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.

14

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:

E. E. Graham

Head, Chemistry Department

Ray Woodruff

Chairman, Examining Committee

Louis DeMunn

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

August, 1967

ACKNOWLEDGEMENT

The author would like to especially thank Dr. Ray Woodruff 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

	Page
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
INTRODUCTION	1
GENERAL CONSIDERATIONS	4
Theoretical Foundations	4
Sensitivities and Detection Limits	6
EXPERIMENTAL	7
Instrumentation	7
Absorption Procedure	10
Standard Solutions	10
RESULTS	11
Solvent Choice	11
Nebulization Rate	11
Furnace Temperature	13
Monochromator Slit Width	14
Lamp Current	15
Sensitivities and Detection Limits	16
Calibration Data	17
DISCUSSION	20
LITERATURE CITED	26

LIST OF TABLES

Table	Page
I. Optimum Absorption Conditions	15
II. Sensitivities and Detection Limits	16

LIST OF FIGURES

Figure	Page
1. Schematic Diagram of Furnace Interior	9
2. Manganese Absorption as a Function of Nebulization Rate . .	12
3. Manganese Absorption as a Function of Furnace Temperature .	13
4. Calibration Curve for Manganese	17
5. Calibration Curve for Cadmium	18
6. Calibration Curve for Copper	18
7. Calibration Curve for Aluminum	19

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

¹The 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 Mislán (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

$$I_v = I_o e^{-K_v l}$$

where

I_o = incident radiation of frequency ν

I_v = intensity after absorption

K_v = absorption coefficient of the vapor at frequency ν

l = absorption path length

According to classical theory the integrated absorption is given by

$$\int K_v d\nu = \frac{\pi e^2}{mc} N_v f$$

where

e = electronic charge

m = electronic mass

c = velocity of light

N_v = 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_v is for all

practical purposes equal to N_0 (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

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

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.

²In 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-manganese (180216) were used as light sources. The lamps were operated from a constant-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 described 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 modified 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°.

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, absolute ethanol, and absolute methanol. The use of water was immediately rejected 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

Figure 2. Manganese Absorption as a Function of Nebulization Rate.

used was 1.56 liters per minute (reading of 13 on flow meter). The calibration data were taken at this value. For evaluating the optimum conditions lower flow rates were used.

A slight change in the nebulization system was used in the work with the rare earths. These elements required a higher furnace temperature for maximum absorption, and at those temperatures the sample could not be drawn into the nebulizer by capillary action. Hence no nebulization occurred. This is probably due to some type of radiation pressure which keeps the liquid particles of sample from entering the furnace. To overcome this difficulty a syringe pump was used to introduce the sample into the nebulizer.

The sample introduction rate was 1.65 milliliters per minute. The flow rate of argon was the same as before.

Furnace Temperature

For each element studied there was a furnace temperature at which maximum absorption was observed. A curve showing the relation between absorbance and temperature for manganese is given in Figure 3. The shape of this curve is very similiar to those observed for the other elements. The absorbance always increases until a maximum is reached, and then it gradually decreases. The explanation of these phenomena is not absolute. However, it is believed that a rational explanation can be put forth which accounts for

Figure 3. Manganese Absorption as a Function of Furnace Temperature.

these facts.

The rise in the curve is the time during which the production of free ground-state atoms occurs in the furnace. The processes involved are the separation of the metal atoms from the solvent and the dissociation of any compounds formed in the furnace by the metal atoms. At the point of maximum absorption the metal atoms are now present as free atoms, most of them being in the ground-state. The fact that this maximum differs for each element is due conceivably to a difference in the energy requirements of free-atom production. There are three processes which contribute to the succeeding decrease in absorption as the temperature is further increased: 1) the number of absorbing atoms per cubic centimeter in the furnace decreases due to the increased kinetic energy of the atoms, 2) the number of atoms in the ground-state decreases because some of the atoms are excited to higher energy states by the furnace, and 3) some of the atoms may be ionized, thereby further lowering the ground-state population.

Monochromator Slit Width

There is no general rule which can be stated with regard to the relation between slit width and absorbance. Copper, erbium, holmium, and dysprosium showed a continual increase in absorption as the slit width was decreased. No change was observed for cadmium as the slit width was varied. Manganese and aluminum showed maximum absorption at relatively large slit widths. It appears that because of the brightness of the interior of the furnace, the line intensity of the hollow-cathode lamp is a strong

influencing factor. If the signal-to-background ratio is poor the slit width must be large and vice versa. A similar situation was observed by Skogerboe (39) when he used flames as line sources.

Lamp Current

The absorbance was measured as a function of lamp current for each element except the rare earths. The usual relationship, i.e., increasing absorbance with decreasing current, was not observed. Rather, there was either no change in the absorbance as the current was varied, or an increase in absorbance with increasing lamp current. The latter effect was shown

Table I. Optimum Absorption Conditions

Element	Slit Width (mm)	Furnace Temperature (°C)	Lamp Current (ma)	Wavelength (Å)
Manganese	0.06	1250	10	2794
Cadmium	0.02	1000	10	2288
Copper	0.02	1720	12	3247
Aluminum	0.095	2140	17.5	3093
Holmium	0.01	ca.2300 ³	20	4103
Dysprosium	0.01	ca.2300 ³	15	4211
Erbium	0.01	ca.2300 ⁴	18	4008

³These values were obtained using a syringe pump to introduce the sample.

⁴Obtained without a syringe pump.

by copper and aluminum. A probable explanation is that the intense light emitted by the furnace causes a poor signal-to-background ration. This ratio is improved by increasing the lamp current. The relationship between absorbance and lamp current was not investigated for the rare earths because operating current was not available for the hollow-cathode lamps of these elements. It was decided to operate the lamps at the current values used by Skogerboe (39).

Sensitivities and Detection Limits

The sensitivity is defined (23) as the concentration in micrograms per milliliter which gives one per cent absorption. The detection limit is the concentration which gives an absorption signal equal to twice the variability of the background. The sensitivities and the estimated detection limits obtained for the elements studied are listed in Table II. Also, the best sensitivities reported by other workers using flames, and the best sensitivities using absorption tubes are listed for comparison.

Table II. Sensitivities and Detection Limits

Element	Sensitivity (ug/ml)	Estimated Detection Limit	Best Flame Sensitivity	Sensitivity with Absorption Tubes
Manganese	0.008	0.002	0.15 (42)	0.005 (28)
Cadmium	0.0022	0.0018	0.04 (42)	0.0004 (18)
Copper	0.008	0.003	0.2 (42)	0.007 (18, 43)
Aluminum	0.03	0.01	0.7 (3)	Not investigated

Calibration Data

The absorbance was plotted against concentration for each of the elements, with the exception of the rare earths for which no data was available, at the wavelength shown by previous workers to give maximum sensitivity. The curves shown in Figures 4 through 6 were drawn by the method of least squares with each point on the curve representing the average of several measurements.

Figure 4. Calibration Curve for Manganese.

Figure 5. Calibration Curve for Cadmium.

Figure 6. Calibration Curve for Copper.

Figure 7. Calibration Curve for Aluminum

DISCUSSION

The application of a high-temperature furnace as sample atomizer to atomic absorption spectroscopy has been shown in this work to be a practical method of analysis. The results reported are only preliminary when one considers how much is needed to fully explore the analytical potential of the method. Many advantages and disadvantages have become evident. Therefore it would be well to consider some of the significant results obtained in this work and the conclusions which can be drawn.

The accuracy of the method has been demonstrated. The sensitivities obtained for the elements studied are considerably better than the best flame sensitivities. They are not as good as the values reported with absorption tubes, although for manganese and copper the difference is slight. The superiority of the absorption-tube technique is probably due to the longer path length used (90cm as compared to our 20cm) and the reflectivity of the absorption tubes which increases the path length still further. The sensitivity of aluminum has been improved by better than a factor of ten with the use of the furnace. This seems to confirm our earlier belief that the great advantage of the furnace technique is the elimination of oxygen from the system, thereby making it especially attractive for the refractory elements. It should be noted that since methanol was the solvent, oxygen was not completely eliminated from the system. It was not possible, because of time limitations, to obtain sensitivity data for other refractory elements, but the work that was done indicates that the method will be very sensitive for these elements as well. All data was taken without the use of any type of electronic aids such as noise suppression and scale expansion. How much

these can improve the method is yet to be seen.

The calibration curves are linear for all elements studied except aluminum. The linearity may be deceptive, however, since these curves were plotted over small concentration ranges. Aluminum was also studied over a small range, but it exhibits considerable non-linearity. There are many causes of such curvature. In the case of the furnace method of atomization, it is thought that the intense light emission from the furnace (including some sample emission) lowers the signal-to-background ratio by increasing the background noise level in the photomultiplier tube. This problem is compounded if the emission from the hollow-cathode is weak. The aluminum emission used in the present work was provided from a multielement tube and was not very intense. The tube had to be operated at maximum recommended current and the slit opened quite wide to obtain maximum sensitivity.

The noise level in the furnace is very low. The major source of noise appears to be in the photomultiplier tube and the associated electronics. Another source is the occasional light scattering caused by the entrance of carbon particles, usually originating from the walls of the absorption tube, into the light path. Generally the maximum noise fluctuation never exceeded four per cent and was usually around two per cent. These noise levels were observed only at zero absorption when adjusting the base line and low concentrations. At larger concentrations noise was not observed. This is an improvement over flame techniques where noise is usually present, even at high concentrations. Some noise suppression was achieved by adjusting a damping control on the recorder.

A major disadvantage is the slow rate at which equilibrium is reached

in the furnace. This rate varies from element to element, but only copper and the rare earths seemed especially slow in reaching equilibrium. This should not be a limiting factor to the analytical potential of the method unless extremely rapid analyses are necessary. There are probably modifications which can be made, particularly in the design of the furnace, which will shorten the time needed to attain equilibrium.

The problem of a "memory effect" has not been fully investigated. This effect has been a serious limitation to the absorption-tube technique where flame components actually deposit on the inside walls of the absorption tube. In the present study only copper and manganese were investigated in this regard. Copper showed some effect but manganese did not. The memory effect exhibited by copper may be due to other factors such as instrumental drift.

The extent of this investigation was limited somewhat by the nature and quality of the instrumentation. The work on the rare earths could not be carried to completion because the absorption tubes deteriorated at the high temperatures needed for these elements. For this reason the size of the absorption tube was changed from an original thin-walled type (O.C. 7.8 mm, I.D. 5.9 mm) to a thick-walled type (O.D. 7.8 mm, I.D. 4.8 mm). The latter also proved unsatisfactory because the power requirements were too great for the welder. It would appear that in order to use the present power supply, a tube with an I.D. in between the two would have to be used. Another possible solution would be to make the tubes of a denser and less conductive form of graphite. In addition to the problems with the absorption tubes, the furnace itself proved to be somewhat troublesome. The furnace as now designed

cannot be operated over long periods of time without considerable deterioration of many of its parts. In particular, three areas needed replacement or reconstruction most often: the connections between the current-carrying wires and the furnace (the wires had to be stripped and reset into the copper connectors about once a month if the current in the wires was low and about every two weeks if the current was high), the outer graphite tube which seemed to change in crystal structure in the center and become very brittle (needed replacement about every two months), and the small graphite pieces which make electrical contact between the absorption tube and the ends of the furnace (replacement was needed about once a month). It is obvious that for it to be a useful analytical tool, the furnace must be more durable. Improvements in the design, especially in the aforementioned areas, should lead to this durability.

In summary, the furnace technique of atomizing the sample for atomic absorption spectroscopy has been demonstrated to be a very sensitive method of analysis. With improvements in instrumentation and technique, even better results can be expected. In the immediate future much work needs to be done to fully explore the potential of the method. Listed below are some of the areas which the author feels to be of particular concern.

Suggestions

- 1) The furnace method should be completely extended to the rare-earth elements and the other elements which form refractory oxides.
- 2) Various types of organic solvents which do not contain oxygen should be investigated, for their effect on absorption and on the absorption tube.
- 3) A study should be made of the nature and extent of interference effects

with the use of the furnace.

- 4) Further investigations should be conducted to elucidate the nature of the chemical reactions occurring in the furnace. In particular, what would be the effect of different anions on the maximum-absorption temperature, and what is the fate of the solvent in the furnace?
- 5) The use of high-intensity hollow-cathode lamps should be studied. In the present work it was found that the aluminum emission was not very intense. This resulted in a poor signal-to-background ratio, and required that the hollow-cathode lamp be operated at the recommended maximum current. A high-intensity aluminum lamp should improve this situation.
- 6) The possibility of analyzing solids with the furnace should be explored. The design of the present furnace could be used with minor modifications to permit the introduction of solids either vertically or horizontally.
- 7) The nebulization system used in this work does not allow one to vary the flow rate of inert gas independently of the nebulization of the sample. Therefore, large flow rates had to be used to obtain a fair amount of vaporized sample. The system can be improved by using a syringe pump to introduce the sample into the nebulizer. This allows the use of much lower flow rates and still results in a large amount of nebulized sample. The use of an ultrasonic nebulizer would probably be the best method. It would allow one to produce large amounts of vaporized sample without excessively large flow rates, and also with better efficiency than other methods.
- 8) The use of different types of absorption tubes in the furnace should be explored. The graphite tubes which were used in this study had to be replaced often because of their rapid deterioration, especially at high

temperatures. A possible solution to this problem might be to coat the graphite tubes with a very thin layer of carbide which should make the tubes more resistant to deterioration.

9) The present power supply for the furnace should be replaced, possibly with a good a.c. supply. The welder which was used was very noisy and inconvenient to use. It was difficult to adjust the furnace temperature to a reproducible value by turning the control handle on the welder. Also the unit requires a very high starting current and is therefore difficult to use in most electrical systems.

LITERATURE CITED

1. Allan, J. E., Fourth Australian Spectroscopy Conference, August, 1963.
2. Allan, J. E., Analyst 83, 466 (1958).
3. Amos, M. D., Willis, J. B., Spectrochim. Acta 22, 1325-43 (1966).
4. Billings, G. K., Atomic Absorption Newsletter 4 (10), 357-60 (1965).
5. Box, G. F., Walsh, A., Spectrochim. Acta 16, 255 (1960).
6. Burgess, D., U. S. Bureau of Mines Bulletin 504 (1962).
7. Chekhovshoi, U. Va., Sheindlin, A. R., Priory i Tekhnika Eksperimenta, No. 1, 197-9 (1963).
8. Chernin, S. M., Mal'tsev, A. A., Priory i Tekhnika Eksperimenta, No. 6, 120-2 (1961).
9. Claassen, H., M. S. Thesis, Montana State College, 1964.
10. David, D. J., Analyst 83, 655 (1958).
11. Dorria, A., Dissertation, University Frankfurt am Main, 1956.
12. Fassel, V. A., Analytical Chemistry 32, 19A (1960).
13. Fassel, V. A., Curry, R. H., Kniseley, R. N., Spectrochim. Acta 18, 1127 (1962).
14. Fassel, V. A., Mossotti, V. G., Analytical Chemistry 35, 252 (1963).
15. Fassel, V. A., Kniseley, R. N., D'Sliva, A. P., Analytical Chemistry 35, 910 (1963).
16. Fassel, V. A., Mossotti, V. G., Spectrochim. Acta 20, 1117-27 (1964).
17. Fassel, V. A., National Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1965.
18. Fuwa, K., Vallee, B. L., Analytical Chemistry 35, 942 (1963).
19. Gatehouse, B. M., Walsh, A., Spectrochim. Acta 16, 602 (1960).
20. Gilbert, P. T., Analytical Chemistry 34 (5), 210R (1962).

21. Goleb, J. A., Brody, J. K., Anal. Chim. Acta 28, 457-66 (1963).
22. Goleb, J. A., Yokoyama, Y., Anal. Chim. Acta 30, 213 (1963).
23. Kahn, H. L., J. Chem. Ed. 43 (1), A7 (1966).
24. Kalmus, H. P., Sanders, M., Electronics 23 (2), 84 (1950).
25. King, A. S., Astrophysics J. 56, 318-43 (1922).
26. King, A. S., King, R. B., Astrophysics J. 82, 377-95 (1935).
27. King, R. B., Stockbarger, D. C., Astrophysics J. 91, 488-502 (1940).
28. Koirttyohann, S. R., Feldman, C., "Developments in Applied Spectroscopy", Volume 3, Plenum Press, New York, 1964.
29. Lockyer, R., "Advances in Analytical Chemistry and Instrumentation", Interscience, New York, 1964, pp. 1-29.
30. L'vov, B. V., Inzhener-Fiz. Zhur., Akad. Nauk Belorus S. S. R. 2 (2), 44-52 (1959).
31. L'vov, B. V., Spectrochim. Acta 17, 761-70 (1961).
32. Mislán, J. R., Atomic Energy Com. Ltd., AECL 1941, 10 pp., 1964.
33. Rann, C. S., The Element, No. 9.
34. Robinson, J. W., Analytical Chemistry 32, 17A (1960).
35. Robinson, J. W., Anal. Chim. Acta 23, 479 (1960).
36. Robinson, J. W., The Element, No. 2.
37. Russel, B. J., Shelton, J. P., Walsh, A., Spectrochim. Acta 8, 317 (1957).
38. Russel, B. J., Walsh, A., Spectrochim. Acta 15, 883 (1959).
39. Skogerboe, R. K., Ph.D. Dissertation, Montana State College, 1963.
40. Skogerboe, R. K., Woodriff, R. A., Analytical Chemistry 35, 1977 (1963).
41. Slavin, W., Atomic Absorption Newsletter, No. 7, 1962.
42. Slavin, W., Atomic Absorption Newsletter, No. 24, 1964.
43. Stupar, J., Mikrochim. Acta. 4-5, 722-36 (1966).

44. Walsh, A., Spectrochim Acta 7, 108 (1955).
45. Walsh, A., "Proceedings Xth Colloquim Spectroscopicum Internationale", Spartan Books, Washington, 1963, p. 127.

MONTANA STATE UNIVERSITY LIBRARIES

3 1762 10015333 5

Atomic absorption spectroscopy with a high-temperature

NAME AND ADDRESS

TC Boyd 21 E Main #
6-710

cop.2