used only with neutral or reducing atmospheres and at high temperatures the carbon of the graphite induces reducing conditions. It is unlikely for an atom of the sample to escape from the absorption volume without contacting the walls. The hot graphite is capable of reducing most species. Graphite reacts with water at high temperatures to form carbon monoxide and hydrogen. It reacts with oxygen to form mixtures of carbon monoxide and carbon dioxide, the higher temperature favors carbon monoxide [52]. It reacts with nitrogen at elevated temperatures to form cyanogen [53]. Air must therefore be excluded since even small amounts of air shorten the lifetime of the heater tubes considerably due to oxidation. Thus, oxidizing atmospheres of any kind are unusable. Graphite has a practical upper temperature limit of about 2400°C. Above this temperature the lifetimes of the heater tubes are considerably shortened. Actually, the lifetime of the tubes is inversely proportional to some unknown function of the temperature. Tubes can be run as high as 3000°C for short periods of time, but their lifetimes might be only an hour or so, compared to tens to hundreds of hours at 2000°C (depending upon the inertness of the atmosphere inside the furnace).

Table 2. Comparison of Oscillator Strengths and Sensitivities in the Flame and in the Furnace

Element	Wavelength Å	Oscillator Strength, f [51]	Sensitivity Flame		Furnace	
			L'Vov [51]*	Varian [47]*	Held [6]*	Watne [36]†
Ag	3281	0.45	0.1 µg/ml	0.036 µg/ml	8x10 ⁻¹² g	4x10 ⁻¹¹ g
Cu	3248	0.31	0.1 µg/ml	0.04 µg/ml	9x10 ⁻¹¹ g	4x10 ⁻⁹ g

* For an absorbance of 1%

† For an absorbance of .1 above blank

PYROLYTIC COATING--AN ATTEMPT AT IMPROVEMENT

In an initial attempt to increase the lifetime and decrease the porosity of the graphite heater tubes, a method of coating them with pyrolytic carbon was developed [24]. Pyrolytic coating is probably the most significant thing that can be used to improve the graphite system short of making everything out of vitreous carbon [36]. Pyrolytic coating is easy and inexpensive. Methane is introduced at one end of a quartz tube in which the object to be coated is suspended; the tube is then heated to about 1000°C in a tube furnace. The flow of methane is adjusted to between 30 and 200 ml/min. depending on the size of the object to be coated (too low a flow will coat only one end of the object, too high a flow cools the object excessively). The object is left for one-half to one hour, and allowed to cool after the methane flow is stopped. (The exhaust gases from this system should be exhausted into a hood, since the vapors are possibly highly carcinogenic.) The best coatings are a silvery color and are much harder than the graphite itself. This increases the durability of the object. It also decreases the porosity. Pyrolytically coated rods retained their threads about five times longer than uncoated rods. They also oxidized more slowly. The following quotation from the paper by Woodruff et al. documents the decrease in porosity.

Air was drawn through the walls of porous graphite tubes using the adapter described in previous papers 2,3. An uncoated National AGKSP [a commercial form of porous graphite] tube, 14 mm long, 6.2 mm o.d. and 4.7 mm i.d. will pass about 1400 cc/min of air with a pressure differential of 30 cm of mercury across it. This air flow (i.e., the porosity of the graphite) is reduced to essentially zero after a 40-min plating period (24).

Pyrolytic coating can also be used to "weld" two pieces of graphite together or to make porous carbon frits. Cups containing such frits are suitable for use as filters which allow the analysis of particulates with the furnace [24].

Pyrolytically coating graphite improves the sensitivity for copper by a small amount. Much of this is probably due to the decreased porosity. Recently, a much less porous form of carbon has become commercially available. It is called vitreous carbon.

Chapter 3

ALTERNATE ATOMIZER MATERIALS

VITREOUS CARBON

When one thinks of carbon, one usually thinks of graphite or diamond, but apparently there is a continuum of structure and properties between these two physically very different materials [55]. Diamond has each atom covalently bonded to four other atoms in an sp^3 configuration. The interatomic distance is 1.54\AA . This accounts for its hardness (10 on Moh's scale of 1-10) and strength, high melting point (actually, at 3900°K , diamond converts spontaneously and completely to graphite in a few milliseconds [56]), and the fact that it is a nonconductor of electricity [57]. Diamond has a specific gravity of 3.52. Graphite has its atoms bonded in sheets of hexagonal sp^2 bonded atoms, the interatomic distance within the sheet being 1.42\AA , but the distance between the sheets being about 3.35\AA [57]. The sheets are thus able to slide over each other with relative ease, accounting for the lubricating properties and softness (1 on Moh's scale) of graphite. Graphite has a specific gravity of 2.26. It is a good conductor of electricity [57].

Vitreous carbon is mesomorphic, i.e., its structure is between amorphous and crystalline. There appears to be a continuum between the amorphous and the crystalline states. Numerous techniques [53-65]

indicate that the structure of vitreous carbon consists of graphite-like sheets in layers with an interlayer spacing of $3.42 \pm 0.03 \text{ \AA}$. The bonding between the layers appears to be at least partially through sp^3 carbons. The layers seem to be made up of distorted hexagonal rings which are bonded differently or folded or both at the ends of the crystallites [59]. The crystallites are those areas which have a definite structure and are about 15 \AA thick and $20\text{--}40 \text{ \AA}$ wide. There are no definite boundaries, only defects, but there is a definite direction on a 100 \AA scale along the layers. The structure is random at greater than 500 \AA [37]. Besides this, there are pores smaller than 30 \AA with smaller interconnecting channels, but they do not penetrate two walls simultaneously. The amount of tetrahedrally bonded carbon decreases with increasing high temperature treatment [63].

Vitreous carbon has a high mechanical strength, 3 to 10 times greater than graphite. It has a very low gas permeability (about the same as hard glass) [57]. It fractures like glass, yet is somewhat plastic; indentations in it tend to disappear. It is hard (6-7 on Moh's scale) and it has excellent abrasion resistance [57]. An attempt was made to grind some cups from a piece of 1/4 inch solid vitreous carbon rod using a 4 mm steel rod and emery dust with water. After about 3 working days, the vitreous carbon had been penetrated about 1/2 cm. Vitreous carbon has a low specific gravity of about 1.45. Its electrical resistivity is between 3-8 times greater than

graphite and its thermal conductivity is about one-tenth as great [57]. It becomes 2-3 times stronger when heated to 2500°C (most materials become weaker at higher temperatures). It has a coefficient of thermal expansion about the same as Pyrex glass [58]. Its thermal properties are constant to near its melting point of about 4000°C [67]. It does not revert to a graphite-like structure upon heating and it has a high chemical resistance. It will withstand heating in air to 600°C with no weight loss. It is not affected by HF or halogens other than fluorine, or by most other non carbide-forming elements. It is readily attacked by alkali metals [38].

Vitreous carbon has been prepared from many different types of starting materials, each of which appears to give a nearly identical final product [54,68-71]. Starting materials include coal tar resin, furfural, phenol-formaldehyde resins, phenol-hexamine resins, furfural alcohol or cellulose. Slow heating (1°C/min. to 1°/hr) to a temperature above 700°C seems to be the key to making this substance [69]. The product from this is given a final high temperature treatment by raising its temperature more rapidly (20°/hr) to a final temperature of above 2000°C, depending upon what the working temperature of the final product will be.

A set of commercial vitreous carbon heater tubes 15 cm long, 1 cm o.d. and 2 mm thick were used in conjunction with a regular graphite shield tube, a regular carbon side tube and regular graphite

cups (a shield tube is a 12 inch long by 5/8 inch i.d. by 1/8 inch thick tube used to align the heater tubes, act as the "T" in the center, i.e., the place where the side tube and the heater tubes joined, and it also kept the graphite felt insulation from directly contacting with regular graphite, this was not a true test of a vitreous carbon system. Nevertheless, this arrangement increased the absorbance of 10^{-8} g of copper about 25%. The amount of the element necessary to give an absorbance of 0.1 above the blank was about 4×10^{-11} g of silver and 4×10^{-9} g copper. Lifetimes of the heater tubes at 2000°C in this particular furnace were about 50 hr for the uncoated graphite, 120 hr for the pyrolytically coated graphite and greater than 260 hr for the vitreous carbon electrodes. Similar results were found by Yamada and Sato [54]. A completely vitreous carbon furnace should be tried in order to determine how much of the problem of lack of sensitivity of copper (and other elements) is caused by carbide formation and how much is caused by the porous nature of graphite. Expense prohibited this study using commercially fabricated parts, but it spurred attempts to make vitreous carbon in this laboratory.

In an initial attempt to make vitreous carbon, a number of different starting materials were mixed and heat treated simultaneously (see Tables 3 and 4). Pure "resol" (see Table 3) appeared to give the best results. The product from this and, to a greater extent, the product from the other mixtures appeared to be bubbly and fragile,

Table 3. First Attempt at Making Vitreous Carbon

Resin	Results after heating about 10°C/hr for 4 days ^{††}
1) Pure novolak* [72]	Large shiny bubbles about 1-2 mm in diameter
2) Pure resol [#] [72]	Smaller bubbles than in 1)
3) Pure furan resin [†] [72]	Almost all evaporated
4) 1/2 novolak, 1/2 resol	Very similar to 1)
5) 1/2 novolak, 1/2 furan resin	Almost all evaporated
6) 1/2 resol, 1/2 furan resin	Finer bubbles, about 1/2 mm diameter
7) 1/3 novolake, 1/3 resol, 1/3 furan resin	Expanded the most. Large bubbles

* Novolak was made from 4.28 g of 88% phenol with 2.82 g of 37% formaldehyde catalyzed with 5 drops of concentrated HCl. After 2 months it was soft and white with a hard red scum.

Resol was made from 4.28 g of 88% phenol with 6.42 g of 37% formaldehyde. After 4 hours, 5 drops of concentrated NH₄OH was added. After 2 months it was yellow and had the consistency of honey.

† Furan resin was made from a 1:4 furfural:furfurol alcohol mixture, by weight. After 2 months, it was orange and had a heavy water consistency.

†† All samples were silvery and shiny. They appeared pyrolytically coated. Under the surface all were shiny and black and hard.

Table 4. Experiment 2 on the Formation of Vitreous Carbon

Resin	Heated at 10°C/hr to 110°C	
1) pure furan	Most distilled. Dark brown	Fairly hard and shiny black with fine bubbles.
2) novolak	Clear and fluid. Hard crust.	Much ash. Friable bubbles. Fairly strong and hard.
3) resol	Clear and hard. No bubbles.	Looks best. Shiny black. Numerous flaws.
4) novolak plus resol	Hard crust. Clear yellow. White crystals inside.	Next best.
5) novolak plus furan resin	Hard black, ejected mass.	Looks like a cinder. Shiny but bubbles all the way through.
6) resol plus furan resin	Like #4.	Major flaws, but looks good. Porous inside but not outside.
7) novolak, resol and furan resin	Dark brown. Hard crust.	Bottom shiny and black. Sides and top porous.
8) furan resin, 1-1.5 ml + 2 drops HCl*	Black. Hard.	Not good. Semiglossy. Black.
9) furan resin 1-1.5 ml + 2 drops NH ₄ OH	Most distilled. Brown. Hard crust.	All distilled except tiny fragment.
10) liquid from explosion of 8)	Hard and black. Not sticky.	Porous inside, nonporous inside.

* Turned dark blue, then brown, then sat for 10 minutes and exploded giving a rubbery black substance and a thick, black liquid.

possibly caused by too rapid heating and too thick a section. Another experiment was attempted: a variety of samples were heated directly to 700°C, but each of the samples distilled, then coated everything inside the quartz tube with what appeared to be pyrolytic carbon.

An attempt was made to make a tube of vitreous carbon by rotating a quartz tube partially filled with resol while heating it in a tube furnace. The heating took place over 4 days. Part of the product stuck to the quartz tube and could not be mechanically removed. Pure oxygen was passed through the tube while heating the tube with a hand torch (natural gas-oxygen). Some of the product burned away much more easily than the rest. Perhaps some was pyrolytic graphite and some was vitreous carbon. In any case, it was not in a form suitable for our purposes.

Having noted the various colored smoke which was a result of the pyrolytic coating process [24], and the fact that a variety of starting materials could be made into vitreous carbon, an attempt was made to make vitreous carbon from natural gas. A 30 cm long by 1 cm diameter stainless steel tube was wrapped with a coating of 1/16 inch asbestos paper. Over this was wound about 15 turns of 0.040 inch nichrome wire in a non uniform spiral (the turns became closer together toward one end). The purpose was to create a rather uniform temperature gradient from one end of the tube to the other. The tube was insulated with a 2 inch layer of quartz wool and a sheet of 0.005 inch

thick sheet of aluminum about 10 cm in diameter to act as a heat reflector. One end was measured at 200°C, the other at 900°C. Temperatures in between were estimated assuming a uniform temperature gradient. Natural gas was passed through a quartz tube placed inside this special heater. The flow rate of the gas was between 200 and 500 ml/min and continued for about 12 hours. Results are tabulated in Table 5. The section between 760 and 810°C looked fairly good, but it stuck to the quartz and had to be burned away to remove it. This approach has possibilities which should be explored further. A quartz tube in the shape of a "T" could be made, carefully heated and supported (quartz starts to sag at these temperatures if heated for a long period of time) and then coated on the inside with the vitreous carbon made from natural gas. The quartz tube could then be etched away with HF. There is a problem of the breakage of the carbon tube possibly due to the difference in coefficients of expansion of quartz and carbon. Perhaps graphite could be used and vitreous carbon coated on the inside.

Having found no economically feasible means of obtaining a vitreous carbon atomizer, some non-carbon materials were explored.

Table 5. Attempt at Making Vitreous Carbon from Natural Gas

Temperature °C	Results
200 - 350	Nothing
350	Light brown smudge starting
400	Dark brown smudge starting
500	Sharp transition where the carbon stops sticking to the quartz
560	Broken carbon
630 - 670	Quartz starts to get cloudy and shows a rainbow
760 - 810	Nice shiny carbon tube, layered but hard
760 - 870	Quartz tube broken and missing (stuck to the stainless steel)
870 - 900	Quartz is clear but has broken carbon in it
Past 900	Temperature decreases rapidly, oils and tars present

METAL OXIDES

Early investigations on this project included attempts to determine the suitability of metal oxides for use in making cups, and if that was found suitable, heater tube construction would be attempted.

The properties desired are a high melting point, good thermal shock resistance, good stability to metals, carbon oxidizing and/or reducing atmospheres, non-porosity, non-volatility, stability to moisture and non-toxicity (see Table 6).

A high melting point is desirable in order to be able to analyze all types of elements, including the more refractory ones such as tungsten, tantalum, etc. Metal oxides with melting points below 1600°C were not considered.

Good stability to metals or carbon is necessary since the tube must be heated in some manner. It was proposed that it could be wrapped with tungsten or molybdenum wire, or placed inside a graphite tube which would then be heated. As the temperature increases, metal oxides become better and better conductors of electricity, and if the tube could be preheated in some manner, the temperature could be maintained or increased by resistance heating, using the metal oxide itself as the resistive element. Radio frequency heating would also be a possibility, but it would require a much more complex system.

Table 6. Properties of Commercial Refractory Oxides Compared with Graphite

Compound	MP °C	Thermal Shock Resistance	Stability			Metals	Advantages/ Disadvantages
			Oxidizing Atm.	Reducing Atm.	Carbon		
Al ₂ O ₃	2015	Good	1950	Good	Fair	Good	
BeO	2550	Excellent	2400	Excellent	Excel.	Good	Toxic, expensive, reacts with water above 1650°
CaO	2600	Fair	2400	Poor	Poor	Fair	Reacts with water at RT
MgO	2800	Fair	2400	Poor	Good	Fair	Sublimes strongly above 1900°
SiO ₂	1728	Excellent	1680	Poor	Poor	Poor	
ThO ₂	3300	Poor	2700	Good	Fair	Excel.	Radioactive; expensive
ZrO ₂	2600	Fair	2500	Good	Fair	Good	Low resistant at hi temp. Can make resistance furnace in ox. atm. Expensive. Crystal structure inversion. Must be stabilized.
Mullite	1830	Fair	1800	Fair	Fair	Fair	
Spinel	2110	Poor	1900		Fair		
Zircon	2420						
Graphite	4000	Excellent	300°C	Excellent	Excel.	Good	Suitable electrical resistivity.

Porosity of the heater tubes would shorten the residence time of the sample in the analytical volume, hence it would lower the sensitivity. It would probably also cause curvature of the analytical curves, since the last of the sample might not have evaporated before the first of the sample had diffused out of the light path. Thus, non-permeability is an important criterion for heater tubes.

Stability to both oxidizing and reducing atmospheres would permit studies under other than reducing (or neutral) conditions, and this would be desirable in itself.

Having heater tubes stable to oxidizing conditions would greatly increase their lifetime, since in the graphite furnace, at least, oxidation of the heater tubes by oxygen, nitrogen or water is the primary cause of heater tube failure.

Zirconium Oxide

Good thermal shock resistance is necessary since the furnace is heated relatively rapidly, and the cups are heated very rapidly from room temperature to the operating temperature of the furnace. This temperature change (possibly 2000°C or greater) is made within a few seconds or, in some cases, within a fraction of a second.

A piece of 3/4 inch o.d. by 1/8 inch wall zirconium oxide tubing 12 inches long was obtained and was wrapped with 5 feet of 20 gauge nichrome wire. The ends of the wire were connected to a variable transformer. After heating to 800°C, the zirconium oxide

cracked in numerous places where the wire touched the tube. Apparently, it could not stand the thermal shock of being heated directly but not uniformly.

Magnesium Oxide

Non-volatility of the heater tube material is also essential to retain a usable lifetime for the system. Magnesium oxide, an otherwise reasonable material to try, vaporizes strongly in non-oxidizing atmospheres above about 1900°C [48].

Calcium Oxide

Non reactivity with moisture is essential for a practical system. Calcium oxide which is one of the least expensive of the refractory oxides and has a relatively high melting point (2600°C [48]). Unfortunately, it will hydrate in air and decompose within a few days.

Beryllium Oxide

Beryllium oxide which is probably the best all around ceramic of the metal oxides is quite toxic, especially through inhalation of the dust or vapors [48]. For this reason its use was not considered.

Thorium Oxide

Toxicity of another kind, radioactivity, is a problem with the highest melting of the oxide ceramics, thorium oxide (melting point 3300°C) [48]. Contamination from it can, however, be monitored with a

geiger counter. Because of its high melting point and excellent resistance to metals at high temperatures, it was decided to try making some thorium oxide cups.

A castable thorium oxide system consisting of a liquid binder and a container of powdered thorium oxide was obtained from the Zirconium Corporation of America.

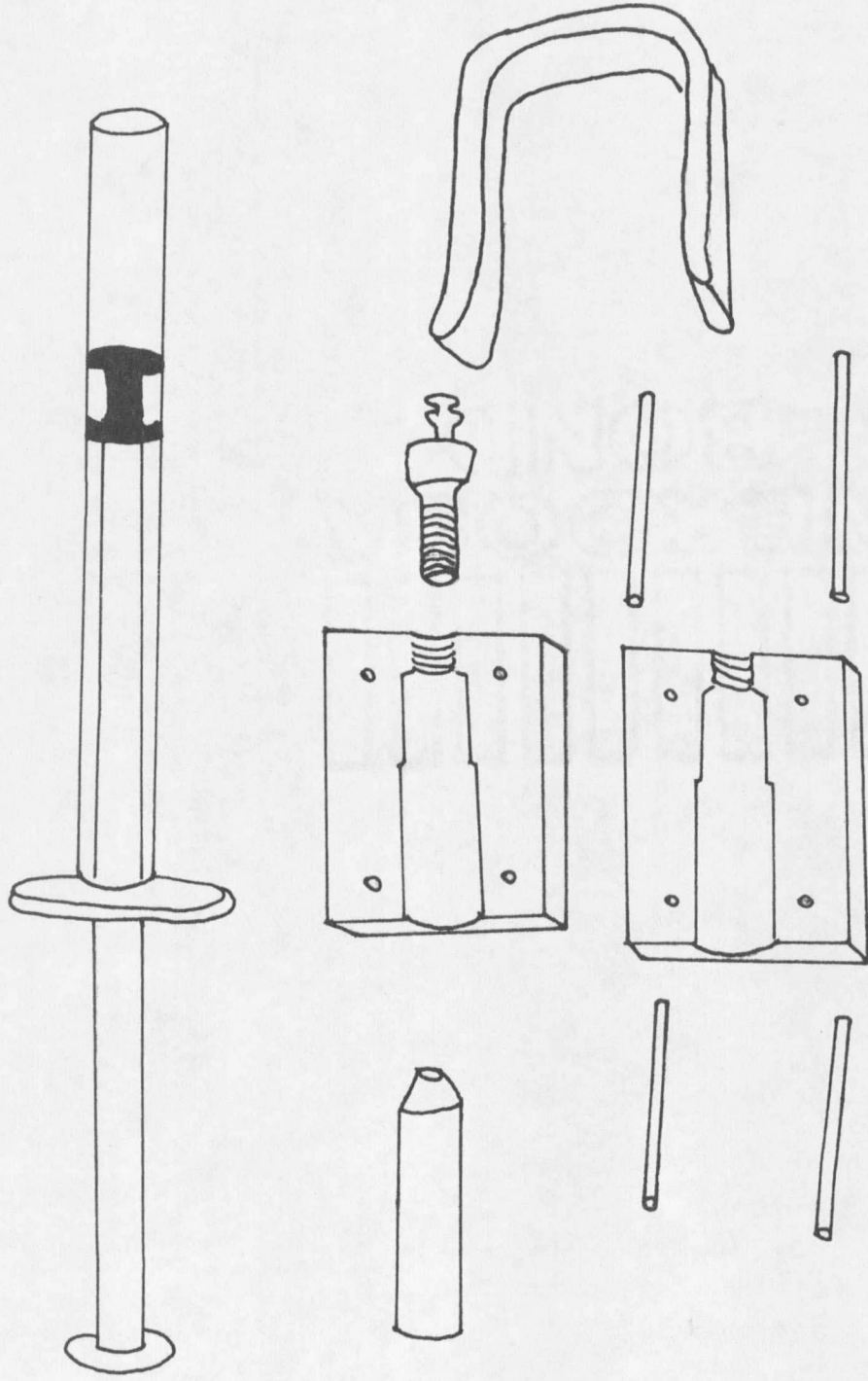
A mold was made by taking two pieces of 3/8 inch thick teflon sheet 1x1 inch square, placing them face-to-face and drilling 1/16 inch hole about 3/16 inch in from each corner through both pieces simultaneously. A steel pin was inserted in each of these four holes to maintain alignment. The whole apparatus was placed in a vice (faces vertical, one edge horizontal) and a 1/4 inch hole was drilled through the joined faces and parallel to them to within 1/8 inch of the other side. This other side was drilled and tapped for 5-32 threads. A 5/16 inch hole was then drilled so that the 1/4 inch diameter section was 1/2 inch long. Two other teflon pieces were machined, so a 5-32 teflon bolt, and the other, a 5/16 inch rod tapering down to 1/8 inch from 3/16 inch diameter in a 5/16 inch length (see Figure 6). This made a splittable mold. A steel clip was made to hold the entire mold together.

The mold was used by spraying the entire inside of the mold with the kitchen product known as PAM, as a mold release agent. The mold was assembled except for the 5/16 inch rod. About 1/3 of a ml of

Figure 6. Thorium Oxide Cup Mold

The two halves of the mold are assembled after being sprayed with a mold-release agent. The four pins maintain alignment and the spring clip holds the mold together. The teflon screw is inserted and about 1/3 of a ml of thorium oxide castable with a light paste consistency is inserted with a cut-off 1 ml syringe. The piece which forms the inside of the cup is then inserted. Disassembly after setting overnight is in reverse order.

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the thorium oxide castable was mixed with enough of the binder to make a thin paste. A 1 ml syringe with the needle end cut off was used to mix the paste and inject it into the mold. After the syringe was removed, the mold was tapped on a hard surface with the threaded end down to remove any bubbles. The 5/16 inch rod was then inserted (the tapered end making the inside of the cup). The entire apparatus was allowed to set overnight. Disassembly was done by removing the 5/16 inch rod, the 5-32 bolt, and then taking the two halves of the mold apart.

Using this system, numerous thorium oxide cups were made. The directions with the castable state that the objects which had been formed should be fired by heating slowly to about 2100°C. The graphite furnace was the only thing we had available which could attain that temperature. A cup was put into a specially prepared graphite furnace and heated to about 2000°C for about 6 hours, then cooled slowly. The cup turned to a blackish powder except for its central core. It smelled like the acetylene made from the reaction of calcium carbide and water. Apparently the thorium oxide was reacting with the carbon in the argon atmosphere to form thorium carbide. It was apparent that thorium oxide could not be fired in direct contact with graphite. An indirect approach was attempted.

The objective was to fire the thorium oxide in a system completely enclosed by a carbide of a different metal. This carbide

would then be in contact with the graphite, and, being a carbide already, no reaction with the graphite should take place. It was hoped the thorium oxide would not react with a metal carbide.

The desirable properties of the carbide were: a melting point greater than 2500°C if possible, and insolubility in water (to insure a stable, manageable carbide). The Handbook of Chemistry and Physics provided the data in Table 7 which lists some of these properties.

A number of small, hollow graphite cylinders with tight fitting caps were made. The size was such that a thorium oxide cup would fit inside, and the cylinder itself would fit inside the heater tube of a graphite furnace. Each cylinder and its cap were soaked in one of the following solutions (see Table 8), vacuum being applied and released a number of times in an attempt to force the solution into the graphite. Each cylinder was dried and then prefired to 2100°C in a graphite furnace. Each cylinder was resoaked and dried and fired a second time.

To each cylinder was then added a thorium oxide cup, the top put on tightly, and the complete set of cups and cylinders fired to about 1900°C. None of the resulting cups were usable (see Table 8).

One thorium oxide cup was heated in a bunsen burner flame. It became white but soft and crumbly after heating to an orange heat. Commercially, thorium oxide is heated to 2500°C over a period of twelve days.

Table 7. Data on Refractory Carbides

Compound*	Melting Point	Color and Form	Solubility
MoC	2692	Grey	sl.s.HNO ₃ , HF, h.H ₂ SO ₄ , HCl
Mo ₂ C	2687	White	as above
Ni ₂ C		Dark grey powder	
NbC	3500	Black or lavender grey powder	s.HNO ₃ , HF
SiC	2700 subl.d.	Col.-blk. hex or cub	s.KOH fus.
TaC	3880	Blk. cub.	sl.s.H ₂ SO ₄ , HF
TiC	3140+90	Grey, Met cub	s. aq.regia, HNO ₃
WC	2870+50	Blk, hex	s.HNO ₃ +HCl, HNO ₃ +HF
W ₂ C	2860	Blk, Hex	s.HNO ₃ +HCl
ZrC	3540	Grey met. cub	sl.s. conc H ₂ SO ₄

* Data in this table from reference 75.

Table 8. Solutions for Preparing Carbides, and Results and Appearance of ThO₂ Cup after Heating

Solution Used	Results	Appearance of ThO ₂ Cup
MoCl ₅	Looks like graphite. Some black powder inside	Porous, black
NbCl ₅	As above with brownish black powder	Black
Ni(NO ₃) ₂	Lighter grey outside. Droplets of metal (Ni) inside	Lighter grey. Somewhat crumbly
Na ₄ SiO ₄	Glassy substance inside fills space. Like graphite outside + metal splashes.	Looks best. Least parts missing. Holds together even if grey.
TiCl ₄ (non aq.)	Silvery grey outside. Thin light grey powdery coating inside.	Couldn't remove crucible from tube.
Zr(NO ₃) ₄	Like graphite outside. Grey coating inside with black and dark grey flakes.	Looks second best.

Since no suitable method of firing the cups was found, the experiment was discontinued.

Metal Oxides--Conclusion

Since the metal oxides appeared unsuitable for our purposes, a less thermally shock sensitive class of substances, thermebals, was investigated.

METALS

The next class of materials for evaluation as heater tube materials was the metals. Half a dozen refractory metals exist which were considered for this project. Four were actually tested. Table 9 shows some of the important properties of these metals and compares them with graphite.

Iridium was not used because of its poor machinability and its extremely high cost (one cup made of iridium by powder metallurgy cost about \$500).

Rhodium was not used in the pure form because of its lack of availability. It was used in the platinum tube as a 10% alloy in which it imparts hardness (pure platinum is quite soft, especially as a 0.005 inch thick foil), and doubles the electrical resistivity. The tube is heated by resistance heating and the resistance of most metals is so low that not much heating is accomplished. The power system we had available was not designed for such a low impedance. Another disadvantage of the metals is that they have higher coefficients of thermal expansion than does graphite. This increased the problems of

Table 9. Properties of Refractory Metals Compared with Graphite

Metal	Melting Point [77] °C	Boiling Point [77] °C	Specific Resistance Ohm-cm [75]	Machinability	Coefficient of Expansion [74] °C ⁻¹	Stability in Oxidizing atm.	Stability in Reducing atm.
W	3410	5930	5.51x10 ⁻⁶	Poor	4x10 ⁻⁶	Poor	Fair
Mo	2610	5560	5.7x10 ⁻⁶	Good	4x10 ⁻⁶	Poor	Excellent
Ta	2996	5425	15.5x10 ⁻⁶	Good	7x10 ⁻⁶	Poor	Good
Ir	2454	5300	6x10 ⁻⁶	Poor	6.5x10 ⁻⁶	Good	Good
Rh	1966	4500	19.8x10 ⁻⁶	?	12.5x10 ⁻⁶ #	Good	Good
Pt	1769	4530	10x10 ⁻⁶	Excellent	8.9x10 ⁻⁶	Excellent	Excellent
Graphite	3727	4830	1.4x10 ⁻⁴	Very good	3x10 ⁻⁶	Poor	Excellent

Non isotropic. 4.67x10⁻⁶ °C⁻¹ along another axis.

maintaining alignment, good electrical contact, and keeping the electrical power conductor to the heater tube cool while allowing the heater tube itself to be as hot as possible.

Tungsten

Tungsten has the highest melting point of all of the metals (3410°C) [73]. It has as low a thermal coefficient of expansion as any of the metals considered [74]. Its main disadvantages are its poor stability to oxidizing atmospheres, its high electrical conductivity (highest of all of the metals considered) [75], and its poor machinability. It also has a tendency toward hydrogen embrittlement. Notwithstanding its disadvantages, the construction of a tungsten furnace was thought to be a goal worth striving for. For these reasons, the first metal furnace attempted was a tungsten furnace.

A vapor-deposited tungsten tube 0.250 inch inner diameter, 0.011 inch wall thickness, and 12 inches long (obtained from Ultramet Corporation, Pacomina, California) was fitted with molybdenum "T" to receive a molybdenum cup. Molybdenum was used instead of tungsten due to the relative ease of machining. This tube was placed in a furnace shell and heated electrically. The tube had a cold resistance of about 0.015 ohm (compared to a graphite tube with a cold resistance of 0.21 ohm). The resistance of the tungsten tube was so low that too much current was being drawn from the mains and the circuit breaker tripped. The 220 volt, 20 amp breaker was replaced by a 220 volt 30 amp breaker

which also tripped. What was needed was a step-down transformer with a 50:1 ratio instead of the 10:1 ratio transformer we had available. This was necessary to improve the impedance match. To test the system, the tungsten tube was operated at reduced power, reaching perhaps, 1000°C for 1 hour. The tube was being heated in an argon atmosphere. After the test period, the power was shut off and the system opened for inspection. The tungsten tube had oxidized to such a degree that it was unusable. This was probably due to slight air or water contamination either in the argon itself or from leaks in the seals of the furnace shell. Apparently tungsten must be operated in a reducing atmosphere so that any atmospheric contamination will be eliminated. Some other electrical power arrangement would be necessary, as well. (The lag-time in obtaining another tube prevented repetition of the experiment at this point.)

Tantalum

Tantalum was the second choice. It has a melting point approximately 3000°C, is less brittle than tungsten (actually it is rather soft, even more so than the platinum tube eventually used), and is more machinable and less expensive than tungsten. Another advantage is its high specific resistance (highest of all of the metals considered). This allows a higher temperature to be reached with the same "power" input. Tantalum has the disadvantages of a high thermal

coefficient of expansion and poor stability to atmospheric contamination.

A 0.230 inch inside diameter by 0.010 inch wall thickness by 12 inch long tube was fitted with a molybdenum "T", since we had no solid tantalum rod available. After applying power, the tube bent so badly that the light beam was occluded. Apparently the softness combined with a high coefficient of thermal expansion and the springiness of the spiral heater tube contacts (see Figures 7 and 8) caused the tube to deform.

An attempt had been made to eliminate the atmospheric contamination problem for this experiment. The argon gas flow was passed through a 1 inch steel tube containing calcium metal. The tube was heated to about 500°C with a tube furnace. This should have removed both water and oxygen from the argon gas flow. It was noted that the tantalum tube was still brittle and had a graining coating which flaked off the outside. Apparently a reducing atmosphere is required here, as well as in the tungsten case. The molybdenum "T" had some yellowish white crystals growing on it. In an attempt to test the composition of these crystals, some of them were analyzed by emission spectroscopy. The emission arc spectrum showed strong molybdenum lines. In a second test, some of the crystals were heated in a bunsen burner flame. They caused a yellow-green flame, characteristic of

Figure 7. Spiral Heater Tube Contact

The spiral heater tube contact was used on the older model graphite furnaces, the tungsten furnace, and on the first tantalum furnace. It consists of a double spiral of 1/4 inch copper tubing which is brazed to a copper chuck in the center of the spiral. The copper chuck makes contact with the heater tube. Water is circulated through the copper tubing to keep the copper chuck from melting. A gas outlet is provided between the water inlet and outlet. A piece of brass is brazed on the outside of the iron housing ring and tapped with a 1/4-20 thread for electrical connection. Surrounding the iron housing ring is a rubber insulating ring which extends about 1/16 inch beyond the iron housing ring. This is held in place with a retaining ring. The entire thickness is about 5/8 inch. The copper spiral tube provides spring tension to maintain contact with the heater tube and take up the expansion due to the extreme temperature changes (see also Figure 1).

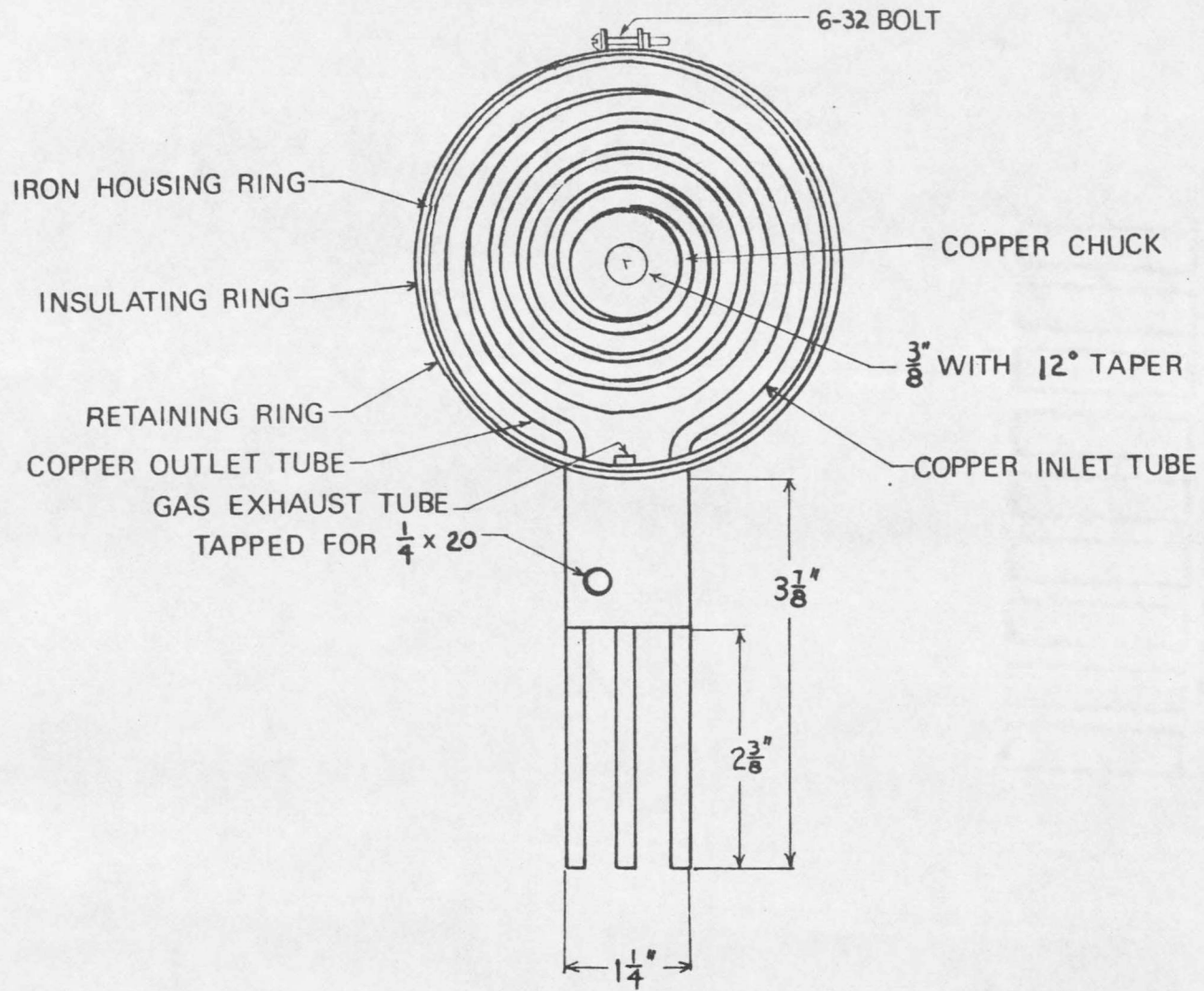
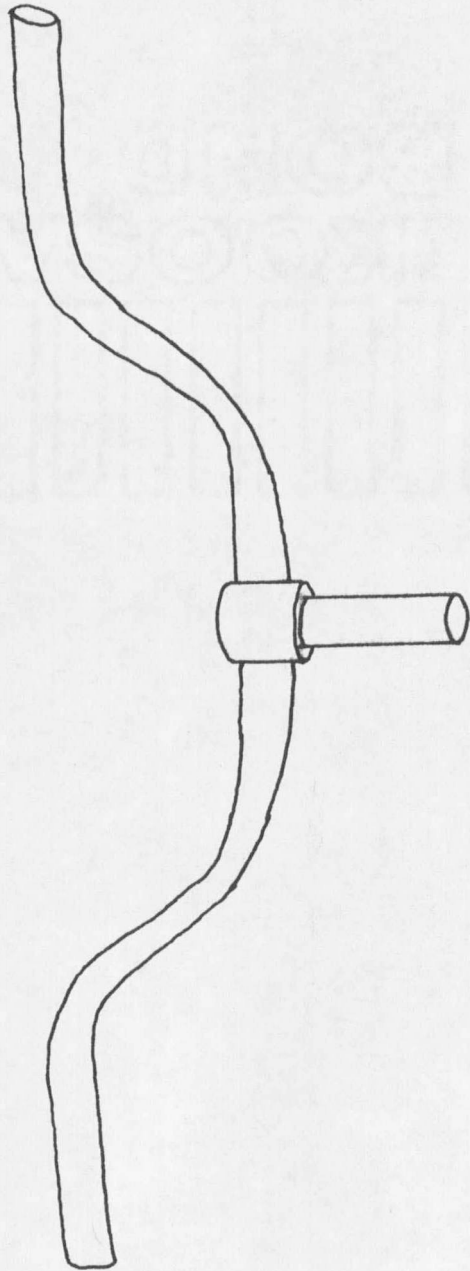


Figure 8. Distorted Tantalum Heater Tube with Molybdenum "T"

The initially straight 1/4 inch tantalum tube was inserted into a specially machined piece made from 3/8 inch molybdenum rod. Close to the end of the rod, a 1/4 inch hole was drilled perpendicular to the axis of the rod. Along the axis of the rod, a 1/8 inch hole was bored to intersect the 1/4 inch hole. The outside diameter of part of the molybdenum rod having the 1/8 inch hole was reduced so that it fit snugly inside a short piece of the tantalum tubing which acted as a side tube.

The tantalum tube distorted when heated. Apparently the springiness of the spiral heater tube contacts combined with the coefficient of expansion to cause the distortion.



molybdenum compounds. In the flame, some of the crystals melted and gave a white smoke characteristic of molybdenum heated in air.

The maximum temperature reached was about 1000°C and required 200 amps at 2.4 volts. No insulation was used between the heater tubes and the furnace shell, but two sheet molybdenum reflectors were installed, one above and one below the heater tube in order to reflect as much of the radiated energy as possible back onto the tube.

In a second attempt with another tantalum tube, electrode contacts with sliding fit, not spring loaded were used. In this case the tantalum tube didn't bend. It did, however, oxidize. These experiments suggest that the furnace shell was leaking air.

Platinum

To avoid the atmospheric problems which plagued the tungsten and tantalum furnaces, and in an effort to compare results (especially vapor pressures of potassium) with those results obtained with the graphite furnace, it was decided to build a platinum furnace. Platinum has the advantages of excellent stability in both oxidizing and reducing atmospheres, and excellent machinability. Its chief disadvantages are its low melting point, its high coefficient of thermal expansion, and its high cost.

Chapter 4

THE PLATINUM ATOMIZER

The platinum furnace consisted of a 16 gauge steel cylindrical outer shell of the "suitcase" style. (One style of furnace shell has the top hinged like a suitcase. In the other style, both ends are removable.) It was 9 inches in diameter and 14 inches long, closed at both ends. To the outside of this was brazed copper tubing for water cooling. On the axis of the cylinder were two openings, one on each end of the cylinder. These served to admit light, electrical power, and as the gas exits for the heater tube. Perpendicular to the axis and in the center of the outside of the cylinder were two other openings, at 90° around the circumference from each other. One served as the entrance port, through which the third electrical connection was made and through which the sample and gas were admitted. The other hole was an observation port through which the "T" junction of the heater tube and the side tube could be observed and the temperature read using an optical pyrometer. Parallel to the cylinder axis but above it and just above the two end and the observation port openings, the cylinder was cut by a plane. The steel of the cylinder was bent out to form two 1/2 inch wide ledges all the way around the cylinder where it was cut by the plane. These two ledges formed the seat for a silicone rubber seal which was molded between them. A piece of steel 3/4 inch wide extended downward from the top half

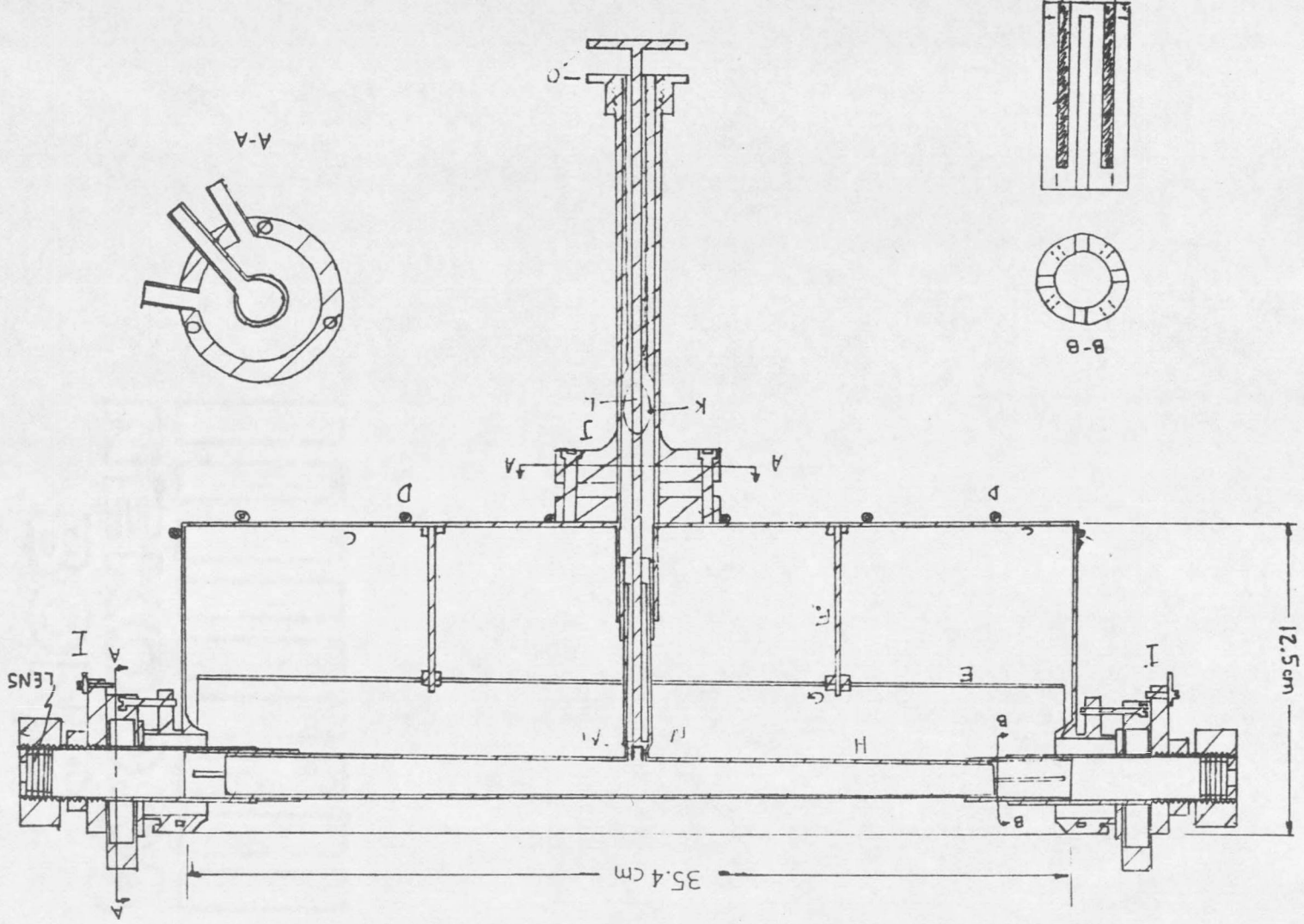
forming a heat shield for the gasket. On the backside of the cylinder (the side opposite the observation port) was a set of hinges which allowed the top of the cylinder (the cylinder had its axis horizontal and the entrance port down) to be opened for any adjustments or changes in the heater tube. The front side had two adjustable latches to secure the top and to make the system gas tight (see Figure 9).

The push-rod pedestal holder served as the sample introduction port, gas entrance, electrical contact and was water cooled. It was machined from a brass rod $5/8$ inch in diameter and 8 inches long. The lower portion was threaded to receive a $1/2$ inch pipe cap. The pipe cap was bored with a $1/8$ inch hole for the push-rod. The lower $3-1/2$ inches of the $5/8$ inch rod were bored with a $1/8$ inch hole. This aligned the push-rod with the centerline of the side tube. The next two inches are bored to $3/8$ inches. From the junction of these two sized holes and up for 1 inch was milled a $3/8$ inch wide slot through one side of the $5/8$ inch rod. This slot acted as the entrance port. Cups were inserted through this slot which was sealed off by sliding a quartz tube (the "window") which was $2-1/2$ inches long and $7/8$ inch o.d. over a set of "O" rings, one of which was above the window and two of which were below. These were greased with a little bit of silicone high vacuum grease (used for its heat resistance). The "O" rings sat in grooves machined into the outside of the $5/8$ inch rod. The upper portion of the $5/8$ inch rod was bored to $1/2$ inch i.d. to

Figure 9. The Platinum Furnace

The platinum furnace consists of an outer shell, C, cooled by 1/4 inch copper tubing, D, brazed to its outer surface. Instead of insulation there are two 0.015 inch thick polished molybdenum reflectors, E, which are semicylindrical and which help reflect the radiation. They are supported by threaded molybdenum rods, F, and secured by molybdenum nuts, G. The platinum tube, H, itself is in the form of a "T". Power is supplied to it through two water cooled lens holders, I, and the pedestal support, J. K is the entrance port and L is the rod which has the pedestal, M, containing a cup, N, on one end and a magnet, O, on the other to hold the pedestal in place. B-B is one of the spring contacts and A-A shows a section of the water cooling and gas inlet/outlet arrangements of the electrical contacts, used both in the lens holders and in the pedestal support.

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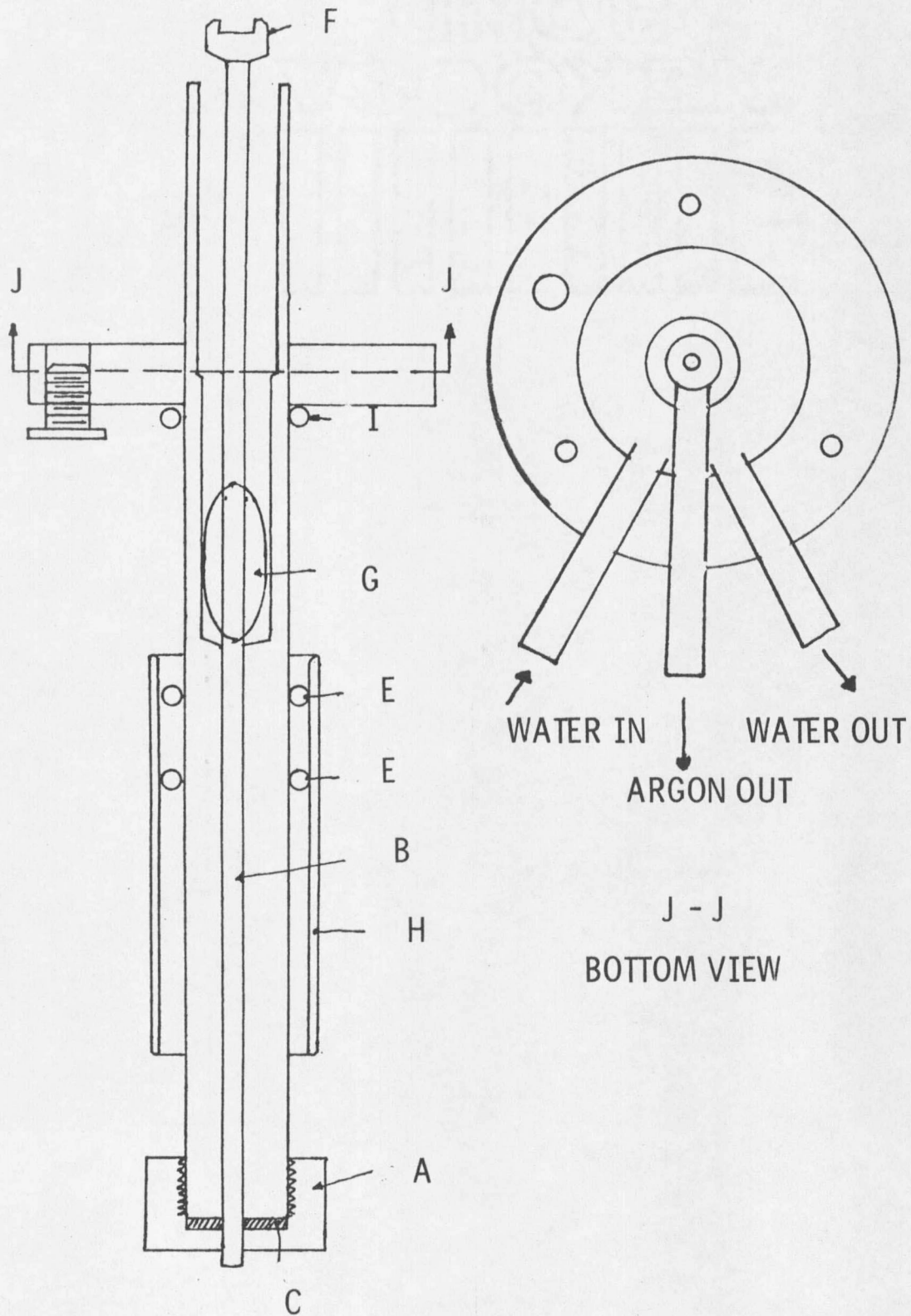


receive the spring contact (see section B-B Figure 9). Coaxial with the 5/8 inch rod and brazed to it above the window was a 3/8 inch thick brass disk 2-3/4 inch in diameter. This had been machined to receive water circulation and gas throughput as seen in section A-A of Figure 9. Electrical contact was made to this disk via a 1/4-20 bolt (see Figure 10).

The electrical contacts on the ends of the cylinder consist of a 5/8 inch inside diameter by 1/8 inch wall thickness by 4 inch long brass tube which is threaded on one end to receive a threaded brass lens holder. About 1 inch from the threaded end is brazed coaxially a 2-1/2 inch diameter by 3/8 inch thick brass disk which has been hollowed out for water cooling as is the entrance port shown in section A-A Figure 9. Perpendicular to the 5/8 inch tube is a 1/8 inch inner diameter tube which penetrates from the outside of the 2-1/2 inch diameter disk to the inside of the 5/8 inch diameter tube. This serves as the gas exit, and was normally connected to a flow meter so the gas input and output could be compared. This gave an idea of how well the furnace was sealed. The 2-1/2 inch diameter disk was bolted with three insulated bolts to a similar sized disk brazed to the case. A rubber gasket between the water-cooled disk and a short piece of brass tubing brazed through the other disk formed a gas seal and electrically insulated the water-cooled arrangement from the case. Changes in the tension of the three insulated bolts changed the alignment for

Figure 10. The Push-rod Pedestal Holder

The push-rod pedestal holder was machined from a brass rod $\frac{5}{8}$ inch in diameter and 7 inches long. The lower portion is threaded to receive a $\frac{1}{2}$ inch pipe cap, A, which was bored to receive a $\frac{1}{8}$ inch hole for the rod, B. A silicone rubber gasket, C, fits inside the pipe cap to make a gas-tight seal. The rod was bored to receive a $\frac{1}{8}$ inch push rod for a distance of $3\frac{1}{2}$ inches from the bottom. This allows fast cooling of the rod and more importantly, provides a large heat capacity to keep "O" rings D and E from becoming too hot. From $3\frac{1}{2}$ inches to $5\frac{1}{4}$ inches from the bottom, the rod was bored to $\frac{7}{16}$ inch to provide clearance for the 0.360 inch pedestal, F. From $5\frac{1}{4}$ inch to the end, the rod was bored to $\frac{1}{2}$ inch for the spring contacts. From $3\frac{1}{2}$ inch to $4\frac{1}{2}$ inch from the bottom was milled a $\frac{3}{8}$ inch wide slot, G, in one wall and 5 inches above the bottom was brazed a $\frac{3}{8}$ inch brass disk, $2\frac{1}{2}$ inch in diameter. This was machined as in section A-A of Figure 5. A $\frac{1}{4}$ -20 hole was tapped into the outer rim of this disk for electrical contact. A $2\frac{1}{2}$ inch long by $\frac{3}{4}$ inch i.d. quartz tube, H (the window), slides over "O" rings D, E, and I to open or seal the entrance port. The disk is bolted to the case with three bolts insulated with bakelite insulators. This allows the case to "float" electrically.



optical purposes. The water-cooled disk was tapped for a 1/4-20 threaded bolt which secured the electrical connection.

The heater tubes were made of an alloy of 90% platinum and 10% rhodium, since this alloy has almost twice the specific resistance of pure platinum [44]. A higher specific resistance is desirable since otherwise the potential drop across the heater tube is so low that little resistance heating is accomplished. The tube was 12 inches long, 0.005 inches wall thickness and 0.375 inches in outside diameter. Welded to this in the center was a perpendicular tube 4 inches long, of similar other dimensions. This was reduced in diameter about 1/2 inch from the joint so that its wall thickness was about 0.020 inches and its inner diameter was about 0.335 inches. This provided a place for the pedestal to seal and increased the heat capacity so the cup would be heated more rapidly. It had the disadvantage of decreasing the resistance at this point, which, in turn, decreased the maximum temperature at this point. On the average, the coldest temperature of the junction was about 200°C lower than the hottest point in the heater tubes. This minimum temperature at the junction was the assumed temperature of the cup.

The fact that platinum welds so easily is both an advantage and a disadvantage. It makes it easy to work with, but using platinum cups in a platinum furnace causes them to weld wherever they touch. (The use of a platinum pedestal was therefore not possible.) If the

contact pressure is not great and the temperature is below about 1100°C, the weld can be easily broken. The problem increases with increasing temperature. This was one of the major problems in the design of the platinum furnace.

The solution of finding a material suitable for use as a pedestal was found in aluminum oxide. The pedestal was, at first, a single crystal to avoid the possibility of any grain boundary diffusion problems. The least expensive and most readily available source of single crystal aluminum oxide is synthetic ruby. The first pedestal was ground from a cut ruby using a diamond saw and two different sized diamond grinding pins. An aluminum oxide thermocouple sheath 1/8 inch in diameter and having two longitudinal holes was used as the push-rod to which the pedestal was attached. Wires of platinum-10% rhodium and platinum-30% rhodium were drawn through the holes and welded at the top to give a thermocouple reading the temperature directly under the cup. The pedestal was attached to the push-rod by using the same liquid binder supplied with the thorium oxide castable, combined with powdered aluminum oxide instead of the recommended thorium oxide. A thin paste was made and allowed to dry overnight and then fired in the furnace during the first analysis. The first pedestal cracked after about two weeks of use. The second and third attempts cracked during machining. A piece of sintered aluminum oxide was successfully manufactured into the fourth pedestal. It,

too, cracked after three or four days, but was repaired using the above binding agent and powdered aluminum oxide as cement. After all of the tests in oxygen had been completed, a molybdenum pedestal was machined and found to work successfully. It could not, of course, be used in air.

First Generation Platinum Atomizer

The first generation platinum atomizer had the ends of the heater tube and the side tube held in alignment by spring contacts (see section B-B Figure 9). It was hoped that the friction fit at two places (where the platinum tube contacted the spring and where the spring contact contacted the 5/8 inner diameter brass tube) would allow for thermal expansion yet maintain good electrical and thermal contact. The system worked at low temperatures, but when approximately 1000°C was reached, arcing due to poor electrical contact caused the brass to melt (due to poor thermal contact) and the melted brass dissolved in the platinum forming an alloy which caused the platinum tube to melt through and burn out at one end.

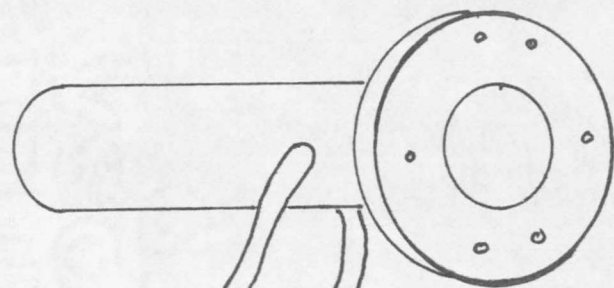
Second Generation Platinum Atomizer

The heater tube "T" from the first platinum furnace was salvaged by cutting about two inches off of the burned out end of the heater tube. Apparently what was needed was better cooling and better electrical contact. Due to limited time, it was decided not to modify

the basic furnace design, rather to add whatever pieces were necessary to make the furnace functional. The pieces had to be such that they could be adjusted for different lengths of the legs of the heater tube and the side tube. The push-rod pedestal holder was removed and the outside of the top end was threaded. A 1-1/8 inch diameter by 1/4 inch thick brass disk was bored and threaded to match. A brass ring 1-1/8 inches outside diameter by 5/8 inch inside diameter by 3/16 inch thick was machined and bored with six holes around its perimeter which matched six holes tapped for 4-40 bolts into the threaded disk. The ring was then sawed in half. A 3/4 inch diameter by 0.005 inch thick platinum disk was cut, and a 1/4 inch hole punched in its center. A tapered object was pushed through the platinum disk to flare the hole and make it fit over the 3/8 inch platinum tube. The two were then welded together. The push-rod pedestal holder was replaced on the furnace shell, the threaded disk threaded on the proper distance, the platinum disk placed on this, then the split rings bolted to the threaded disk (see Figure 11). This arrangement was found to provide good electrical contact, and sufficient thermal contact (for the side tube) to prevent melting of the brass. The ability of the 0.005 inch platinum disk to buckle slightly provided some ability to absorb the expansion of the tube. It was enough for the side tube but not for the heater tubes themselves.

Figure 11. Second Generation Platinum Furnace with Water Cooled Split Ring Electrical Contacts

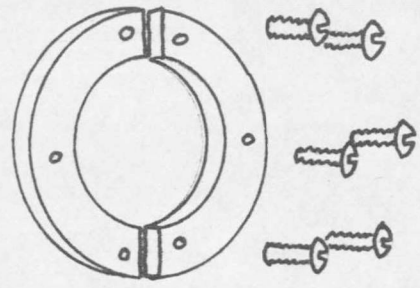
This heater tube contact was double walled. Copper tubing 3/16 inch o.d. conducted water to and from this contact to allow cooling. The copper tubing was passed through the silicone rubber gasket of the outer shell--a poor design. The outer portion of the large tube fit snugly inside the original lens holders and replaced the spring contact, B-B, of Figure 9. Once these contacts were in place, the platinum heater tube with the extra platinum disk welded on to it was held tightly against the flat plate end by a split ring arrangement and six bolts. The entire piece, excluding the copper tubing, was made of brass and silver-soldered together.



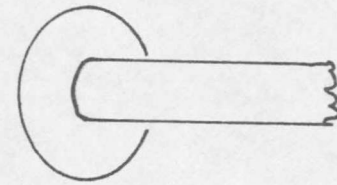
Water in

Water out

Double Wall
Water cooled
Electrical
Contact



Split Ring



Platinum Heater Tube

The ends of the heater tubes are farther from the point of water cooling on the cylinder ends, hence water-cooling had to be brought closer to the heater tubes. A brass cylinder with hollow walls was constructed. It had an outside diameter allowing a friction fit into the electrical contacts at the cylinder ends. This allowed adjustment for different lengths of heater tubes. A brass disk and split ring similar to that used on the side tube was constructed and silver-soldered to the hollow cylinder. Two 3/16 inch diameter copper tubes connected to the hollow cylinder and led out through the silicone rubber gasket for connection to the water line and drain. Slots had to be cut in the steel heat shield which extended down from the top part of the steel shell so that these tubes would be electrically insulated from the case. Three-quarter inch platinum disks were welded onto the ends of the heater tube in a manner similar to that on the side tube (see Figure 11).

This system was found to function satisfactorily. Three problems still exist. The water lines through the silicone rubber gasket are very difficult to seal yet keep electrically insulated from the case. Second, the platinum disks do not allow sufficient absorption of the expansion of the long platinum heater tube, so the tube wrinkled and bent, partially occluding the light path. Third, oxygen entering the furnace from leaks around the gasket (and/or through the entrance port when it was open) combined with the hydrogen which was

mixed with the argon in certain experiments (to make the conditions inside the furnace reducing) on the hot platinum surface (which undoubtedly acted as a catalyst) and formed large amounts of water. The water condensed on the cold water tubes inside the furnace as well as on the case and rusted the inside of the steel shell of the furnace.

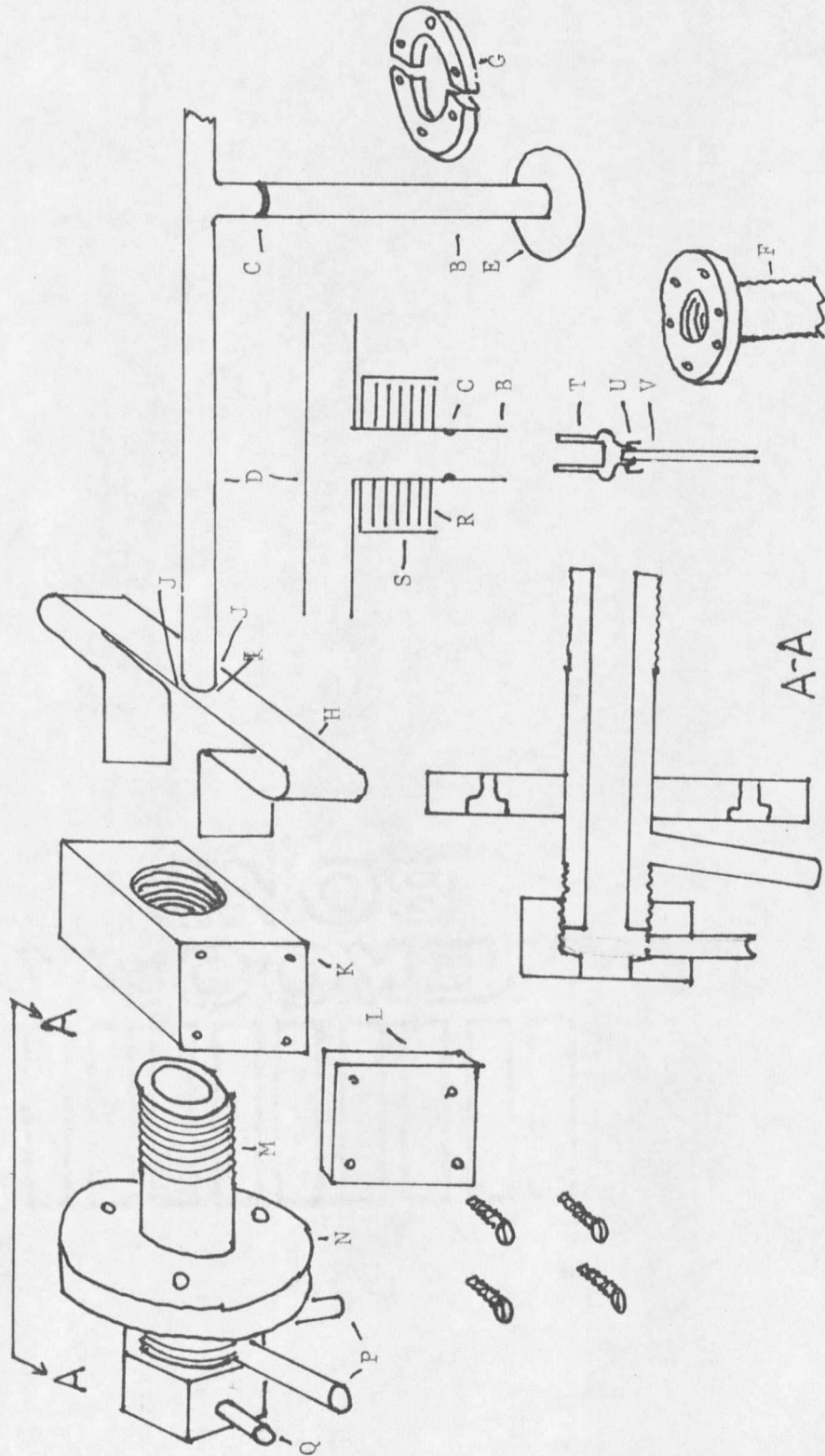
Third Generation Platinum Atomizer--Suggestions

The proposed third generation platinum atomizer should be able to solve all three of these difficulties as well as two others which have plagued all Woodruff furnaces, namely the desirability of getting the heater tubes hot all the way to the ends and making the temperature of the heater tube uniform, and to make the junction of the "T" as hot as the rest of the heater tube. An ideal system would have the heater tube and side tube be uniform temperature over its entire length, yet have such a large heat capacity that insertion of a cup would not lower the temperature of the side tube at the "T". This would allow the cup to rapidly reach the temperature of the heater tubes.

The furnace should be redesigned as follows (see Figure 12). To solve the rusting problem, the furnace should be made entirely of brass. Stainless steel would also work, but stainless steel is much more expensive and is much more difficult to work with. (It cannot be brazed or silver soldered, it must be TIG welded--tungsten-inert gas

Figure 12. Third Generation Platinum Furnace Construction Details

An indentation is made in the side tube, B, at the appropriate place to serve as the pedestal stop and seal, C. It is filled with platinum wire. The side tube is welded directly to the mainheater tube, D, avoiding the build-up of the platinum as much as possible. A disk of platinum foil, E, is welded to the bottom of the side tube in the same manner as in the second generation furnace and is attached to the push-rod pedestal holder, F, with a split ring, G, as before. A strip of platinum, H, of width equal to one half the circumference of the heater tube, and of equal thickness, is bent into a "U" on each end, and a hole is punched through its center. One of these strips is welded to each end of the heater tube, I. The portion of the strip directly above and below the welds may be narrowed to increase the heating at this point and to allow the heater tube to become hot all the way to the end. The springiness in the "U" should easily take up the three or four millimeters of expansion while maintaining the alignment. The ends of the "U" are secured to a brass piece, K, by a brass plate, L, and four brass bolts. The brass piece, K, is threaded to fit over a doubled walled water cooled electrical contact, M (see section A-A), which consists of a brass disk, N, with holes for attachment to the furnace via insulated bolts, and a hole for attachment of the electrical cable. This brass disk, N, is silver-soldered to the double walled water cooled electrical contact, M. The tubes, P, for entrance and exit of cooling water are attached outside the furnace shell. On the end opposite the brass piece, K, is a threaded lens holder and gas exit, Q. R is a stack of press-fit platinum disks to increase the heat capacity without appreciably affecting the resistance. S is a shield to limit convection of the stack. Other radiator plates similar to R may need to be placed on the heater tube and side tube at hot spots to make the temperature more uniform. T is the aluminum oxide pedestal, U is a platinum pin, and V is the aluminum oxide rod.



welded.) The suitcase design should be retained except the seal support should be made much thicker. The 16 gauge steel bent under certain conditions which probably caused some of the sealing problems encountered.

The expansion problem can be solved by changing the electrical connection. A strip of platinum having the same thickness as the heater tube and having a width equal to $1/2$ its circumference should be bent in a modified "U" shape (see Figure 12). This would allow excellent electrical contact at the ends (which would be attached to a piece of water-cooled brass), yet allow the alignment to be preserved and expansion to take place without distortion of the heater tube. By just slightly narrowing the width of the contact strip as it approaches the heater tube, the goal of having the ends of the tube as hot as the middle could easily be accomplished. The side tube connection can remain as it was.

The gasket sealing problem can be solved by not running water tubes through it, and by making the seal support more rigid. A foam silicone rubber gasket may be required.

The electrical contact-lens holder-water-cooled gas exit end pieces should be redesigned as in Figure 12. This will allow good electrical contact, good water cooling, and good gas sealing, as well as easy optical alignment.

To make the temperature uniform along the heater tube and the side tube, platinum "radiator" disks may be required. Press fitting them at the hot spots should increase the surface area at these points, which will increase the rate of radiation hence cool the tube.

If the disks are very close together, however, and not vertical to allow convection, the radiation from one should be absorbed by the next, for the most part, and the heat capacity of the system at this point should be increased without appreciable decrease in temperature (see R and S of Figure 12). This could be done to enable the cups to come to thermal equilibrium rapidly without the junction of the "T" being appreciably cooled. It is important that the disks be thin and not touch so that the electrical resistance of the tube is not appreciably decreased. The tube should not be built up in thickness (as it was before) to enable it to reach the same temperature as the test of the heater tube. To stop losses due to convection, the top disk should be slightly larger and a platinum cylinder, S, extending downward to cover the other disks could be used. It should be determined whether or not this would cause more losses due to radiation than were saved by stopping convection, however.

Some sort of "stop" is needed to seat the pedestal against inside the platinum side tube. What is proposed is to use a dull tubing cutter to depress a ring in the platinum side tube at the appropriate place. A small piece of platinum wire should then be

welded on the outside of the side tube but inside this depression to keep the platinum seal from being pushed out by the pedestal.

The order of assembly is proposed as follows: A graphite rod is inserted into the 12 inch heater tube. The hole for the side tube is drilled. The platinum around the hole is flared out, if possible, so that it is over the side tube. A similar piece of graphite rod is inserted into the side tube. The two are then welded together using the minimum amount of platinum wire to make the weld and seal the tube. The piece of graphite is removed from the side tube. A piece of low melting plastic or easily dissolvable plastic is machined with a rounded groove at the place for the seat. This is inserted, the platinum tube depressed into the groove, and the plastic melted or dissolved out. A piece of platinum wire with a length equal to the circumference of the inside of the groove is welded in place. A number of thin platinum disks are press fit above the seat and for perhaps 1/4 inch below to increase the heat capacity. The disks are bent so they do not touch. A disk is welded to the bottom of the side tube and the platinum strips are bent into shape, punched, and welded in place. The tube is put in place and heated and any hot-spots are observed. A disk can later be press fit over the spot to increase the cooling. Welding should not be necessary--they will weld themselves in place upon heating.

The pedestal must be redesigned so that there is no possibility of a platinum cup touching the side tube walls. One possibility would be to make the pedestal from a short length of thin-walled alumina tubing which had a thick end. A hold could be made in the end for insertion of the alumina rod. The bottom of the pedestal should be smaller than the outer diameter to enable a platinum pin to be inserted through a hole bored in it and in the alumina rod. (A diamond drill, which is available, will be necessary.) The ends of the platinum wire pin should be bent down so that it cannot contact the side tube wall.

ELECTRONICS--POWER

The power source is 220 volts alternating current (VAC) 3-phase from the mains. Forty amps per phase is available.

Due to the low resistance of the heater tubes in these furnaces (0.21 ohms for the graphite furnace across the main tube, and 0.019 ohms for the platinum furnace across the main tube), one needs high currents at low voltages. The relatively low temperature of 1200°C on one of the graphite furnaces required 90 amps at 18 volts. The power, however, is proportional to the square of the current. Using 250 amps at 10 volts per leg is not uncommon for a graphite furnace. The platinum furnace, due to its order-of-magnitude lower resistance, requires more current. As an example, consider the above

graphite furnace operating at 90 amps through a resistance of 0.21 ohms. Power is equal to the resistance times the square of the current, hence $0.21 \times 90^2 = 1700$ watts. To expend the same amount of power in the platinum furnace, with its resistance of 0.019 ohms, would require $\frac{1700}{0.019} = 300$ amps. The low resistances of the heater tubes are extremely difficult to measure and were measured with a special low-resistance measuring ohm meter designed by the author specifically for measuring the resistance of heater tubes (see Figure 13).

The low current necessary is provided by stepping down the 220 VAC 3-phase line voltage through three variable transformers connected in the delta configuration. The variable output of each variable transformer is applied to the two primaries of a 10:1 step-down transformer which are in series with each other (each step-down transformer has two primaries and two secondaries wound on the same core). The secondaries of each transformer are connected in parallel. One side of the connected secondaries of each transformer goes to a common point (point S in Figure 4). The other side is connected to one leg of the platinum furnace.

The current through each leg is measured by a transducer in series with an a.c. volt meter. The transducer is made by removing the coil from a 110 to 6.3 volt filament transformer, cutting out the center section of the laminated core, replacing the primary coil over

Figure 13. Low Resistance Tester

This device will measure resistances from 0.01 to 10.0 ohms. It is powered by three nine volt transistor radio batteries and it will fit in a 5x4x2 box. External calibration resistances are built into the box and put in series such that one can check one low, one medium, and one high value on each range as well as zero. The lower known resistances can be made from measured lengths of nichrome resistance wire of known resistance/length.

The procedure for use is as follows:

- 1) Short probes
- 2) Switch to the first range (0-10 ohms)
- 3) Push test button and zero meter
- 4) Attach probes to known resistance
- 5) Push test button and calibrate
- 6) Repeat 1-5 until there is no change
- 7) Attach probes to unknown resistance
- 8) Push test button to measure
- 9) Repeat 1-8 except 2 with succeeding ranges until proper range is reached

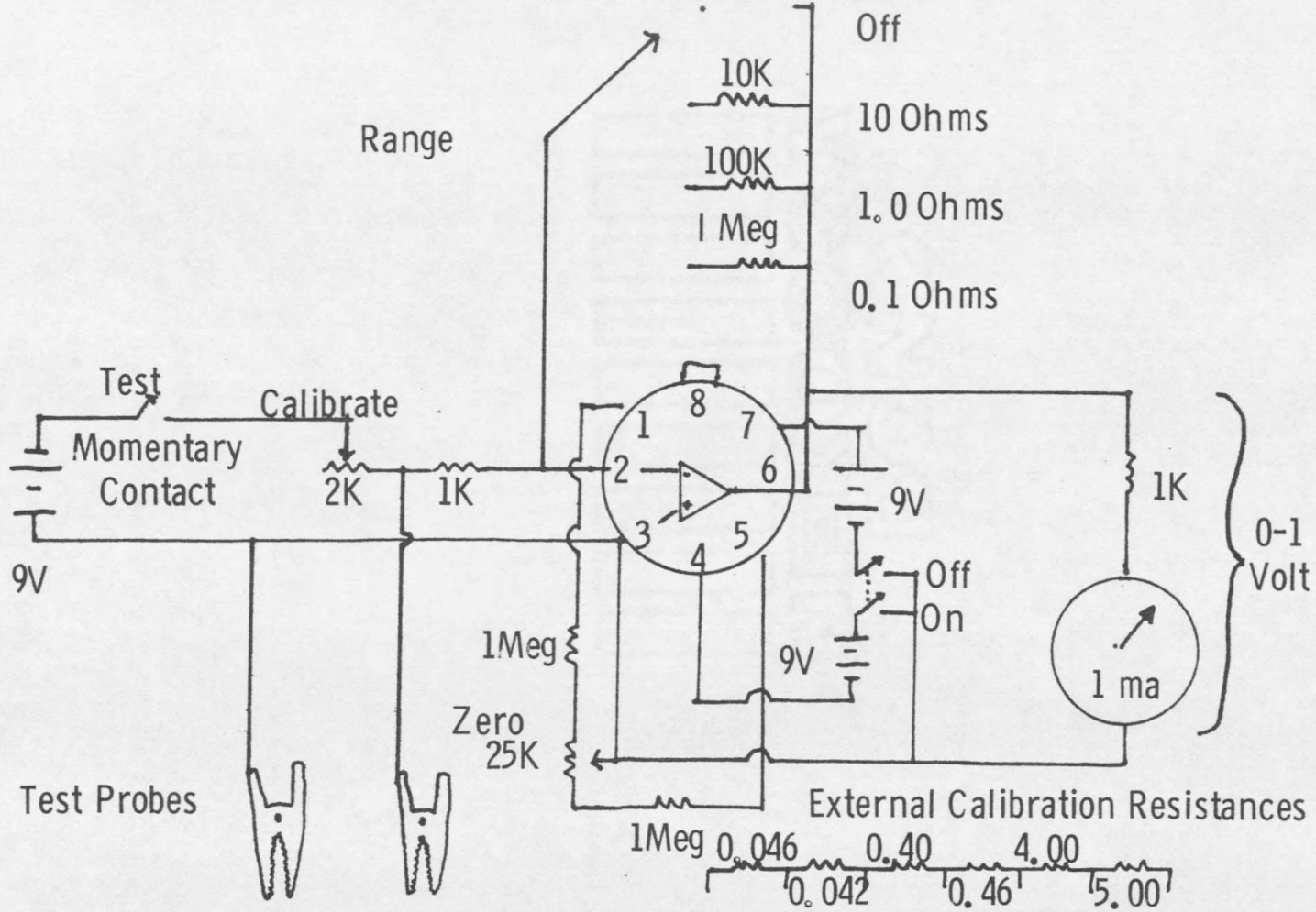
Read 0 to 1×10^1 ohms (range 1)

$\times 10^0$ ohms (range 2)

$\times 10^{-1}$ ohms (range 3)

Care must be taken that contact resistance between probes and heater tube is much less than the resistance to be measured.

LOW RESISTANCE TESTER



one of the outside sections of the core and passing the cable powering one leg of the platinum furnace through the core of this transducer. A variable resistance is added in series with the meter and the system calibrated against a known current meter (see Figure 5).

ELECTRONICS--ANALYTICAL

The signal from the R955 photomultiplier tube powered by an Ortec high voltage power supply at -700 volts goes to a lock-in amplifier. The amplifier does three things; it locks in on a signal of a certain frequency, it amplifies the signal, and it produces the necessary frequency to pulse the hollow cathode power supply, which in turn, pulses the hollow cathode. The amplified signal from the lock-in amplifier goes to a log amplifier which takes the log and makes the signal proportional to absorbance. The output signal from the log amplifier is fed into a chart recorder. On a separate channel of the chart recorder is recorded the temperature from a thermocouple inside the pedestal. The signal from the thermocouple is amplified by an operational amplifier before going to the recorder (see Figure 3).

RESULTS OF A TYPICAL ANALYSIS

Cadmium

As a typical analysis, cadmium was analyzed. Due to its low boiling point, cadmium has a relatively high volatility hence is suitable for use at low temperatures. Concentrations of cadmium covering 3-1/2 orders of magnitude were prepared and analyzed by pipeting into platinum cups, drying under an infrared lamp, then analyzing in the platinum furnace. The peaks on the chart recorder paper were copied and the copied peaks cut out and weighed. The results are shown in Table 10 and Figure 14. The scatter is caused at least in part by the fact that the pedestal was not raised enough to seal. This was to avoid the platinum cups sticking to the inside of the side tube. (A pedestal of a different design would rectify this and should give more precise results.) The detection limit is estimated to be about 2×10^{-12} grams for cadmium in this experiment. The line is the least squares fit for the data. To check for other sources of scatter, 1x1 inch squares of the paper upon which the graph was copied were cut out and weighed. The average of ten squares was 0.0574 with a standard deviation of 0.0006; about a 1% error. As another check, a reproducibility study was done on the different lambda pipets used in making some of the dilutions used in the cadmium study and later in the open cup potassium study. The results are shown in Table 11. The standard

Table 10. A Typical Analysis--Cadmium

Peak Code	Cadmium (grams)	Weight of Peak	$\bar{x} \pm s$
P	5.0×10^{-12}	.0801	
O	1.0×10^{-11}	.0685	
N	2.0×10^{-11}	.0554	
L	5.0×10^{-11}	.0911	
D	1.0×10^{-10}	.0629	
K	1.0×10^{-10}	.0441	
M	1.0×10^{-10}	.0903	
R	1.0×10^{-10}	.0575	.064 \pm .02
C	2.0×10^{-10}	.0800	
J	2.0×10^{-10}	.1169	.099 \pm .03
B	4.0×10^{-10}	.1413	
E	1.0×10^{-9}	.1415	
F	1.0×10^{-9}	.2011	
G	1.0×10^{-9}	.1526	
H	1.0×10^{-9}	.1386	.151 \pm .03
I	1.0×10^{-9}	.1275	
A	1.0×10^{-9}	.1419	
U	1.0×10^{-8}	.3453	

Figure 14. Graph of the Cadmium Data

Since the plot covers 3-1/2 orders of magnitude, the inset in the upper right hand corner was made. This point and those at 1×10^{-9} gm. Cd have been moved one major division along the slope. The slope of the curve is 2.71×10^7 , the intercept is 0.093, and the correlation coefficient, r , is 0.88.

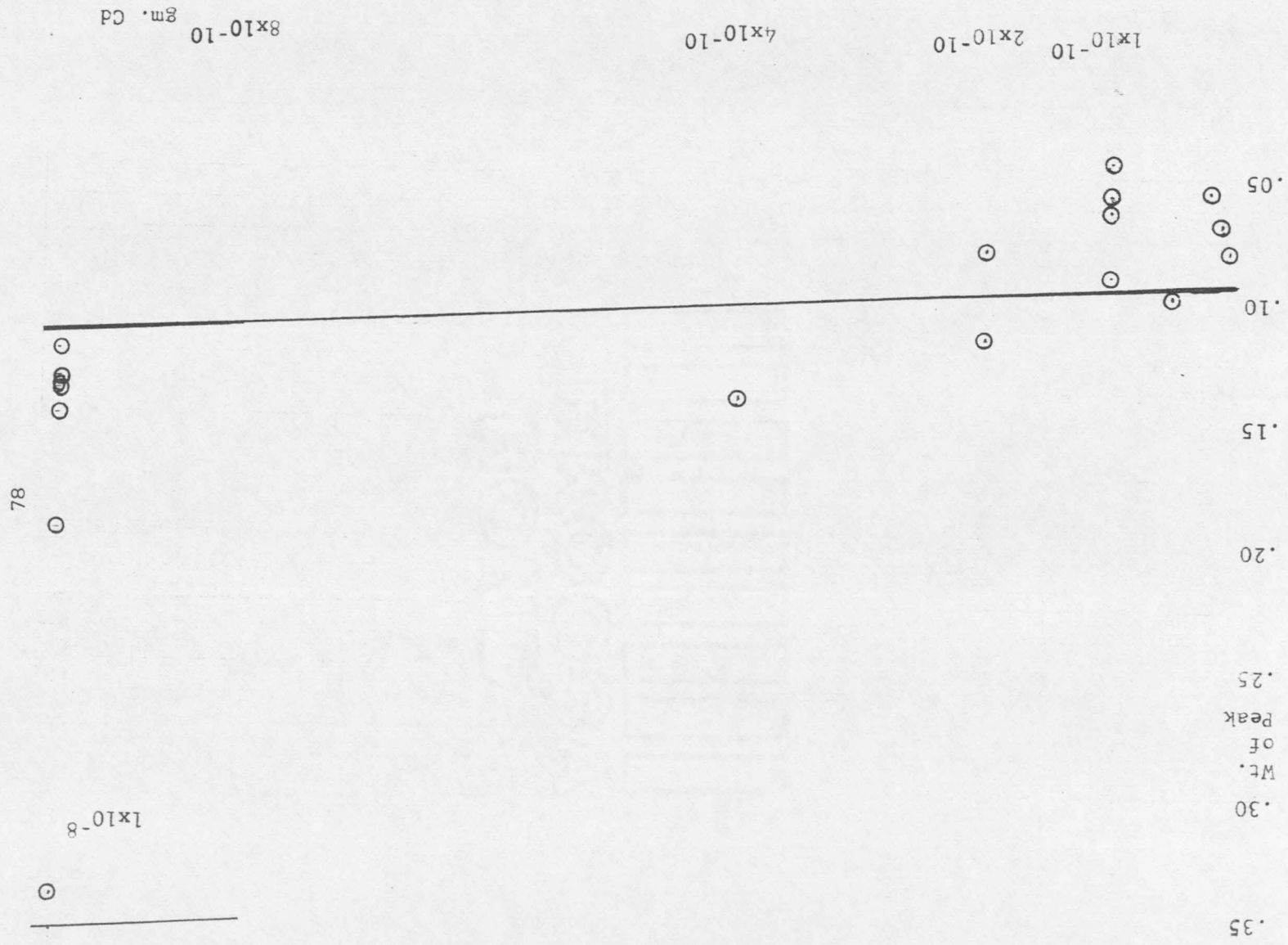


Table 11. Reproducibility Study, λ Pipets (at 20.5°C)

<u>100 λ Oxford Sampler</u>		<u>10 λ Eppendorf</u>	
<u>Grams of Water</u>		<u>Grams of Water</u>	
Total	Difference	Total	Difference
7.6589	.0974	8.8693	.0105
7.7563	.0981	8.8798	.0097
7.8544	.0979	8.8895	.0116
7.9523	.0975	8.9011	.0101
8.0498	.0968	8.9112	.0101
8.1466	.0985	8.9213	.0100
8.2451	.0969	8.9313	.0107
8.3420	.0973	8.9420	.0102
8.4393	.0977	8.9522	.0100
8.5370	.0972	8.9622	.0096
8.6342		8.9718	
1000 ($\bar{x} \pm s$)	97.5 \pm .5	1000 ($\bar{x} \pm s$)	10.3 \pm .6

<u>20 λ Eppendorf</u>		<u>5 λ Eppendorf</u>	
8.6549	.0207	8.9771	.0053
8.6756	.0201	8.9824	.0047
8.6957	.0199	8.9871	.0053
8.7156	.0200	8.9924	.0051
8.7356	.0188	8.9975	.0051
8.7544	.0211	9.0026	.0054
8.7755	.0210	9.0080	.0044
8.7965	.0207	9.0124	.0052
8.8172	.0205	9.0176	.0053
8.8377	.0211	9.0229	.0049
8.8588		9.0278	
1000 ($\bar{x} \pm s$)	20.4 \pm .7	1000 ($\bar{x} \pm s$)	5.1 \pm .3

deviations range from a low of about one-half of one percent to about six percent.

Copper

As another application of the technique, the analysis of copper at 872°C at 3248Å⁰ was attempted. Ten nanograms of copper could not be detected under these conditions. From experience with the graphite furnace it is known that copper requires a higher temperature for analysis. From some unpublished work in this laboratory with a graphite furnace, the optimum temperature was found to be above 2600°C, obviously above the limit for platinum which melts about 1770°C.

Chapter 5

APPLICATION OF THE PLATINUM ATOMIZER TO POTASSIUM VAPOR PRESSURE MEASUREMENTS FOR MHD

MAGNETOHYDRODYNAMICS

Magnetohydrodynamics (MHD) is a more efficient means of generating electricity from the combustion of a fuel. The prospective fuel is coal. The system is envisioned to work basically as follows.

Powdered coal is mixed with a small amount (about 1%) of a "seed" compound. The mixture is blown into a combustion chamber where it is mixed with hot air (which may be enriched with oxygen). The coal burns and the seed compound vaporizes and at least partially ionizes. The expanding gas (now a plasma) exhausts down the MHD channel where powerful magnets cause the paths of the positive ions to bend in one direction and the paths of the electrons and negative ions to bend in the opposite direction. Electrical contacts collect the electricity thereby produced, which is in the form of direct current. The current is converted into alternating current of the proper voltage and frequency and fed into the power grid. The heat in the exhaust from the MHD channel will then drive a conventional steam turbine electrical generation plant whose electricity will also be put into the power grid. The gases are treated to remove the seed compound and pollutants, then exhausted into the atmosphere, some of their residual heat being used to preheat the air for burning in the combustion chamber.

The hot, liquid slag containing dissolved seed is processed to remove the seed for recycling, and the slag is discarded or used in making road beds, building blocks, etc.

THE IMPORTANCE OF POTASSIUM TO THE MHD PROJECT

The seed compound must be an easily ionizable substance whose use is economically feasible. Its purpose is to increase the conductivity, hence the efficiency of the electrical generation in the MHD channel [83]. The problem is one of temperature and one of materials. At a few thousand degrees kelvin, the exhaust gases from burning coal is only very slightly ionized. Higher temperatures increase the degree of ionization, but materials for construction of the channel (its conductors and insulators) will melt in the range between 2000 and 3000°K [83]. The addition of a seed compound which is much more easily ionized than the exhaust gases themselves, increases the conductivity of the plasma making it feasible to operate the channel in the 2000°K range [83].

A potassium compound has been chosen for the seed because it is the best compromise in terms of ease of ionization and cost. Its ease of ionization (100 kcal/gram-atom) is the third from the lowest of all elements. Only rubidium (96 kcal/gram-atom) and cesium (90 kcal/gram-atom) being lower. Sodium has an ionization energy of 119 kcal/gram-atom [77].

If one uses the cost of the metal in 1964 as a rough guide to the relative cost of the compounds of these elements, sodium is lowest (\$0.15-0.20/lb), potassium is about ten times greater (\$2/lb), and rubidium and cesium are more than 50 times more expensive than potassium (\$100/lb and \$100-150/lb, respectively) [78].

It is not economically feasible to use a seed compound just once through the channel, hence it must be recovered from the exhaust gas and the slag in which it will dissolve. In order to know how best to recover the seed, and how much is recoverable, knowledge of the vapor pressures of potassium over the slags under various conditions is necessary. Obtaining these kinds of data was one of the objectives of this research group. Another objective was to develop a system to monitor the potassium atom concentration in the channel while it is operating. Both of these require the measurement of potassium in the vapor state, hence a system to make these measurement is necessary. Development of a system for this purpose was the objective of the later portion of this thesis research.

THE WOODRIF FURNACE--A MODEL FOR THE MHD CHANNEL FOR VAPOR PRESSURE STUDIES

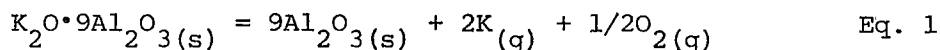
Systems operating in the range of 1500 to 2500°K which would be suitable for studies of the vapor pressure of potassium are not common. The Woodriff furnace was proposed as a good candidate, due to

its long pathlength, constant temperature mode of operation and its ability to operate in this temperature range.

The difference in the slopes of log of absorbance due to potassium vs. $1/T^{\circ}K$ curves in the graphite furnace with data obtained by other methods (such as mass spectroscopy or thermal gravimetric analysis as used by the National Bureau of Standards (NBS) indicated that the residence time was reduced possibly due to the graphite reacting with the potassium vapor. Thus, the effective vapor pressure appeared lower with the graphite furnace. In order to test this theory and to test the effects of different conditions (oxidizing, neutral, reducing, presence of hydrogen and/or water vapor, etc.) on the vapor pressure of potassium, a completely non-carbon system was needed. The platinum furnace previously described has proved to be the most suitable non-carbon system developed so far, because of its ability to operate under the different conditions mentioned above. In an initial test it has reproduced the NBS vapor pressures within limits of experimental error on an NBS standard sample and thus eliminated the problems found with the graphite atomizer.

COMPARISON OF THE RESULTS OF THE GRAPHITE AND PLATINUM
ATOMIZERS IN DETERMINING THE VAPOR PRESSURE OF
POTASSIUM

A vapor pressure standard was needed to calibrate the platinum and graphite atomizers. According to E. R. Plante of the National Bureau of Standards [45], vaporization of K_2O takes place independent of the composition of the sample for the $K_2O \cdot 9Al_2O_3$ -alumina system, and is dependent only on the temperature. Therefore, this makes an excellent standard. (This is analogous to the boiling point of a pure liquid which depends only upon the pressure and not on the amount of material present.) According to Plante [45], the reaction taking place is



and the potassium vapor pressure is given by:

$$\log P_K(K_2O \cdot 9Al_2O_3) = -21453/T^\circ K + 7.4866 \quad \text{Eq. 2}$$

Since absorbance is directly related to concentration and concentration is directly related to pressure, a plot of $\log P_K$ vs. $1/T^\circ K$ should be a straight line.

In order to measure the vapor pressure of potassium, the sample to be analyzed was placed into a Knudsen cell. A Knudsen cell is a closed cup about 6 mm outside diameter and 10 mm high with a pinhole in the top. It was made from 0.010 inch thick platinum sheet. The

ends were 1/4 inch diameter disks made by cutting the platinum sheet with a paper punch. One end was welded on and a 0.22 mm hole was drilled through its center. The sample was placed into this Knudsen cell and the bottom welded on using a heat sink to avoid overheating the sample.

Equilibrium of potassium vapor and oxygen with the solid sample (Equation 1) was established within the cell. Through the pinhole effused an amount of vapor assume to be proportional to the vapor pressures of the gaseous species within the cell. The second important assumption was that the loss of this vapor from the cell did not disturb the equilibrium within [34].

An experiment was set up in which the same sample (of $K_2O \cdot 9Al_2O_3$ -alumina sent to us by R. Plante of the National Bureau of Standards) in the same Knudsen cell was analyzed in the graphite furnace and then in the platinum furnace at various temperatures. The samples were put into the graphite or platinum furnace and allowed to reach equilibrium as evidenced by a plateau in the absorbance.

The platinum furnace reached equilibrium much more rapidly than the graphite furnace for these samples for a given temperature. Equilibrium might be reached in 1 to 10 minutes in the platinum furnace as opposed to perhaps 45 minutes in the graphite furnace. This was probably due to the graphite absorbing the potassium then releasing it at a later time until a potassium-graphite to potassium vapor

equilibrium was established. This similar problem does not occur in the platinum furnace where only the rate of diffusion controls the attainment of equilibrium.

The results of this experiment are shown in Table 12 and plotted in Figure 15.

Using a least squares fit for log absorbance vs. $1/T^{\circ}K$ gave the following equations:

$$\text{Graphite:} \quad \log \text{ abs.} = \frac{-7950}{T} + 3.78 \quad \text{Eq. 3}$$

$$\text{Platinum:} \quad \log \text{ abs.} = \frac{-22400}{T} + 14.1 \quad \text{Eq. 4}$$

$$\text{N.B.S.:} \quad \log P_K = \frac{-21453}{T} + 7.4866 \quad [45] \quad \text{Eq. 5}$$

The pressure, P_K , of potassium in Equation 1 is not exactly equal to the concentration (hence the absorbance if Beer's law is followed) but it is within a few percent [43]. The change in enthalpy, ΔH , for the above reaction can be calculated from the slopes of the log absorbance vs $1/T$ curves (see Figure 15) using the equation [46]:

$$P = C e^{-\frac{E_a}{RT}} \quad \text{Eq. 6}$$

where P is the pressure or absorbance, C is a constant which is determined by the geometry of the system, E_a is the activation energy or change in enthalpy, R is the gas constant, 1.987 calories/g- $^{\circ}K$, and

Table 12. Results in the Platinum and Graphite Furnaces for the Same Sample of $K_2O \cdot 9Al_2O_3$ -alumina

<u>Platinum Furnace</u>			
<u>Temperature, °C*</u>	<u>°K</u>	<u>1/T°K X10⁻⁴</u>	<u>Absorbance</u>
1070±10	1343±10	7.45±.05	0
1110±10	1383±10	7.23±.05	.008±.0007
1155±10	1428±10	7.00±.05	.023±.0007
1170±10	1443±10	6.93±.05	.040±.0007
<u>Graphite Furnace</u>			
1100±10	1373±10	7.28±.05	.011±.0007
1210±10	1483±10	6.74±.05	.020±.0007
1310±10	1583±10	6.32±.05	.066±.0007

* As read with an optical pyrometer.

Figure 15. A Comparison of the Log Absorbance vs. $1/T^{\circ}K$ for Potassium in the Platinum and Graphite Furnaces with the Values Obtained by the National Bureau of Standards.

The sample was $K_2O \cdot 9Al_2O_3$ -alumina in cup C with a 0.17 mm hole.

The slope of the line in the graphite furnace is -7950, and the intercept is 3.78. The correlation coefficient is $r = .70$.

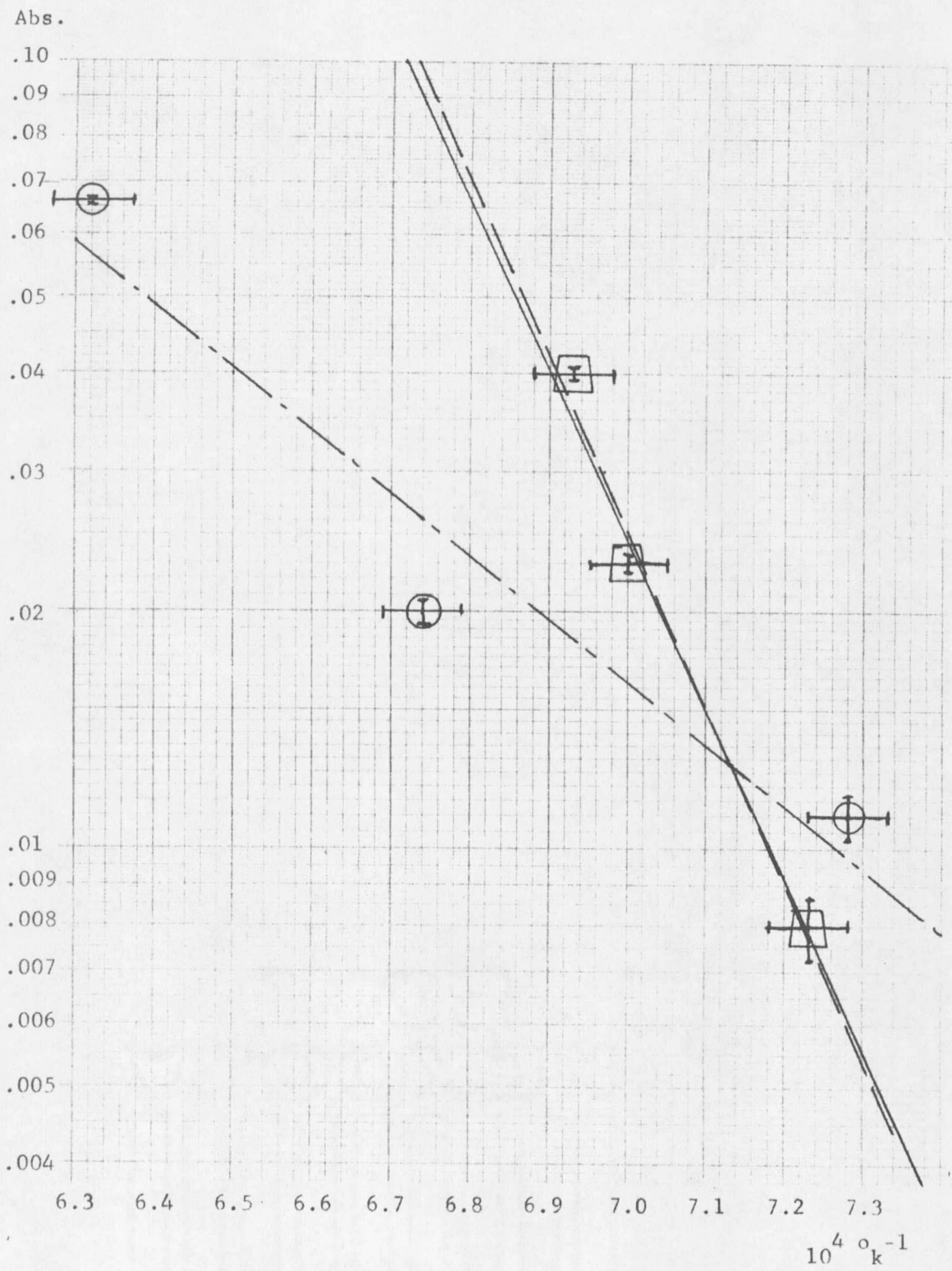
The slope of the line in the platinum furnace is -22,400, and the intercept is 14.1. The correlation coefficient is $r = .99$.

The values from the N.B.S. are slope is -21,453 and intercept is 7.4866 [45].

○ Graphite furnace ————

□ Platinum furnace ————

N.B.S. ————



T is the temperature in °K. Taking the natural log of both sides, then converting to base-10 logs gives:

$$\log P = \frac{-E_a}{2.303R} \left(\frac{1}{T}\right) + C' \quad \text{Eq. 7}$$

where C' is a constant. Equation 7 is in the form of $y=mx+b$ hence the log of the absorbance or pressure plotted against $1/T$ should be a straight line. The resulting ΔH 's are:

Graphite: 36.1 ± 10.3 kcal/mole of gas formed,

Platinum: 102.6 ± 16.8 kcal/mole of gas formed,

N.B.S.: $98.2 \pm$ kcal/mole of gas formed [45].

Equations 3 and 4 were derived from a least squares fit for the $\log A$ vs. $1/T$. The $\log A$'s for graphite and platinum were equated and the temperature at this point was determined. The temperature was substituted back into one of the equations to obtain the absorbance. This gave the point at which the two lines crossed. This point lies at an absorbance of 0.0128, $1/T = 7.13 \times 10^{-4}$ corresponding to a temperature of 1401°K. Using an arbitrary absorbance of 0.1 for platinum and 0.05 for graphite, the respective temperatures were calculated. A straight line was then plotted between the common point and these other two points. This gives the line of least squares fit for the given points.

Since our principal interest was in the slope of the curves, the N.B.S. curve was translated such that it, too, passed through the common point. This was done by inserting the absorbance and $1/T$ values of the common point into Equation 2, and solving for the intercept.

The results indicate that the process which is occurring within the platinum furnace is similar to that measured by the N.B.S. using mass spectrographic analysis and gravi thermometric analysis, i.e., that it is diffusion controlled only. This process is the vaporization of potassium and oxygen gas from the potassium oxide in β -alumina, and it is completely diffusion controlled. It is not complicated by other factors, such as condensation and revaporization from carbon grains in the graphite, with that consequential change in enthalpy as shown by a different temperature dependence of the slope of the log absorbance vs. $1/T$ curve for graphite (see Figure 15).

The ability to reproduce the results of the N.B.S. work is critical to the MHD effort at Montana State University. It means that standard samples which have a known temperature dependence for their vapor pressures can be used to calibrate the furnace, which, in turn, can act as a secondary standard for actual coal slag samples. By using a variety of samples and conditions, thermodynamic data can be obtained which will be useful in selecting the best method for seed recycling.

THE EFFECT OF OXIDIZING VS. REDUCING CONDITIONS ON THE
SENSITIVITY OF THE FURNACE FOR POTASSIUM

The knowledge of whether or not it is possible to analyze for potassium under oxidizing conditions as well as under reducing conditions is critical for the MHD project, since it is proposed to analyze for potassium continuously by using part of the exhaust stream as the analysis volume. (For highest economic efficiency, the MHD channel should be operated under oxidizing conditions other things being equal.) Since potassium has been analyzed in the graphite furnace, it is apparent that it is possible to do the analysis under reducing conditions. Analysis for potassium under oxidizing conditions had never been attempted in our laboratory, since the graphite furnace by its nature, cannot be operated under oxidizing conditions.

In an attempt to determine whether analysis for potassium is even possible under oxidizing conditions, a number of open cup analyses were performed using different sets of conditions. One series of experiments was done in the open air (oxidizing conditions). The second series was performed in an atmosphere of argon-4% hydrogen (reducing conditions).

The results clearly indicate that it is possible to analyze for potassium under oxidizing conditions (see Table 13). They also indicate that within experimental error (roughly $\pm 50\%$) that the sensitivity for potassium under these two sets of conditions is the same.

Table 13. Comparison of the Sensitivity of the Platinum Furnace for Potassium Under Oxidizing and Reducing Conditions

Peak Code	Potassium (grams)	Weight of Peak	$\bar{x} \pm s$	Atmosphere
S	5.5×10^{-6}	.0082		air
N	5.5×10^{-6}	.0159	$.013 \pm .005$	air
O	5.5×10^{-6}	.0161		air
M	2.2×10^{-5}	.0311		air
R	2.2×10^{-5}	.0238	$.047 \pm .034^*$	air
T	2.2×10^{-5}	.0863		air
U	2.2×10^{-5}	.0334		Ar-4% H_2
V	2.2×10^{-5}	.0446		Ar-4% H_2
W	2.2×10^{-5}	.0661		Ar-4% H_2
X	2.2×10^{-5}	.0843	$.060 \pm .021^*$	Ar-4% H_2
Y	2.2×10^{-5}	.0820		Ar-4% H_2
Z	2.2×10^{-5}	.0499		Ar-4% H_2
G	4.4×10^{-5}	.0791		air
H	4.4×10^{-5}	.0877		air
I	4.4×10^{-5}	.0763	$.071 \pm .016$	air
L	4.4×10^{-5}	.0456		air
Q	4.4×10^{-5}	.0675		air
J	1.1×10^{-4}	.1177		air
P	1.1×10^{-4}	.1441	$.131 \pm .019$	air
A'	2.0×10^{-4}	.2465		Ar-4% H_2
A	2.0×10^{-4}	.2185	$.232 \pm .014^\#$	Ar-4% H_2
B	2.0×10^{-4}	.2300		Ar-4% H_2
C	2.0×10^{-4}	.1574		air
D	2.0×10^{-4}	.3308	$.228 \pm .091^\#$	air
F'	2.0×10^{-4}	.1942		air

*,# Comparison of these two sets of averages for the same amount of potassium shows that, within experimental error, there is no difference in sensitivity in air or in Ar-4% H_2 , that is, between oxidizing and reducing conditions.

The large scatter in the points can be attributed to two different factors. First, the pedestal was not seated when these experiments were done, because the platinum cup kept sticking to the platinum walls of the side tube, necessitating the shut-down of the furnace to retrieve them. This meant that all of the potassium vapor did not necessarily vaporize into the analysis volume. This situation could be solved by redesigning the pedestal, but the materials to rebuild the pedestal in a different form were not available at the time this work was done. The second cause of the large scatter in the points was probably because the system had varying amounts of water vapor present at different times. It was not realized at this point in the experimentation the tremendous effect that water vapor has on the sensitivity of the furnace for potassium.

Two important conclusions can be drawn from this experiment: it is possible to determine potassium under oxidizing conditions and the sensitivity for potassium under oxidizing vs. reducing conditions does not vary more than 50%.

THE EFFECT OF WATER VAPOR ON THE SENSITIVITY ON THE FURNACE FOR POTASSIUM

Throughout the experiments with potassium, the furnace had not given the reproducibility one should expect from the Woodriff furnace. That was not too surprising since the first models of most complex systems of equipment have problems. Much of the equipment used with

the furnace (the light system, analytical electronics and power supply) had been refined over long years, and should not have been the source of any trouble. It was apparent that there was a factor working in the platinum system which was not a problem with the graphite furnace.

The observation was made that sometimes a given Knudsen cell containing a given sample gave results which saturated the system at a given temperature, yet at other times that same sample gave almost no signal at the same temperature.

The effect was very startling one time when open cup potassium samples were being analyzed. In trying to arrive at an order-of-magnitude sensitivity of the furnace for potassium, one sample of 1×10^{-4} g of potassium (a tremendous amount, relatively speaking) was introduced into the furnace when the atmosphere was argon-4% hydrogen. The chart recorder "pegged" and remained pegged for 8 minutes after the cup was moved down and allowed to cool. After this time the recorder began charting the usual exponential decay.

At this point, the window (the quartz tube covering the entrance port; see Figure 10) was opened to remove the cup, and an extreme drop in sensitivity was noted on the chart recorder. When the window was closed, the pen returned (after a time) to where it would have otherwise been on the exponential decay. From this point it followed the exponential curve until the window was again opened. Opening and closing the window successively damped the sensitivity and

then returned it to normal (see Figure 16). It was apparent that there was one of two factors working at this point. Either opening the window depressurized the system slightly making the argon-hydrogen mixture take a different path, or air was entering the system and causing a tremendous effect.

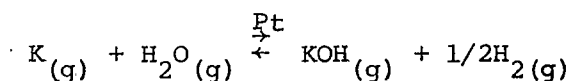
Disconnecting the gas supply momentarily had little effect. Plugging the exit flow of the gas had more effect, but it was much smaller than that caused by opening the window.

It had been noted that when doing analysis in the argon-hydrogen atmosphere, that water was being deposited on the water-cooling tubes inside the furnace to such an extent that there were puddles in the bottom of the furnace. This seemed somewhat strange since there was an 1100°C heater tube less than ten cm away. On the other hand, the water circulating through these tubes was cool. The production of water from the hydrogen in the atmosphere plus any oxygen leaking in being catalyzed on the hot platinum surface was not unexpected, but the amount of water produced was very unexpected. It had been thought that the slightly pressurized system would tend to keep the external oxygen out. Apparently it does a poor job of it.

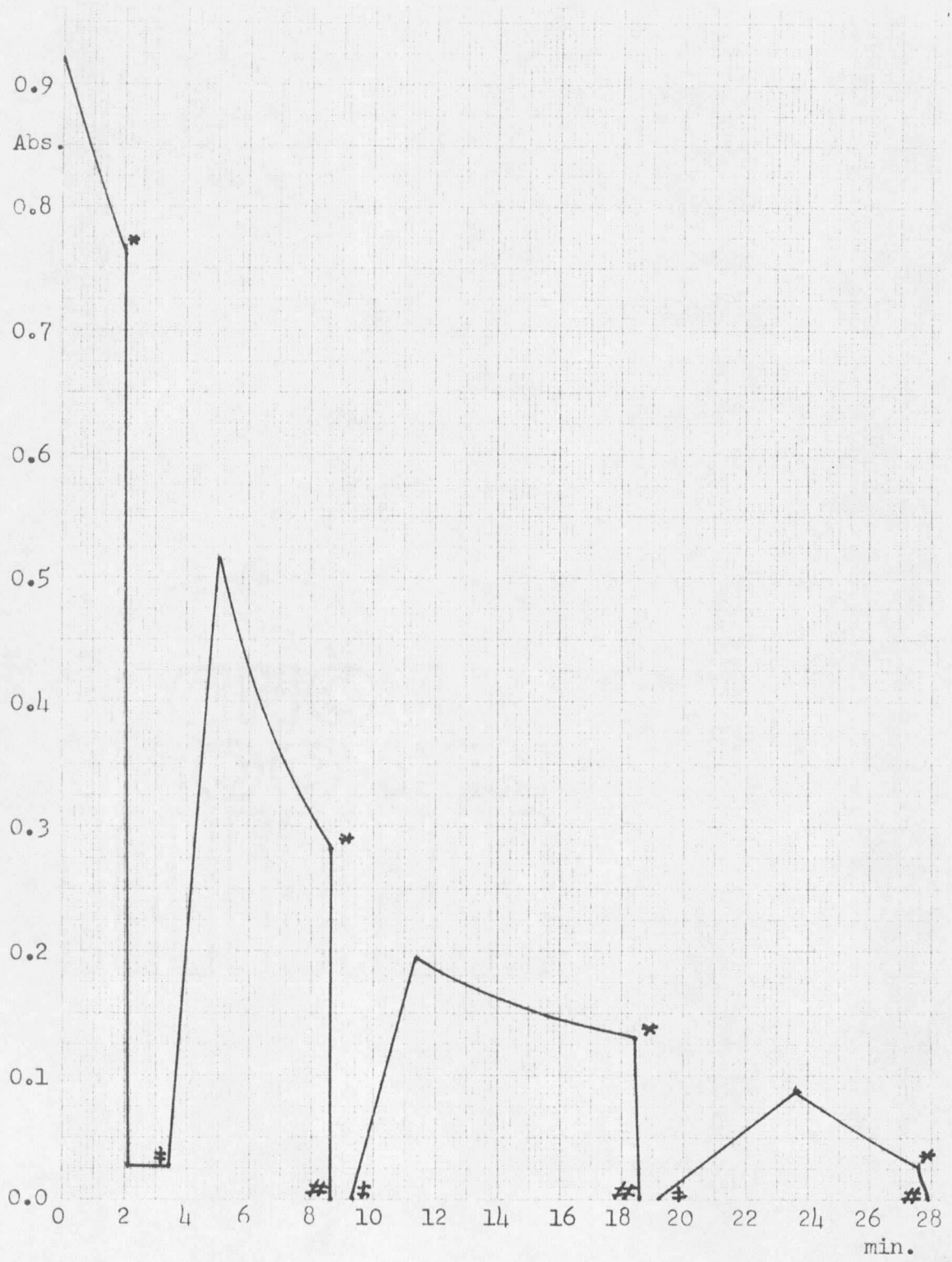
To test whether it was indeed water that was causing the problem, two of the Knudsen cells were introduced after purging the system with the argon-hydrogen atmosphere for about four hours. The window was not opened during these experiments. After equilibrium had been

Figure 16. Effect on the Vapor Pressure of Potassium of Opening the Sample Port to Air in the Presence of Hydrogen

One tenth of a milligram of potassium was introduced into the furnace in an open platinum cup. This caused the recorder to limit. The cup and pedestal were lowered and the recorder remained limited for eight minutes before time $t = 0$ on this plot. After the eight minute period was passed, the recorder recorded the normal exponential decay. At the points marked *, the window of the sample port was opened (initially to remove the cooled cup). This introduced air which depressed the amount of potassium vapor in the light path. At points marked ‡ the window was closed, and the amount of potassium vapor slowly returned to the value it would have had at that time if the window had not been opened. This indicates that an equilibrium was occurring, probably the following:



This reaction may be catalyzed by platinum. At points marked #, the baseline dropped below zero on the recorder. The temperature of the furnace was 1157°C . A more sophisticated study of the atmospheric dependence of this reaction should reveal important kinetic and thermodynamic data.



established and a plateau obtained, the gas stream was disconnected and quickly connected to a system (previously purged with argon-hydrogen) which bubbled the gas stream through the water (see Figure 17). With cup C containing the $K_2O \cdot 9Al_2O_3$ -alumina sample and operating at $1100^\circ C$ the effect was dramatic. A drop in sensitivity of about one and a half orders of magnitude was noted. The reaction was apparently reversible, since removal of the gas stream from the water-bubbling system returned the absorbance to approximately where it had been before. Bubbling the gas through water cooled to $0^\circ C$ instead of room temperature (21.5 or $23^\circ C$) reduced the effect and increased the absorbance, as would be expected since the vapor pressure of water is lower at a lower temperature. (The vapor pressure of water is 21.1 torr at $23^\circ C$, 19.2 torr at $21.5^\circ C$, and 4.6 torr at $0^\circ C$ [79]!) These few simple experiments seem to indicate that the amount of suppression of the absorbance is not directly proportional to the vapor pressure of water, however, a more controlled and quantitative experiment should be done to test this point.

It was apparent at this point that the amount of water in the atmosphere inside the furnace (or oxygen which was converted to water when hydrogen was present) was a major factor in the inconsistent results the furnace had been giving. This is not a problem with the graphite furnace, because the graphite itself reacts with water at high temperatures forming a mixture of hydrogen and carbon monoxide

Figure 17. Effect on the Vapor Pressure of Potassium of Adding Water Vapor to the Entering Gas Stream

First group: Sample $K_2O \cdot 9Al_2O_3$ -alumina in cup C.

Temperature: $1108 \pm 5^\circ C$.

Gas flow: 200 ml/min Ar + 8 ml/min H_2

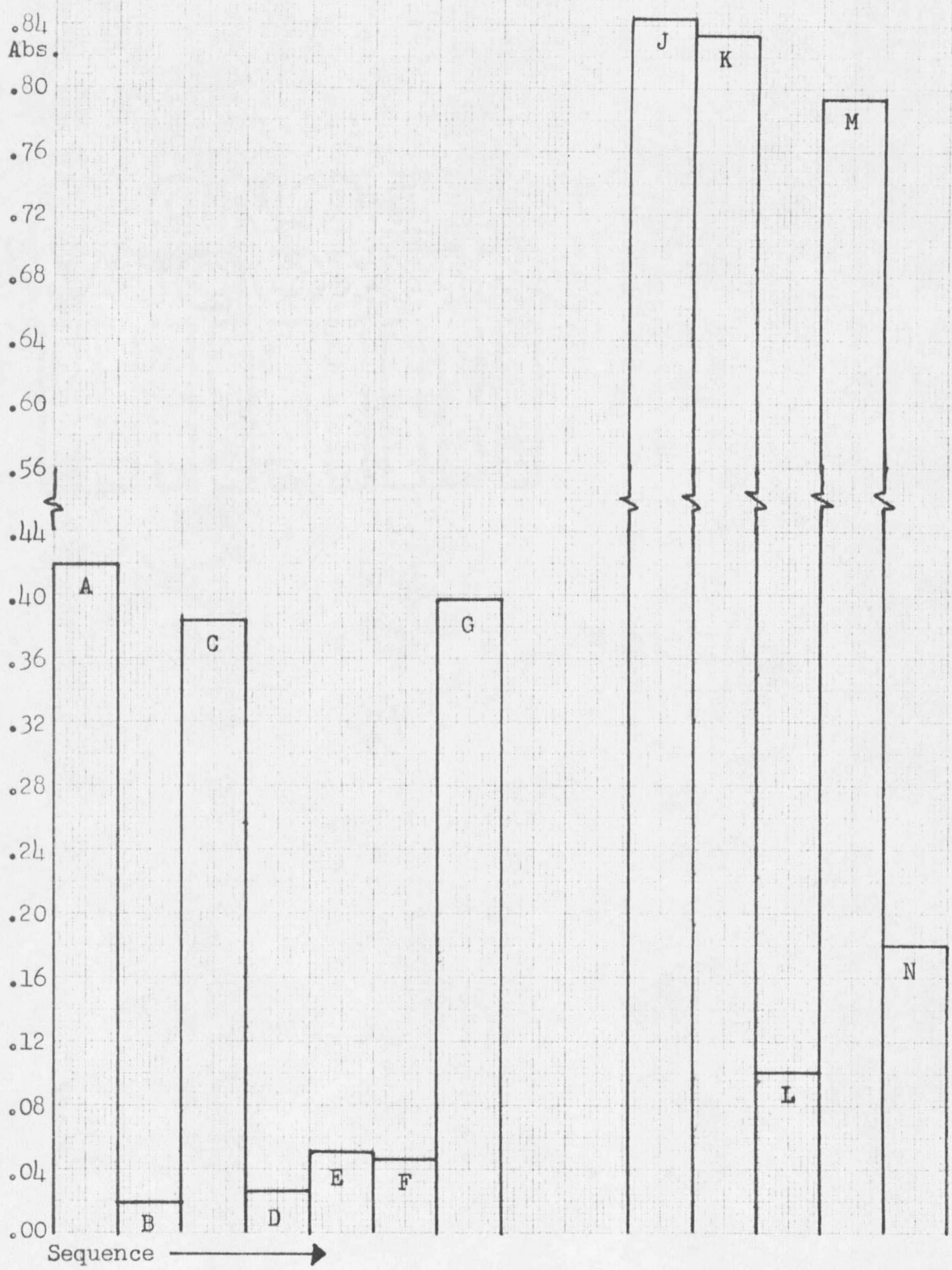
- A: No water added
- B: Gas bubbled through water at $23^\circ C$
- C: No water added
- D: Gas bubbled through water at $0^\circ C$
- E: Gas bubbled through water at $0^\circ C$ and H_2 flow doubled
- F: Gas bubbled through water at $0^\circ C$
- G: No water added

Second group: Sample 1.5A Al:K=3:2 April 6, 1976 in cup H.

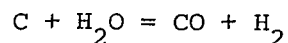
Temperature: $928 \pm 10^\circ C$

Gas flow: 200 ml/min Ar + 8 ml/min H_2

- J: No water added
- K: No water added
- L: Gas bubbled through water at $21.5^\circ C$
- M: No water added
- N: Gas bubbled through water at $0^\circ C$



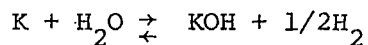
called water gas according to the equation [80]:



The effect of this is to shorten the lifetime of the heater tubes in the furnace, but no water is present to suppress the absorption of potassium. The hydrogen produced has little effect (see the section on oxidizing vs. reducing conditions).

THE EFFECT OF THE HYDROGEN-WATER VAPOR COMBINATION ON THE SENSITIVITY OF THE FURNACE FOR POTASSIUM

Another experiment was performed while the gas stream was bubbling through water at 0°C. The amount of hydrogen in the gas stream was approximately doubled. This caused an increase in the absorbance. Decreasing the amount of hydrogen to approximately its original value decreased the absorbance again (see Figure 17). This fact plus the effect of water suggests that the following reaction is taking place in the gas phase:



and the reaction is reversible.

An additional experiment is recommended in this series. That is one where a plateau is reached in an argon-4% hydrogen atmosphere using one of the Knudsen cells, and then with no water present, the hydrogen concentration should be doubled. Since there was little

change in sensitivity when the system went from air to argon-4% hydrogen, little change in the sensitivity for potassium would be expected if no water was present when the hydrogen concentration was changed.

RESULTS OF THE VAPOR PRESSURE STUDIES OF POTASSIUM

The two graphs for the standard $K_2O \cdot 9Al_2O_3$ -alumina samples are plotted in Figure 18 from data in Tables 14 and 15. One sample had been used for many hours in the platinum and the graphite furnace (where its temperature reached about $1500^\circ C$). The other was a fresh sample of the same material in the same cup (Knudsen cell), and had not been heated above $1000^\circ C$.

The results from the old sample closely match those of the National Bureau of Standards. Our work gives a slope of $-21,400$. That of Plante at the N.B.S. is $-21,453$ [45]. The fact that the intercepts do not match (17.2 for our work, 7.4866 for that of Plante [45]) is of no consequence, since the intercept is dependent upon the geometry of the particular system used (changing the hole diameter, for instance, would change the intercept. It would not change the slope; see also Figure 15).

The reason that the renewed sample does not have the same slope as the old sample is not certain. It has been suggested that perhaps the alumina is not in the correct crystal structure and needs to be heated to become the form which forms an equilibrium system with the

Figure 18. Graphs of Log Absorbance vs. $1/T^{\circ}K$ for Samples of $K_2O \cdot 9Al_2O_3$ -alumina.

Data from Table 14.

Symbol Δ

Sample (Old $K_2O \cdot 9Al_2O_3$ -alumina)

Cup C with 0.22 mm hole

Atmosphere Ar-4% H_2

Platinum furnace

Slope = -21,400

Intercept = 17.2

Correlation coefficient, $r = 0.958$

Data from Table 15.

Symbol O

Sample (Renewed $K_2O \cdot 9Al_2O_3$ -alumina)

Cup C with 0.22 mm hole

Atmosphere Ar-4% H_2

Platinum furnace

Slope = -6,600

Intercept = 5.42

Correlation coefficient, $r = 0.977$.

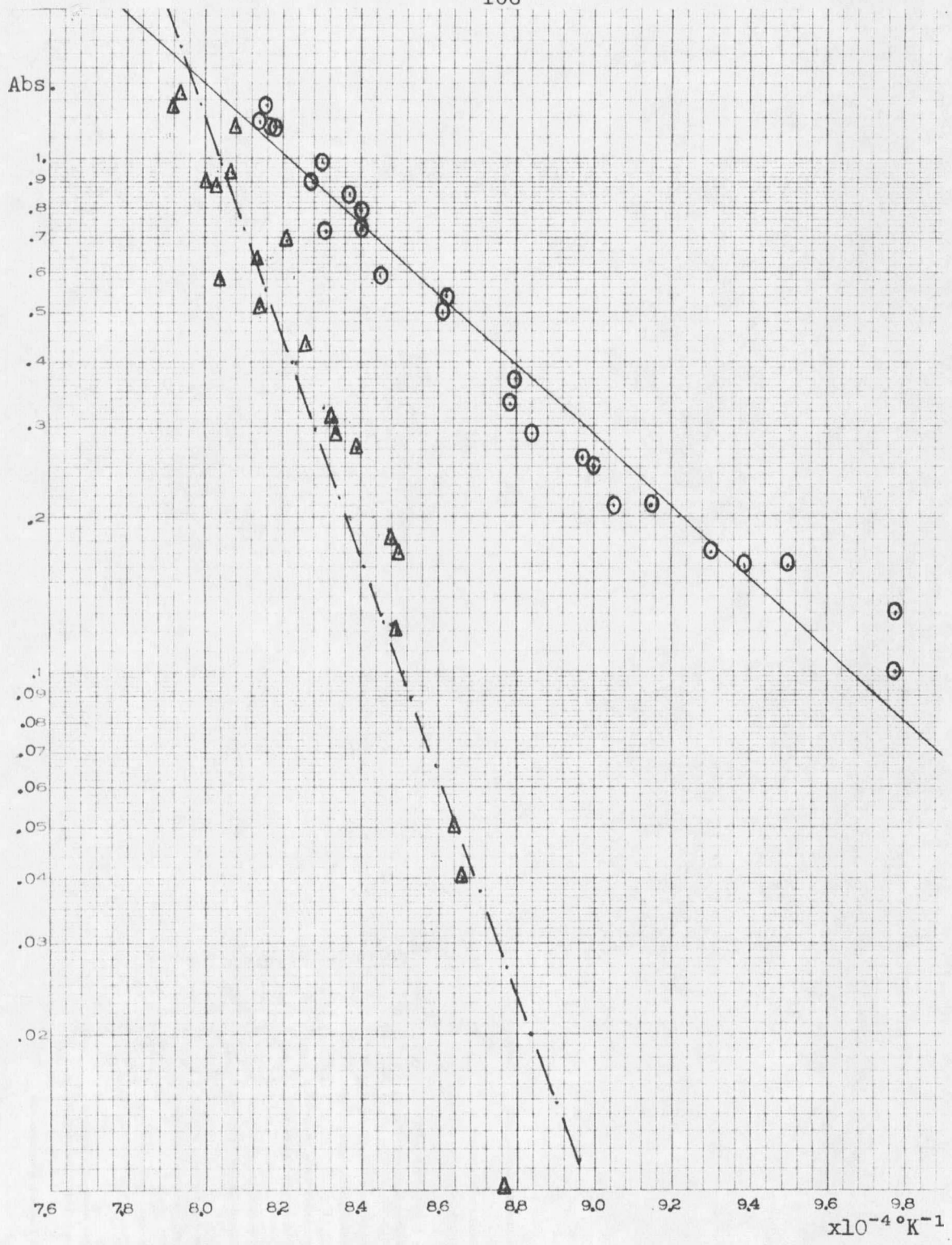


Table 14. Potassium Vapor Pressure Data with Sample
(Old $K_2O \cdot 9Al_2O_3$ -alumina) Cup C

Temperature °C	Peak Height Divisions	Absorbance	$1/T^{\circ}K$ ($\times 10^{-4}$)
1004	101	1.32*	7.38
945	53	.69	8.21
965	88	1.15	8.08
919	21	.27	8.39
903	13	.17	8.50
955	48	.63	8.14
987	101	1.32	7.94
972	68	.89	8.03
937	33	.43	8.26
912	14	.18	8.44
955	39	.51	8.14
976	69	.90	8.01
905	9	.12	8.49
839	0	.00*	8.99
966	72	.94	8.07
990	97	1.27	7.92
971	44	.58	8.04
928	24	.31	8.33
867	1	.01	8.77
882	3	.04	8.66
928	22	.29	8.33
884	4	.05	8.64

* These values not used in the calculations--recorder was limited.
See Figure 18 for a graph of this data. Symbol Δ .

Table 15. Potassium Vapor Pressure Data with Sample (Renewed
 $K_2O \cdot 9Al_2O_3$ -alumina) Cup C

Temperature °C	Peak Height Divisions	Absorbance	1/T°K (x10 ⁻⁴)
750	8	.10	9.78
802	13	.17	9.30
832	16	.21	9.05
858	22	.29	8.84
888	38	.50	8.61
935	69	.90	8.28
948	88	1.15	8.19
952	98	1.28	8.16
932	75	.98	8.30
922	65	.85	8.37
918	60	.79	8.40
888	41	.54	8.61
864	28	.37	8.80
842	20	.26	8.97
820	16	.21	9.15
780	12	.16	9.50
918	56	.73	8.40
955	91	1.19	8.14
950	89	1.17	8.18
957	>101	>1.32*	8.13
930	55	.72	8.31
910	45	.59	8.45
865	25	.33	8.79
838	19	.25	9.00
792	12	.16	9.39
750	10	.13	9.78

* This value not used in the calculations--recorder was limited.
 See Figure 18 for a graph of this data. Symbol O.

$K_2O \cdot 9Al_2O_3$ component [46]. According to Cotton and Wilkinson, anhydrous Al_2O_3 exists in two forms, $\alpha-Al_2O_3$ and $\lambda-Al_2O_3$. (A note in that text says, "' $\beta-Al_2O_3$ ' is actually $Na_2O \cdot 6Al_2O_3$, see R. Scholder and M. Mansmann, Z. anorg. Chem., 321, 246 (1963)"). The $\alpha-Al_2O_3$ is stable at high temperatures and is definitely metastable at low temperatures. The $\alpha-Al_2O_3$ can be prepared from any other forms (including hydrated forms) by heating above $1000^\circ C$. The $\lambda-Al_2O_3$ is formed by dehydration of hydrated oxides at low temperatures ($\sim 450^\circ$) [82]. Apparently the history of the sample is important. This problem is not noticed in the graphite furnace since it is not usually operated at a temperature less than 1000° . The platinum furnace, however, was never operated over about 1300° for fear of melting the heater tube. Once the temperature of the heater tube is made more uniform, temperatures nearer the melting point of the heater tube (which is not known exactly, since it is an alloy of platinum (mp 1770) and rhodium (mp 1966)) [77].

The difference in the history of the sample may be causing the same effect in the higher potassium 1.5A Al:K=3:2 April 6, 1976 sample as well. Note that it, too, has a higher slope for the higher set of temperatures (see Figure 19 and Tables 16 and 17). Note also that once the phase transformation has been made, the supposedly higher potassium level sample does indeed evolve a higher level of potassium at the same temperature.

Figure 19. Graphs of Log Absorbance vs. $1/T^{\circ}K$ for Samples of
1.5A Al:K=3:2 April 6, 1976.

Data from Table 16.

Symbol +
Sample (1.5A Al:K=3:2 April 6, 1976)
Cup H with 0.22 mm hole
Atmosphere Ar-4% H_2
Platinum furnace²
Slope = -9,230
Intercept = 7.40
Correlation coefficient $r = 0.958$

Data from Table 17

Symbol ×
Sample (1.5A Al:K=3.2 April 6, 1976)
Cup H with 0.22 mm hole
Atmosphere Ar-4% H_2
Platinum furnace²
Slope = -13,400
Intercept = 9.26
Correlation coefficient $r = 0.967$

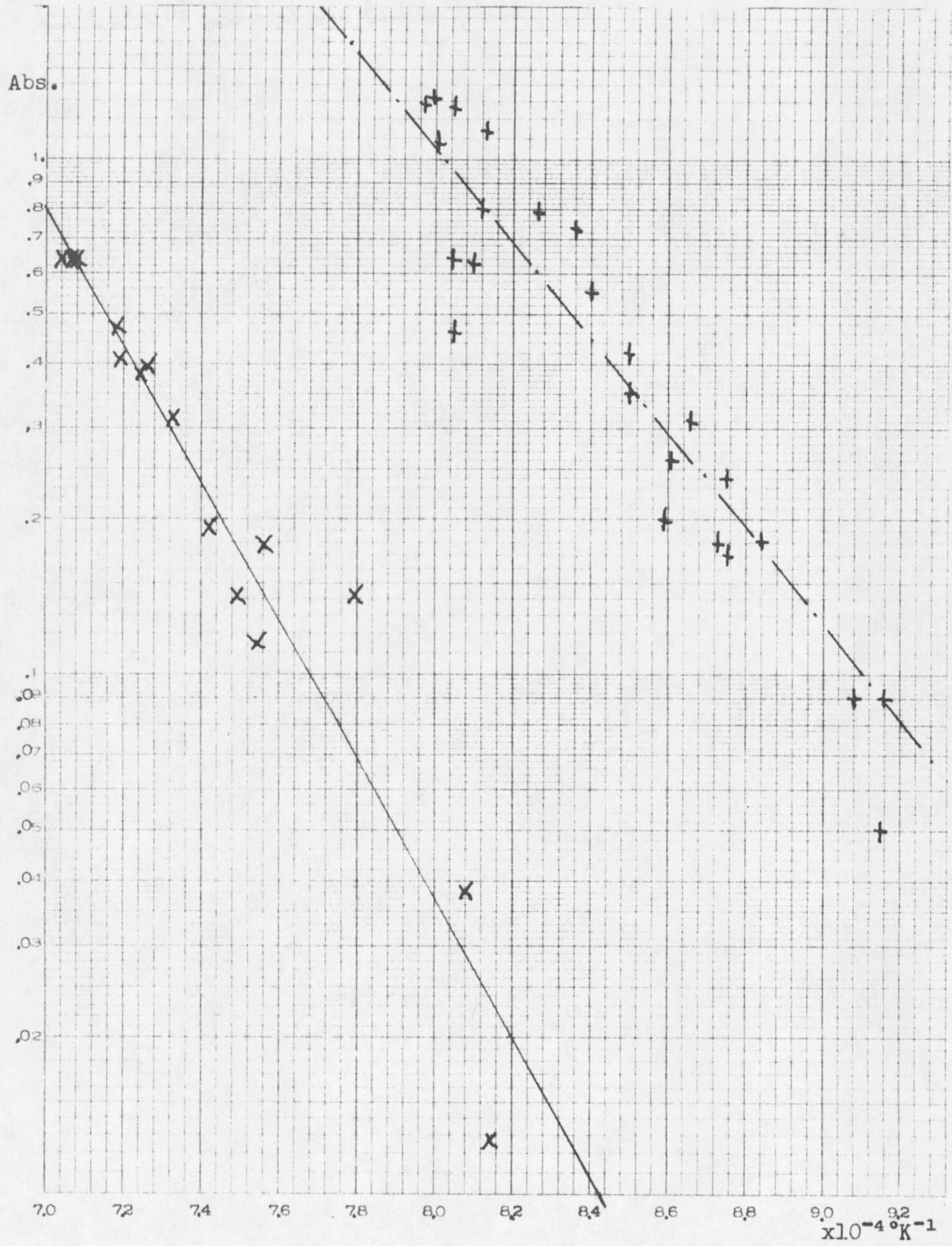


Table 16. Potassium Vapor Pressure Data with Sample (1.5A Al:K=3.2
April 6, 1976) Cup H Lower Temperature

Temperature °C	Peak Height Divisions	Absorbance	1/T°K (x10 ⁻⁴)
820	4	.05	9.15
891	15	.20	8.59
962	48	.63	8.10
970	49	.64	8.05
975	83	1.09	8.01
982	98	1.28	7.97
979	100	1.31	7.99
958	61	.80	8.12
970	35	.46	8.05
888	20	.26	8.61
872	14	.18	8.73
870	13	.17	8.75
828	7	.09	9.08
770	4	.05	9.59
904	27	.35	8.50
938	60	.79	8.26
970	98	1.28	8.05
957	86	1.13	8.13
923	56	.73	8.36
917	42	.55	8.40
903	32	.42	8.50
882	24	.31	8.66
870	18	.24	8.75
858	14	.18	8.84
819	7	.09	9.16
794	5	.07	9.37

See Figure 19 for a graph of this data. Symbol +.

Table 17. Potassium Vapor Pressure Data with Sample (1.5A Al:K=3:2
April 6, 1976) Cup H Higher Temperature

Temperature °C	Peak Height Divisions	Absorbance	1/T°K (x10 ⁻⁴)
955	1	.0128	8.14
965	3	.0384	8.08
1010	11	.1409	7.79
1050	14	.179	7.56
1140	50	.640	7.08
1092	24.5	.314	7.33
1142	50	.640	7.07
1148	50	.640	7.04
1062	11	.1409	7.49
1075	15	.192	7.42
1120	37	.474	7.18
1053	9	.115	7.54
1117	32	.410	7.19
1108	30	.384	7.24
1104	31	.397	7.26

See Figure 19 for a graph of this data. Symbol x.

Chapter 6

CONCLUSIONS, SUMMARY, AND SUGGESTIONS FOR FURTHER WORK

Of the numerous materials tested for use in the construction of vaporization chambers for constant temperature atomic absorption furnaces, graphite and platinum have given the best results. Tungsten and vitreous carbon show promise for non-oxidizing atmospheres and should be tested further.

This research has shown the value of pyrolytically coating the graphite heater tubes, cups and rods used in the conventional Woodriff furnace. Not only is the lifetime of the parts increased by this relatively simple procedure, but an increase in sensitivity and a decrease in porosity are also gained. Indications are that a completely vitreous carbon system would be even better, though it would be much more expensive.

The platinum furnace will not take the place of the graphite furnace but is a valuable complement to it. It will do some of the same analyses that the graphite furnace will do, but it will do other types of analyses as well, such as the study of the effects of atmospheric changes on the vaporization of potassium. It should be a useful tool for other physical chemistry studies as well as normal analytical chemical applications. Studies such as those of the kinetics and equilibria of high temperature gas phase, gas-liquid, gas-solid (or

any combination of these) reactions could be done. The platinum furnace can produce results comparable to results obtained with a mass spectrograph, a much more expensive instrument, and with it results have been obtained similar to those obtained by the National Bureau of Standards on N.B.S. samples. It has provided some necessary and timely data for the MHD program. With it potassium can be analyzed in the presence of oxygen (under oxidizing conditions). With it the presence of water vapor in the combustion products have been shown to cause a possibly serious problem. It has also been shown that the reaction of potassium with water is possibly reversible at high temperature.

With the knowledge gained in two prototype platinum furnaces, a third model should be built. This third generation platinum furnace should have heater tubes with a long lifetime, it should have a more uniform temperature along the length of the heater tube and side tube than is possible with the graphite furnace, and it should have none of the problems with oxidation inherent in a graphite system. It should be limited only by its temperature range, and, of course, its cost.

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