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

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 K2O.9Al2O3-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°C before the γ-Al2)3 is converted to α-A12O3, 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 O2(g) from K2o 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 AH'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.

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Approved:

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MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1977

ACKNOWLEDGMENT

I would like to thank my wife, Carol, for her patience and support.

Dr. Ray Woodriff deserves special thanks both for the encouragement offered and for being a good example of a scientific researcher.

Thanks also to Dr. John Amend, especially for the excellent example he set as a teacher.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Pyrolytically coated graphite, vitreous carbon, tantalum, tungsten and platinum were tried as heater tube materials in a long pathlength, 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°C before the γ-Al_2O_3 is converted to α-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 Woodriff 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 Woodriff 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 Woodriff furnace.

All previous Woodriff 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 Sensitivies

Element	Furnace Temperature	Wave Length, Å	Nanograms for 1% Absorption Furnace [6]	Nanograms for 1% Absorption 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 atmopshere. 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 Woodriff 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 Woodriff Furnace with Graphite Heater Tubes

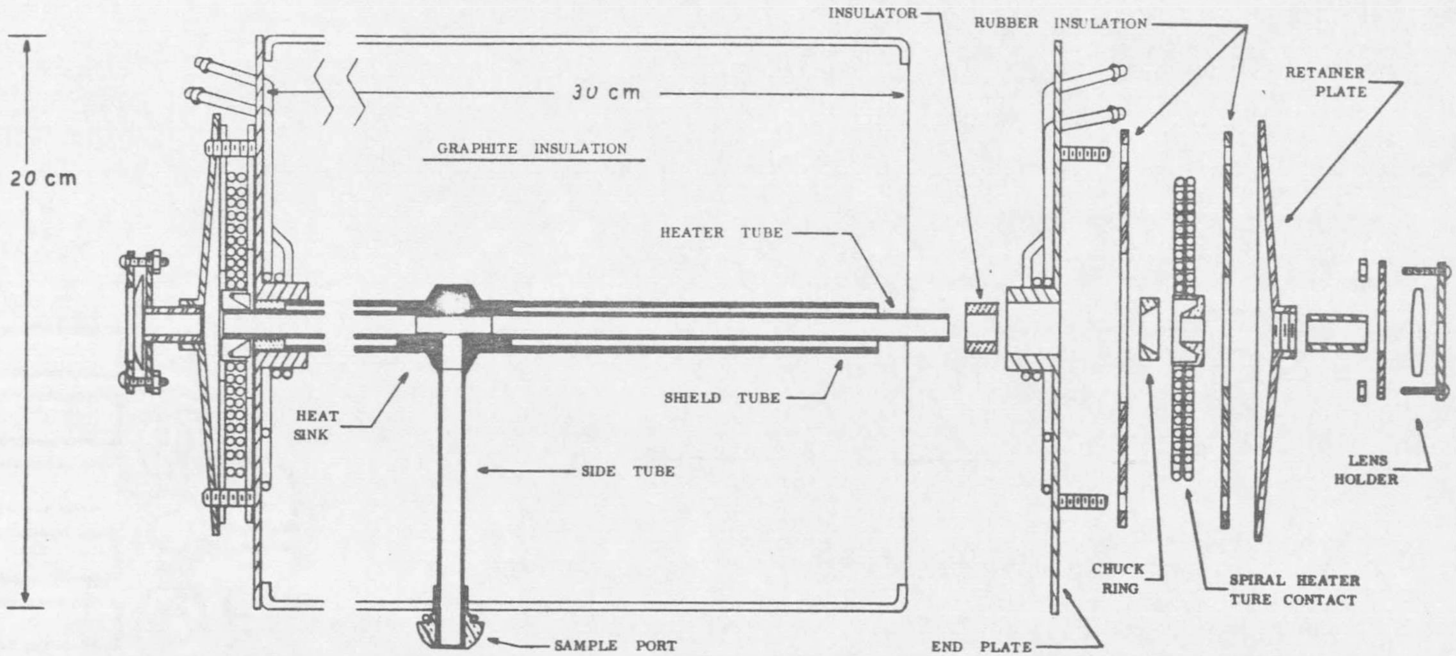

Figure 1 Furnace Model 2.

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.