Atomic absorption spectroscopy with a high-temperature furnace
by Gerald John Ramelow

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry
Montana State University
© Copyright by Gerald John Ramelow (1967)

Abstract:
A graphite-tube resistance furnace was constructed and used in place of a flame as the atomizer for atomic absorption spectroscopic analysis.

The applicability of the furnace technique is demonstrated. Optimum operating conditions were determined for several elements. The sensitivities obtained are comparable or better than those reported for other techniques. The preliminary data indicates that the method is especially suited to those elements which form refractory oxides.

ATOMIC ABSORPTION SPECTROSCOPY WITH A
HIGH-TEMPERATURE FURNACE

by

GERALD JOHN RAMELOW

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemistry

Approved:

Head, Chemistry Department

Chairman, Examining Committee

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

August, 1967

ACKNOWLEDGEMENT

The author would like to especially thank Dr. Ray Woodriff who served as advisor for his continual assistance and guidance throughout the project.

Gratitude is also extended to the National Science Foundation for their financial support of this investigation, and to all those individuals who directly or indirectly aided in the completion of the work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

A graphite-tube resistance furnace was constructed and used in place of a flame as the atomizer for atomic absorption spectroscopic analysis. The applicability of the furnace technique is demonstrated. Optimum operating conditions were determined for several elements. The sensitivities obtained are comparable or better than those reported for other techniques. The preliminary data indicates that the method is especially suited to those elements which form refractory oxides.

INTRODUCTION

Atomic absorption spectroscopy has rapidly become a widely used method of chemical analysis. Since its introduction (2, 10, 37, 44), it has grown in both scope and refinement. It has been extended to elements which are difficult or impossible to analyze by ordinary flame emission (12, 13, 14, 15, 16, 40). However, the full potential of the atomic absorption method has not been realized, primarily because of the use of flames as atomizers.[1] Some of the more important limitations of flames are:

1) The signal-to-noise ratio is limited because of the high noise level in the flame (6, 15).

2) There is possible light scattering by solid and liquid particles of sample in the flame (4, 42).

3) There is little control over the environment of the absorbing atoms (11, 45). For example, in rare-earth analysis oxygen cannot be eliminated because it is a component of the flame.

4) The background is high over many regions of the spectrum because of absorption by the flame gases and molecular species formed in the flame (1).

5) The degree of dissociation of many compounds in the flames normally used is small (30).

6) Sensitivity is limited because of the short absorption path length in the flame (33, 18).

Fuwa and Vallee and others (18, 43) have attempted to increase the

---

[1]The term "atomization" refers to the production of an atomic vapor, composed of free atoms, while "nebulization" refers to the production of an aerosol fog, composed of liquid particles.

effectiveness of the flame by using it with an absorption tube which increases the effective absorption path length. A total consumption burner is inclined at an angle of fifteen to seventy degrees into the end of a ceramic or metallic tube. Very high sensitivities have been reported for this method, but it is limited by the possibility of light scattering and absorption by the flame gases and combustion products. Also, the absorption tube is colder than the flame gases so there is deposition on the walls of the tubes. This reduces the reflectivity of the tube and hence the sensitivity. It may also contribute to a "memory effect."

The need to replace the flame by some other sampling method has often been emphasized (29, 41, 42, 45). In practice two types of replacement methods have been used. The cathodic-sputtering technique developed by Walsh and co-workers (19, 36, 38, 45) and Goleb (21, 22) uses essentially a second hollow-cathode discharge to obtain an atomic vapor. This method requires solid metal samples.

In the method of L'vov (30, 31) the atomizer consists of a graphite crucible into which is inserted an electrode containing evaporated sample on the tip. An atomic vapor is formed by striking an arc between the electrode and an auxiliary electrode. L'vov obtained very high sensitivities for the elements he studied, including refractory elements.

The construction of laboratory furnaces has been described (7, 8, 25, 26, 27). However, only Mislan (32) has used a furnace as a means of atomizing the sample for atomic absorption. His apparatus consisted of an ordinary wire-wound combustion furnace fitted with a separate sidearm heater. It was used only for the determination of cadmium. The sensitivity

obtained was about the same as previously reported using flames.

In the present study a graphite-tube resistance furnace is used in place of the flame as the atomizer. This report gives the results of experiments performed to determine the best operating parameters and the sensitivities obtainable for various elements.

GENERAL CONSIDERATIONS

Theoretical Foundations

In atomic absorption analysis a parallel, modulated beam of radiation of constant intensity emitted by the element being determined is passed through an atomic vapor of the same element. The atoms in this vapor are capable of absorbing the incident radiation at the characteristic wavelengths, and the degree of absorption is a measure of the concentration of the element (34, 35). The general absorption equation is given by

$$I_\nu = I_o e^{-K_\nu \ell}$$

where

I_o = incident radiation of frequency ν

I_ν = intensity after absorption

K_ν = absorption coefficient of the vapor at frequency ν

ℓ = absorption path length

According to classical theory the integrated absorption is given by

$$\int K_\nu d\nu = \frac{\pi e^2}{mc} N_\nu f$$

where

e = electronic charge

m = electronic mass

c = velocity of light

N_ν = number of atoms per cubic centimeter capable of absorbing radiation in the frequency range ν to $\nu + d\nu$

f = oscillator strength (the average number of electrons per atom capable of being excited by the incident radiation

Thus for a transition initiated from the ground state, where N_ν is for all

practical purposes equal to N_o (the total number of atoms per cubic centimeter), the integrated absorption is proportional to the concentration of free atoms in the absorbing medium and independent of temperature.

To measure the integrated absorption, the width of the absorption line must be considered. The factors which influence the width are: 1) natural width of the line, 2) Doppler broadening, 3) pressure broadening, and 4) Stark broadening. At temperatures between 2000 and 3000°K, the width of an absorption line is of the order of 0.02Å. Since most spectrographs are incapable of such high resolution, it is not possible to measure the integrated absorption. Instead the peak absorption is measured using a line source which emits spectral lines of a smaller half-width than the absorption line.

If it is assumed that only Doppler broadening is important in determining the width of an absorption line,[2] the absorption coefficient is given by

$$K_\nu \doteq \frac{2\lambda^2}{D_\nu} \left(\frac{\ell n2}{\pi}\right)^{1/2} \left(\frac{\pi e^2}{mc^2}\right) N_\nu f$$

where
K_ν = absorption coefficient at the center of the line

D_ν = Doppler line width at frequency ν

Since the Doppler line width is proportional to the square root of the temperature (44), K_ν is not affected by small temperature changes and there is a linear relation between absorption and concentration.

---

[2]In flames this is not true, except at low temperatures, because of pressure broadening. In a furnace of the type used in this work pressure broadening should not be significant, except possibly at high temperatures.

Sensitivities and Detection Limits

One of the prime advantages of the atomic absorption technique is the high sensitivity obtainable for many elements. Fassel (17) has recently compared detection limits obtainable by both emission and absorption techniques for a large number of elements. His data show that for many elements (including manganese, cadmium, and copper) the sensitivity has not been greatly improved by atomic absorption. This is especially true for the refractory elements where the absorption method is often less sensitive. The stable oxides formed in flames by the refractory elements have made the detection of these elements by emission and absorption very difficult.

In a high-temperature furnace oxygen can be eliminated from the system by operating the furnace in an inert atmosphere. Under such conditions the refractory oxides cannot form for elements such as aluminum and some of the rare earths. The sensitivities obtainable will be much greater than with the use of flames because most of the atoms will be present as free atoms.

In actual practice there are many parameters which affect the absorption process such as: furnace temperature, sample introduction rate, slit width, lamp current, and type of solvent. A study of the atomic absorption technique using a high-temperature furnace must include an evaluation of the effect of these parameters on the absorption process. Sensitivities can then be determined for various elements at the optimum operating conditions, enabling one to evaluate the relative practicality of the method.

EXPERIMENTAL

Instrumentation

Light Sources

Westinghouse single-element hollow-cathode lamps for erbium (WX5486),
holmium (WX5487), and dysprosium (WX5465), and multi-element lamps for
copper-zinc-lead-cadmium (WL23146) and calcium-magnesium-aluminum-lithium
(WL23158), and a Beckman multi-element lamp for copper-zinc-iron-maganese
(180216) were used as light sources. The lamps were operated from a con-
stant-current power supply (Lambda Electronics Corp., Model 71-B).

Detector and Power Supply

An RCA 1P28 photomultiplier tube was used as the detector. The power
supply used was originally constructed by Skogerboe (39) from a design de-
scribed by Box and Walsh (5).

Amplifier

To prevent the detection of any sample emission from the furnace,
the incident light was modulated at 39 c.p.s. and the amplifier tuned to
this frequency. Thus only the modulated signal is amplified and any 120
c.p.s. signal due to artificial light or full-wave rectified ripple in the
amplifier power supply is rejected. The design of the amplifier is a mod-
ified version (39, 9) of that described by Kalmus and Sanders (24).

Recorder

The recorder was a Bristol Dynamaster (model 1PH560). It has two
chart speeds and a 0 to 10 millivolt full-scale deflection with one-third

second response.

Monochromator

The basic unit was a Beckman DU. It was equipped with a photomultiplier attachment.

Furnace

A graphite-tube resistance furnace was constructed to serve as the sample atomizer. It is capable of reaching temperatures in excess of 3000°C. A schematic diagram of the interior of the furnace is given in Figure 1.

Furnace Power Supply

The power to the furnace was supplied by means of a P and H arc welder. It has a maximum output of 450 amperes.

Nebulizer

The nebulizer used was of our own design and was constructed of glass. A 500 milliliter round-bottom flask was used as a spray chamber to facilitate the condensation of any large liquid particles before they could enter the furnace. The nebulizer and spray chamber were connected to the sidearm of the furnace.

Optical Pyrometer

In order to accurately measure the high temperatures in the furnace, a Pyro optical pyrometer (model 87C) was used. This instrument has three centigrade temperature ranges: 780° to 1200°, 1000° to 1900°, and 1800° to 3200°.
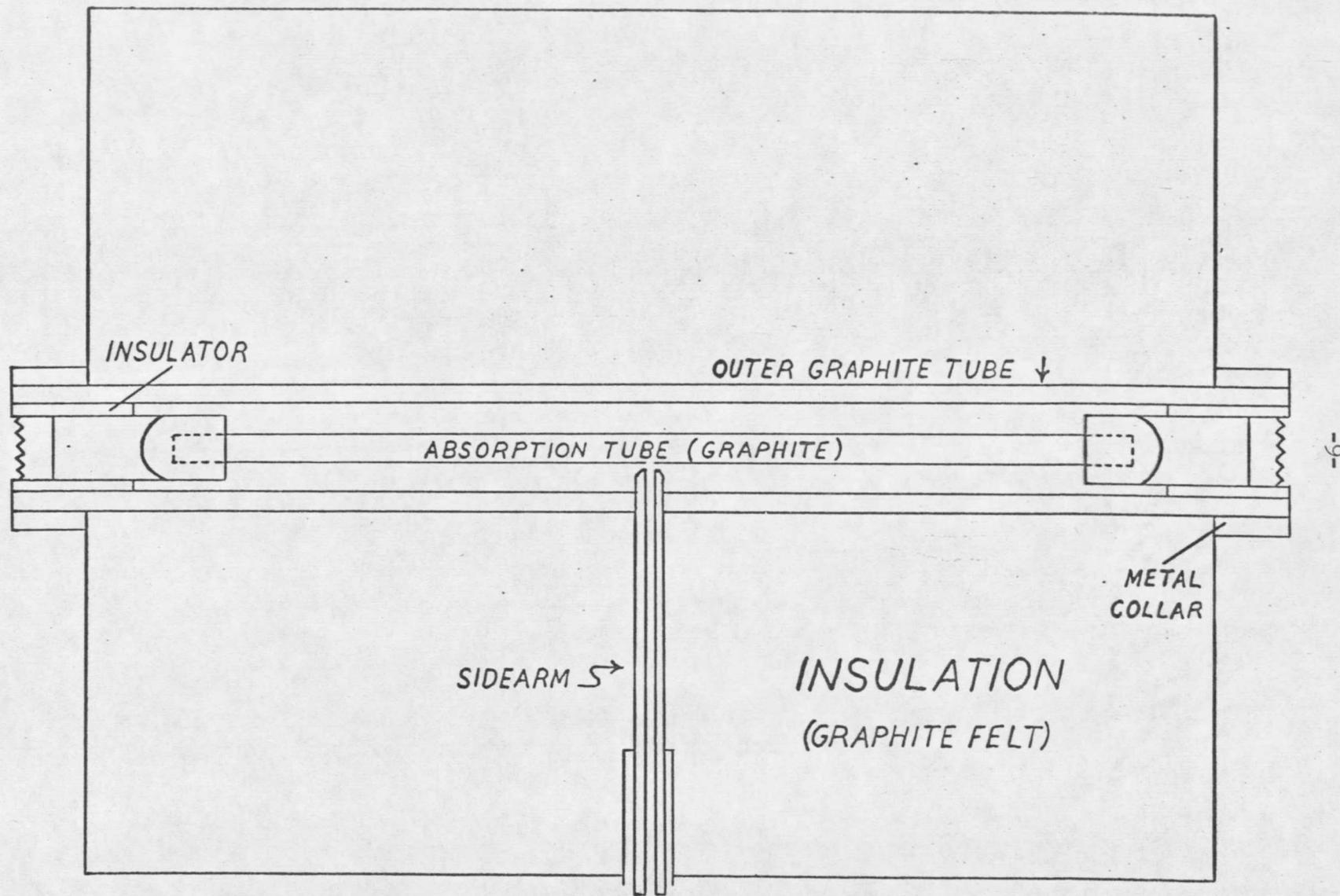
INSULATOR

OUTER GRAPHITE TUBE ↓

ABSORPTION TUBE (GRAPHITE)

-9-

METAL
COLLAR

SIDEARM S→

INSULATION
(GRAPHITE FELT)

Figure 1. Schematic Diagram of Furnace Interior

Absorption Procedure

A chosen spectral line of the element being investigated is located carefully on the monochromator. The light intensity is adjusted to one hundred per cent transmittance by varying the photomultiplier voltage while aspirating pure solvent. The amplifier gain is set at its maximum value. The sample is then introduced and the absorption is recorded on the chart.

Standard Solutions

The stock solutions for manganese, cadmium, copper, and aluminum were prepared by dissolving the pure metal in an appropriate acid (hydrochloric or nitric), evaporating to dryness or near-dryness, and diluting to volume with absolute methanol. The rare-earth stock solutions were prepared by dissolving the pure oxides in perchloric acid, evaporating to dryness, and diluting to volume with absolute methanol. The standard solutions for all elements were prepared by transferring volumes of stock solution (measured with lambda, volumetric, or graduated pipets) to volumetric flasks, and diluting to volume with absolute methanol.

RESULTS

Choice of Solvent

Three solvents were considered for use with the furnace: water, abso-
lute ethanol, and absolute methanol. The use of water was immediately re-
jected because it caused a rapid deterioration of the graphite absorption
tube around the sample entrance. Absolute ethanol was used in the preliminary
work, but was abandoned for two reasons: 1) a large deposition of carbon
on the absorption tube was observed around the sample entrance; and 2) the
solvent was converted into minute carbon particles in the furnace which
deposited inside the furnace. These particles caused some light scattering,
resulting in a corresponding decrease in the source intensity. Absolute
methanol seemed to be the best solvent. It is relatively inexpensive and
easily obtained. Some carbon deposition is observed on the absorption tube,
but this is almost entirely compensated by the normal deterioration of the
tube. Also, formation of carbon particles does not occur, even at the low
temperatures used for some elements.

Nebulization Rate

As the rate of nebulization increases, the absorbance increases.
Figure 2 shows the type of curve obtained when absorbance is plotted against
flow rate of nebulizing gas. There is a two fold reason for this: 1) at
higher nebulization rates there is more sample present as an aerosol fog
which can enter the furnace, and 2) the gas that nebulizes the sample also
carries it into the furnace. In practice the highest flow rate of argon