FUNDAMENTAL INVESTIGATION OF NONFLAME AND FLAME ATOMIZATION WITH COMPUTER-CONTROLLED SPECTROMETRIC SYSTEMS

Dissertation for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY AKBAR MONTASER 1974



This is to certify that the

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has been accepted towards fulfillment of the requirements for

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Major professor

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ABSTRACT

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By

Akbar Montaser

The use of nonflame atomic vapor cells for atomic absorption (AA) and atomic fluorescence (AF) spectrometry has become increasingly widespread in recent years. The major use of these vapor cells is for analysis of nanograms of elements in small samples, such as in microgram or microliter samples. In order to take the full advantage of nonflame atomization, computer-controlled AA/AF spectrometric systems, which utilize electrically heated nonflame atomizers, were designed and evaluated.

A fundamental investigation of nonflame atomization was performed in order to characterize the physical and chemical processes, to isolate and minimize the interaction of parameters, to design new atomizers and to introduce new fast multielement analysis techniques. As a direct result of this investigation, three new nonflame atomizers, four new heating techniques for nonflame atomizers and a new multielement technique, which can employ flame and nonflame devices, were proposed, fully evaluated and characterized.

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The author gratefully achieved dates the sublance, encodingement and finledship of Professor S. R. brouch during the source of this investigation.

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He would like to express his practicular to hisrigan state university

To my Wife, Father, and Mother, they made all the sacrifices.

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deta acquisition, data (I.e INTRODUCTION) the control over instru-

Computer automation of routine analytical measurements is of great practical importance because measurement throughput can be increased significantly and measurement reliability can be greatly enhanced. The laboratory minicomputer is making possible entirely new instrumental measurements which were inconceivable merely a few years ago. The area in which computer-aided experimentation promises to bring about the most profound changes, however, is in the automation of fundamental research studies. Less emphasis has been placed on the automation of fundamental studies because such studies involve widely varying experimental conditions, decision-making based upon what is known about the system, decision-making based upon prior experiments, and decision-making concerning the goals of the experiment, which may change as new information is acquired.

This type of complete automation would greatly facilitate fundamental chemical studies. The influence of all experimental variables could be investigated in a logical manner using the proper statistical design scheme. In addition experimental variables could be optimized for different goals either in real time or by an iterative procedure. Finally, the complete automation of a chemical experiment could make the investigation of effects which are very difficult to study manually a routine matter.

In many types of chemical experiments the obstruction to complete automation comes in the steps of sample preparation and sample handling which occur prior to the instrumental measurements. The automation of these steps along with the more conventional steps of

data acquisition, data processing and real-time control over instrumental variables would then allow computer feedback in a "closed-loop" type system. The study of matrix interferences in atomic spectrometry or the study of ionic strength effects in chemical kinetics are examples of studies which are tedious to perform manually because of the timeconsuming sample preparation and handling steps. Consequently many of these studies never get performed or get carried out in a rather haphazard manner. Complete computer automation should greatly ease the burden in performing such experiments.

In this thesis the development of computer-controlled nonflame atomic absorption (AA) and atomic fluorescence (AF) spectrometric systems, which feature a high degree of automation, is described. Although a chemical combustion flame can also be utilized with all of these systems, the systems are designed to operate with electrically heated nonflame atomizers, such as filaments and furnaces. Despite the advantages of flames, namely convenience and reliability of operation, variety of available flames, low costs, and adequate sensitivity and precision, the flame atomizers exhibit some severe disadvantages which limit the attainable sensitivity and convenience in their use for trace-metal analysis. First, in sample-limited situations, such as the analysis of biological samples, the volumes of available samples may frequently be less than that required for analysis in the flame. Flames are also seldom able to atomize solids directly. Second, the transport of the sample solution to the flame and the production of a vapor of the analyte in the flame are highly inefficient. Third, the presence of flame gas radicals results in formation of stable species such as monoxides and monohydroxides,

which consequently decreases the free atom fractions. Therefore, precise control over the chemical environment of the analyte and concomitant atoms in flame cells is not possible. Fourth, the achievable analyte atom concentration in flames is limited by the dilution effect and the expansion of flame gases. Fifth, in atomic fluorescence the presence of molecular quenchers in analytical flames decreases the fluorescence quantum efficiency and thus the fluorescence signal. Furthermore, in both AA and AF, spectral interferences are caused by emission from the flame and the analyte. This can be minimized, however, by modulating the radiation source(s) and using a phase-locked detection system.

When a nonflame atomizer is utilized, the transport efficiency and the subsequent desolvation of the sample are nearly 100% complete. It is also possible to have precise control over the chemical and spectral environment of the system as well as electrical control over the temperature. The environment of the atomizer is simple to adjust for maximum production of free analyte atoms and for the highest quantum yield in atomic fluorescence. The *major* use of nonflame atomic vapor cells, however, is for the analysis of nanograms of elements in small samples, such as in microgram or microliter samples. Full utilization of all of these advantages for both routine analysis and fundamental investigations is not possible without a fully computercontrolled system. Therefore, in all of the systems described here, the entire system operation, data acquisition, data treatment and optimization are performed under computer control with no operator intervention.

A fundamental investigation of nonflame atomization was undertaken

in an attempt to better understand the complicated physical and chemical processes, to separate the interdependence of parameters, to design new atomizers, and to introduce fast multielement analysis methods. As a direct result of these fundamental investigations, three new nonflame atomizers, four new methods of programmed heating and a new multielement analysis technique were proposed and fully investigated. The new filament atomizers made from graphite braids, threads, or tape incorporate all the fundamental and practical advantages of other nonflame atomic vapor cells as well as several advantages which are not present in other furnace and filament atomizers. The widespread application of one of these vapor cells, the graphite braid atomizer, was demonstrated by the determination of 15 elements by atomic absorption and atomic fluorescence and by its application to biological samples.

The various heating techniques introduced are applicable to any electrically heated nonflame atomizer. Application of these techniques to a platinum loop and a graphite braid atomizer showed that the method of programmed heating influences the atomizer lifetime, the time required for the atomizer to reach a steady state temperature and the separation and optimization of atomization parameters. A new multielement analysis technique which operates in the time-division multiplexed mode has performed a multielement analysis for 4-8 elements in less than 3 seconds. The application of this method to flame and nonflame atomizers is also presented.

explanation of the phenomenon was presented in 1859 by Firchhoff and Bunsen who leid the four II. HISTORICAL mochanical analysis. It was not until 1955, however, that the analysical potentialities of alcond

The contents of Chapter II are divided into five parts. In the first part, the history of atomic absorption and atomic fluorescence is reviewed along with the fundamental principles behind these techniques. In Part two, the advantages and disadvantages of flame atomizer as well as the previous work on the separated flames are discussed. The various nonflame atomization techniques are reviewed in the third part, and the advantages and drawbacks of each method are presented along with the practical application of various nonflame atomizers. The fourth part reviews the radiation sources for AA and AF. The previous work on pulsed lasers and pulsed hollow cathodes is discussed in more detail. Finally multielement analysis by AA and AF is briefly reviewed in the fifth part.

A. Atomic Absorption and Atomic Fluorescence Spectrometry

In their analytical context, atomic absorption (AA) and atomic fluorescence (AF) spectrometry are methods for determining the concentration of an element in a sample. In AA, an atomic vapor is produced from the sample by an atomizer. The vapor is then excited by means of an external light source, and the fraction of the radiation absorbed as a result of radiational excitation is monitored at a wavelength that is specific and characteristic of the element under investigation. Atomic absorption was observed as early as 1802, when Wollaston observed dark lines in the sun's spectrum, but the exact

explanation of the phenomenon was presented in 1859 by Kirchhoff and Bunsen who laid the foundations of spectrochemical analysis. It was not until 1955, however, that the analytical potentialities of atomic absorption were proposed by Walsh (1), and independently, but somewhat later, by Alkemade and Milatz (2,3). Since that time several publications have dealt with the application of AA to the solution of practical problems, and the method has proven to be an indispensable analytical tool. Several books (4-11) have been written on the subject and atomic absorption spectrometers are presently available from more than twenty instrument manufacturers throughout the world.

Atomic fluorescence spectrometry differs from AA only in the means of measurement of the characteristic signal. The analyte atoms are radiationally excited as in AA, but the measured parameter is a portion of the atomic fluorescence radiation resulting when a fraction of the excited atoms undergo radiational de-excitation. The phenomenon of fluorescence by free atoms was first noted in sodium vapor above molten sodium by Wood (12) in 1905, and atomic fluorescence in flames was observed during 1924-1961 for about ten elements (13-16). It was Alkemade (17) who suggested the analytical utility of the phenomenon in 1962 and for the first time, Winefordner, Vickers and Staab (18-19) demonstrated AF as an analytical technique in 1964. The pioneering work of Winefordner and coworkers was closely followed by work done by West and coworkers (20-21). A number of excellent review articles have been published (24-28), and numerous chapters have dealt with the subject in atomic spectroscopy books (10,11, 29-32). It is obvious that since AF was introduced nine years after the development of AA, there have been a smaller number of publications, and the

method is still relatively new and untried in practical applications. In contrast to AA, commercial atomic fluorescence spectrometers are not available. However, prototype multichannel systems have been demonstrated (23,257,258). Although the unavailability of commercial instruments can be partly responsible for the lack of widespread acceptance of AF as an analytical tool, it is the author's opinion that the origin of the problem has been closely tied to the lack of suitable atomizers and radiation sources for AF.

The instrumentation involved in AA and AF mainly depends on the desire to perform single or multielement analysis, but in general, it consists of a radiation source(s), an atomizer, a wavelength isolation device(s), a detector(s) and a readout. Both techniques require entrance optics to focus an image of the source upon the vapor cell. Electrically or mechanically modulated light sources and suitable electronics are needed in order to minimize the response to thermal emission from flames and from some of the nonflame atomizers for analysis of elements with analytical lines above 3000 Å. Although a greater signal is obtained with a dc electronic system and an unmodulated source, the effect of both white noise and 1/f noise can be more severe. Since similar instrumentation is used for both AA and AF, a review of some of the basic components will be given in later sections.

B. Flame Atomizers

In atomic absorption and atomic fluorescence spectrometry the achievable sensitivity and precision are limited by the techniques with which atoms of the analyte element are produced from the sample

and by the characteristics of the external radiation source. The methods of atom production are discussed in this section, and a review of the radiation sources for both AA and AF appears in a later section. Flame and nonflame atomizers have been the subject of many review articles (24,25,27,33,34) and chapters (9, 31, 35). The purpose of an atomizer is to provide a stable, noise-free system to convert the sample into free atoms. At the present time, all commercial instruments are equipped with flame atomization systems, though nonflame attachments are also available.

1. Advantages of Flames

The popularity of flame atomizers originates from the following advantages:

a) The attainable signal-to-background and signal-to-noise ratios are sufficiently high to provide adequate sensitivity and precision for the wavelength range of 2000-3000 Å.

 b) They are convenient to use, reliable and relatively free from memory effects.

c) Most burner systems are inexpensive, small and stable.

d) The wide variety of flames in terms of composition and temperature allows the selection of proper optimum conditions for many different analytical purposes.

Despite their advantages, the flame atomization systems exhibit some disadvantages which limit the attainable sensitivity and convenience in their use for analysis. A discussion of these drawbacks appears later in this section.

Since flame atomization systems have been mostly used in

conjunction with AF in our investigation, this discussion will be limited to those combustion type flames which are the most suitable for AF. For such flames it is desirable to have a minimal concentration of quenchers, a long residence time of the atomic vapor in front of the observation window and a low background emission. Since the radiance of the external source in AA is many times greater than the radiance of the flame, the effect of flame background is not as critical as in AF. In other words, since the atomic fluorescence and flame radiances are comparable, the detection power of any AF system may be limited by the atomizer background.

In a conventional flame, the background emission comes from both the primary and secondary reaction zones. Virtually all the hydrocarbons are broken down in the primary cone and produce among others. unburned products such as carbon monoxide and hydrogen. As a result of the diffusion of atmospheric oxygen towards the center of the flame (37) and the combustion of unburned products in the secondary zone. emission bands result, the most intense of which comes from OH bands in the region of 3100 Å. If the flame is sheathed (37) with an inert gas, the secondary combustion is prevented and atomic fluorescence measurements may be made in the secondary zone where background emission is extremely low. It should be noted, however, that the temperature of the primary cone decreases with increasing sheath gas flow rate. The extent of the cooling effect depends on the sheath gas, flame composition and the height of observation (38). Despite the disadvantages of a lower temperature, separated flames of this type have been used in studies of fluorescence yields (39) and studies

of atomization efficiencies (40). They have proven to be useful in the determination of metals forming refractory oxides (22) and have been evaluated for atomic emission, atomic absorption and atomic fluorescence (41-46). A modified version (47) of the sheathed burner designed by Larkins (48) was used throughout this investigation.

2. Fundamental Disadvantages of Flame Atomizers

a. Precise control over the chemical environment of the analyte and concomitant atoms in a flame cell is not possible. The degree of control of chemical composition that can be obtained by variation of the fuel-to-oxidant ratio causes the simultaneous change of flame temperature as well as flame spectral emission and absorption characteristics. Since all analytical flames possess a considerable concentration of flame gas radicals such as 0, 0H, etc., which combine with an appreciable fraction of many elements to produce stable monoxides, monohydroxides, etc., the free atom fraction, β , is less than unity (52). It has been shown (53) for copper that 10^8 atoms should produce 1 percent absorption whereas in practice the best reported sensitivity limit corresponds to 10^{15} atoms. In other words, the efficiency of atomization is 10^{-5} %.

b. The aspiration efficiency, c, is less than unity. Because of the short residence time of solute particles within the flame gases (54), solutions with a high concentration of analyte and/or other components in the sample matrix may undergo incomplete solute vaporization. Scattering of exciting radiation by solute particles can be considerable. The total consumption nubulizer - burner unit is inefficient in the sense that large droplets are produced so that, even in many instances, solvent evaporation is remarkably incomplete. Pneumatic nebulizers seldom provide an aspiration efficiency of more than 15% with aqueous solutions. The remaining test solution is merely wasted.

by the dilution effect of a relatively high flow rate of unburnt gas used to transport minute volumes of sample solution to the flame. As can be seen from Equation 10 in Chapter III, the flame gas expansion also limits the atom concentration.

of molecular quenchers such as CO, CO_2 , and N_2 , which decreases the fluorescence quantum efficiency, Y, in AF (55,57). The decrease in the parameter Y results in a decreased fluorescence signal and signal-to-noise ratio.

e. Continuous variation and control of flame temperature is not possible.

3. Practical Disadvantages of Flame Atomizers

a. There is considerable absorption background with flames employing carbonaceous fuels. At wavelengths below 2000 Å, an appreciable reduction in intensity results owing to absorption of radiation by flame gas products. Furthermore, because of chemiluminescence reactions, such as the oxidation of CO with O_2 , flames exhibit considerable amounts of emission from their primary and secondary zones. Flames also produce thermal excitation of elements having resonance lines at wavelengths greater than about 3000 Å. Since the emission from these elements is constant with time, its contribution can be

minimized by modulating the AA or AF source and using a phase-sensitive amplifier locked to the modulating frequency.

b. The volume of sample solutions may frequently be less than that required for analysis in flames. This is especially true in clinical chemistry.

c. Explosion hazards are always present with flames of high burning velocity. In closed automated systems where no operator is present, it may not be desirable to employ flames as the atom cells. Efficient exhaust systems are required to remove the released toxic products.

d. Flames usually produce audible noise, although they can be made to operate fairly quietly.

e. Flame atomizers are seldom able to atomize samples directly.

C. Nonflame Atomizers

The first application of nonflame atomizers dates back to 1908 when King (49,51) suggested the use of a graphite furnace for the investigation of atomic spectra and the measurement of oscillator strengths. In the last two decades, there has been considerable research into new nonflame atomizers and their application to the solution of analytical problems. In fact, the disadvantages of the flame mentioned in the previous section have directed many workers to devise new techniques for atomization of samples.

In a nonflame atomizer, it is possible to have precise control over the chemical and spectral environment of the system as well as electrical control over the temperature. The environment of an
atomizer is simple to adjust for maximum cß, and the quantum yield is maximized by use of an inert gas. A nonflame atomizer, particularly the filament-type atomizer, should have lower background and background flicker than a flame. The major use of nonflame atomic vapor cells would seem to be for the analysis of nanograms of elements in small sample sizes, such as micrograms or microliters. It is because of these advantages that the use of nonflame atomizers has gathered considerable momentum in recent years. The major nonflame atomizers are furnaces and filaments. These atomizers are reviewed in this section along with the cold vapor cell technique, the electrical discharge and other less popular nonflame methods.

1. Furnaces

a. <u>The L'vov Furnace</u>. Several satisfactory long path length graphite furnaces of the type used by King have been designed and tested for analytical use in both AA and AF. The sensitivity of the King furnace, and open end furnaces in general, is determined by the amount of substance existing in the vapor phase. Thus, the increase in the amount of sample would be limited by the fact that the volume of vapor becomes comparable with the internal volume of the furnace. Because of vapor loss by diffusion from both ends, error occurs. For a 10 cm long tube, the loss of Hg in an atmosphere of N₂ is reported to be about 4 percent in a time duration of 100 msec at a temperature of 2000 °K (58). Various models of the original King graphite furnace have been used by L'vov and coworkers in extensive AA studies, and the results have been reviewed (9,59). Open ended graphite tubes 30 to 100 mm in length and 2.5 to 5.0 mm in i.d.,

depending on the analytical requirements, have been employed. In the original L'vov furnace (58), the sample is volatilized into a heated tube with a carbon arc. A tantalum or tungsten foil, placed inside the tube, diminished the loss of sample vapor by diffusion through the walls of the graphite tube. The samples to be analyzed are placed on the electrode either in solution form or as a powder. Solution samples are placed on the ends of a carbon electrode and evaporated to dryness. The tip of the electrode is first coated with a solution of polystyrene in benzene in order to prevent the sample solution from soaking into the carbon. The electrode carrying the sample is introduced into a conical opening in the middle of the furnace. The tube is heated to 2000-3000 °C by an ac current supplied by a 10 kW transformer, and the electrode is simultaneously heated from outside by means of a dc arc. The furnace is placed in an argon chamber which contains two quartz windows to permit radiation from the primary source to pass through the furnace.

In a revised version of the graphite cell by L'vov and Lebedev (9), the tantalum or the tungsten foil was discarded, and the tubes were fabricated entirely from pyrolytic graphite or else they were lined both from inside and outside with a layer of pyrographite. The pyrolytic graphite has the advantage of having low permeability, high heat conductivity and high resistance to oxidation. This diminishes diffusion of vapor through the walls, provides uniform heating of the tube and ensures a longer lifetime of the atomizer. A more efficient method of heating was also employed. A two channel atomic absorption spectrometer was used to correct for non-selective molecular absorption and scattering of source radiation. The spectrometer also allows

the simultaneous recording of the absorption of two elements, one of which can be an internal standard. In addition to the extensive use of the graphite furnace for trace element analysis, L'vov and coworkers investigated (9) the Lorentz width of resonance lines, the determination of absolute values of oscillator strengths and estimation of atomic diffusion coefficients. The furnace has been used for the determination of 40 elements by AA thus far.

b. The Woodriff Furnace. Woodriff and coworkers developed a graphite tube furnace for AA in which a tube is heated continuously by an arc-welder or by a power supply that can provide 200 A at 24 V. The furnace body is made of double-walled stainless steel, is insulated with graphite felt and is water cooled. The sample is introduced into the tube, 150 mm in length and 7 mm in i.d., through a side arm which is located in the center of the tube furnace. Although the sample can be nebulized into the side arm, it was found (60,61) that water solutions eroded the graphite rapidly while ethanol solutions caused the tube to get thicker. Furthermore, no nebulization occurs at high temperatures. In order to overcome the nebulization problem, a syringe pump was used to introduce solution into pneumatic and ultrasonic nebulizers. The sample can also be introduced into the tube with a carbon cup (61,63). Normally, 20-50 µl of solution are pipetted into the cup and evaporated to dryness under an infrared lamp. The cup is twisted onto a small graphite rod and is inserted into the furnace through the sample port. The side arm narrows just before it opens into the optical path, and the rim of the sample cup makes a tight contact with this construction. Thus, the inside of the cup becomes an integral part of the tube furnace. The sample

evaporates quickly and expands in both directions along the optical path. Occasionally a small flake of carbon will fall through the light path as the cup strikes against the retainer ring. With the background correction technique (63,64), this problem can be corrected.

The furnace has been used for the determination of seventeen elements (62,63), and no significant matrix effects were observed from the presence of relatively large amounts of Al, Cr, Cu, Fe, Ni, Mn, Zn, Mg on the absorption signal obtained for 10^{-9} g of silver. The furnace has been employed for the determination of trace level of Pb in the atmosphere (65) and in fish tissue (66) and for the determination of sub-nanogram quantities of silver in snow (67). The lifetime of the most improved version of the furnace has been reported to be 10 months (67). The furnace is commercially available from Woodriff Frontier Products (Box 1305, Boyeman, Montana).

c. <u>The Massmann Furnace</u>. A somewhat simpler version of the L'vov furnace was designed by Massmann for both AA and AF (68,69). In contrast to the L'vov design, samples are inserted directly into a tube through an orifice 2 mm in diameter, and evaporation of samples is accomplished by resistance heating of the tube walls instead of an arc. The absorption tube is 55 mm in length, of 6.5 mm i.d., and the wall thickness is 1.5 mm. The tube, mounted in a water cooled chamber, is purged with argon, but the optical path through the tube is open to the atmosphere. For AF work, a cup-shape graphite cuvette is employed. Both the tube and cuvette can be heated in a few seconds to 2600 °C by a current of up to 500 A. If it is assumed that the sample is completely evaporated during the heating period, the cell is ready for the next sample after a cooling time of 20-30 sec.

The lifetime of the graphite tube depends on the maximum required temperature and ranges from 200-300 analyses. Sample solution volumes of 5-50 µ& were used for AF work and 5-200 µ& for AA studies. For solid samples larger than 1 mg, unacceptable background absorption levels were encountered which were minimized by simultaneously measuring the intensity of a nearby nonabsorbing line (70). Detection limits for 16 elements by AA and 9 elements by AF have been obtained by Massmann. The relative standard deviations of the measurements were matrix and concentration dependent and ranged between 4 and 12 percent.

A graphite furnace similar to that described by Massmann is commercially available for atomic absorption spectrometers (71) and was first used for the determination of copper and strontium in milk. It is claimed that the furnace can be used for the determination of 60 elements (72). Massmann type furnaces have been used for the direct determination of trace metals in sea water (73) and high purity water (74), for the determination of lead in the atmosphere (75) and in blood (76) and milk (77), for the analysis of chromium in urine (78) and for the measurement if iron and copper in high purity silica (79). Interferences were found to occur with most elements when present in large amounts (73,80) and solvent extraction prior to analysis is recommended. Other practical applications of this atomizer have been discussed elsewhere (81).

d. <u>Induction Furnaces</u>. From an analytical point of view, two types of induction furnaces (82,85) have been employed for both atomic absorption and atomic emission spectrometry. In these furnaces, the vaporization and atomization of the sample is accomplished by inductive heating of a graphite cuvette or tube. Morrison and Talmi (82-84)

have described the construction of an induction furnace for AE and AA. The inductively heated graphite cuvette, located in an helium environment, serves as a thermal means of vaporization and atomization, while the excitation of the atomized sample is achieved mainly by the helium plasma formed by an RF field. The furnace consumes 4.5 KW, operates at 3 MHz, and is capable of reaching a maximum temperature of 2500 °C. A maximum of 300 samples can be analyzed before the properties of the furnace are changed significantly (83). Samples can be introduced every 30-60 seconds. For absorption measurements, the light from a hollow cathode lamp passes through the plasma plume located over the mouth of a graphite crucible and is absorbed by the sample vapor. The attenuation of the primary radiation is monitored by a conventional AA spectrometer. The system has been used for the determination of 19 elements by AE and 6 elements by AA, but the absolute sensitivities are inferior (82,83) by one to four orders of magnitude to those obtained with some of the nonflame atomizers. Accuracies on the order of 5 percent have been obtained with microsamples of geological, metallurgical and biological materials (83).

Headrige and Smith (85) have reported the construction of an induction furnace for the analysis of volatile elements in solution and volatile matrices by AA. Except for the heating method, the general arrangement of the furnace is similar to that described by L'vov, and it can achieve a maximum temperature of 1900 °C. The furnace has been used for the determination of cadmium in zinc-based alloys.

e. <u>Furnaces With Continuous Sample Introduction</u>. Some problems associated with nonflame atomizers for both AA and AF spectrometry have included the complexity of design, poor reproducibility of

measurements and poor accuracy due to appreciable matrix interferences. The poor reproducibility of measurement mainly originates from discrete sampling. A more reliable and convenient method, used with both AA and AF, involves the continuous nebulization of sample solutions into heated tubes. Mislan (86) has described the construction and performance of an AA spectrometer that incorporates a 36 cm tube of 2.5 cm i.d. heated to a maximum temperature of 1250 °C by a wire wound resistance furnace. Sample solutions were transferred to the absorption tube through a conventional indirect-spray chamber assembly. The device was used for the determination of Cd. and excellent detection limits were obtained. Black et al. (87) used a heated chambercondenser sample introduction system (88) to nebulize aqueous samples continuously through a platinum furnace. The furnace was electrically heated and could achieve a maximum temperature of 1600 °C. The atomic vapor was excited by means of an electrodeless discharge lamp which was focused just above the top of the furnace. Two furnace designs were evaluated and compared with respect to limits of detection, ranges of linearity of analytical curves and interferences. The platinum furnaces have been used for the analysis of Cd. Zn. Cu. Hg and Fe in atomic fluorescence. The relative standard deviations were reported to vary between 1.2 to 3.9 percent. thed by Hoportific Here the sidears of

A graphite tube, located in a water cooled assembly, has been described by Murphy et al. (89) for the determination of Zn, Cu and Bi by atomic fluorescence. The tube was heated by the power from a 3 KW transformer, and the sample aerosol and argon were introduced into the chamber tangentially, exiting up through the tube. The atomic vapor, emerging from the top of the furnace was excited by

primary sources such as hollow cathodes, Xe arc lamps, and electrodeless discharge lamps. The resulting atomic fluorescence signals were compared for a photon counting and a lock-in amplifier system. The best detection limits obtained for Zn, Cu, and Bi were 2.7 x 10^{-7} , 3.2 x 10^{-5} , and 1 x 10^{-3} µg/ml, respectively.

f. Other Furnaces. A variety of furnaces have been used for atomic absorption studies (90-94). Hudson reported the use of a stainless-steel absorption cell heated by a resistance wire for the determination of the atomic absorption cross section of Na vapor (90). Choong and Loong-Sing employed a fused silica absorption tube for the investigation of the absorption spectrum of silver vapor (91). Recently, an automated atomic absorption spectrophotometer has been described for the acquisition of thermodynamic data (92). The instrument can provide automatic measurements of elemental vapor pressure changes with temperature. Using this system, Pemsler and Rapperport (93) have demonstrated that concentrations of extremely small impurities in well characterized metals and alloys can be determined by AA in a sealed cell. The method was illustrated by the determination of 80 ppb of Zn in 99.9999% copper.

Robinson and coworkers employed a furnace design which was basically similar to that described by Woodriff. Here the sidearm of the furnace was filled with carbon chunks or rods, and the furnace was heated by an RF coil to about 1400 °C. The sample gas or liquid, was introduced into the sidearm and was reduced to metallic elements. The atomic vapor then entered a quartz absorption tube heated by a nichrome resistance heater. The system has been used for the determination of Pb. Cd. and Hg in air (95.97) and for the determination

of Cd in sea water and urine (98). Background correction was used to correct for molecular absorption. The effect of chemical interferences for 11 anions on the Cd signal was studied and most of the ions produced no interference (98).

2. Filament Atomizers

The history of filament-type nonflame atomizers originates from the work of Bunsen in flame emission spectrometry in 1859. A wide variety of these atomizers, in which a rod, a loop, or a cup carries the sample, have been proposed in recent years. These atomizers, fabricated from graphite or metallic filaments and strips, are normally electrically heated, and the resulting atomic vapor passes into an unconfined volume in the absorption or fluorescence light path. As a result, with filament-type atomizers, transient analytical signals are obtained. Because of the unconfined nature of the analytical cell volume, there will be less memory effect as well as a considerably greater dilution of the analyte than with the furnace atomizers. Also, $\epsilon\beta$ should be greater with the furnace atomizers. Furthermore, if a large temperature gradient exists between the hot filament and the cooler volume in which AA or AF measurements are made, it may be difficult to achieve freedom from interference effects with the filament atomizers. These interferences should decrease if a flame surrounds the atomizer.

a. <u>Gold, Silver and Copper Wire or Foil Atomizers</u>. Ulfuarson (99) employed a gold foil for the determination of Hg in small quantities of biological materials. After the digestion of the biological samples and extraction with dithizone in chloroform, the sample is transferred

to an ignition tube, and the chloroform is evaporated. The mercurydithizone complex is then destroyed by heating and Hg forms an amalgam with a gold filter. The foil is then heated to vaporize the mercury into the optical path of an AA spectrometer. Biological samples containing as low as 10 ng of Hg per g can be analyzed with this method.

A similar system using tin (II) chloride as a reducing agent has been used for the determination of Hg in geological materials. The mercury is collected on a silver (100) or gold wire (101) and is subsequently released by heating the wire in a closed furnace. The detection limit was reported to be 1.0 ng of mercury.

Brandenberger and Bader (102) used a copper wire for the quantitative amalgamation of Hg. The wire was electrically heated and AA measurements of as low as 0.2 ng of mercury were performed.

Stephens (102) described the use of a copper loop which is heated by a capacitor bank initially charged from a conventional 0-450 V variable power supply. The system can provide heating pulses of a few microseconds and was used for the determination and identification of inorganic and organically-bound mercury by AA spectrometry.

b. <u>Tungsten and Platinum Atomizers</u>. The amalgamation or the electrolysis technique described above can also be used for the determination of elements other than mercury. Using an electrically heated platinum or tungsten wire, Brandenberger (104) reported the determination of Cd, Zn, Pb, Tl, Cu, Ag, Au and Pt in AA spectrometry. Bratzel et al. (105,106) have described the application of a filament technique, similar to that described by Brandenberger, for AF spectrometry. After the analyte solution is placed on an electrically heated platinum or tungsten wire loop, the sample is vaporized and swept into the

fluorescence light path where atomic fluorescence is excited by an electrodeless discharge lamp. The device was used for the determination of ll elements.

Williams and Piepmeier (107) evaluated a rigid spiral-wound tungsten filament for the analysis of Ca, Cr, Cu, Fe, Mg, Mn, and Sn by AA and presented a method of compensating for background tungsten emission. A tungsten-rhemium alloy wire loop (108,109) has also been used for the determination of Cd, Pb and Ni by AA.

Cantel and West (110) have described the use of a tungsten filament atom reservoir (TFAR), 60 mm long and 2.2 mm in diameter, for atomic absorption spectrometry. The sample is delivered to a 1 mm deep notch (\sim 2 mm wide) at the center of the filament, and the TFAR is heated by dissipating electrical energy. The TFAR atomizer has been used for the determination of traces of Zn, Pb, Cu and Ag, and its performance was compared to the carbon filament atom reservoir for the analysis of lead. It was reported that the lifetime of a TFAR was almost indefinite and that greater sensitivity and fewer matrix effects were observed with the TFAR system.

c. <u>Tantalum Atomizer</u>. Donega and Burgess (111) have assembled a filament device which incorporates a sample boat, 50 mm long and 6 mm in width, cut from a graphite sheet, or from tantalum or tungsten foil. The device can be used with volumes of liquid samples as large as 50-100 μ . The sample boat is heated electrically with a current of 30 to 50 A at 12 V, which is sufficient to heat the boat to about 2200 °C in less than 100 msec. The atomizer is mounted in a quartz chamber which can be purged with inert gas in the pressure range of

1 to 760 torr. Although operation at low pressures provides low background interference, the residence time of the atoms in the effective absorption volume decreases and dictates that the detector system be of fast response. The method was used originally for the determination of 10 elements by AA.

Using a tantalum strip, Hwang et al. (112) have recently reported the determination of AA sensitivities and detection limits for 37 elements. Tankeuchi et al. (113) compared nickel, tungsten, tantalum and platinum as strip materials. Only small signals were obtained with platinum, and neither nickel nor platinum could be used at very high temperatures. Tantalum and tungsten showed similar results, but the tantalum strip was easier to fabricate and was chosen as the strip material. Samples as small as 0.5 μ can be delivered to the atomizer. The strip requires 80 W of power to reach a temperature of 2400 °C (114). The system was used for the determination of traces of Al, Cr, Cu, Fe, Mg and Mn and for interference effect studies (113-115). With the exception of the effect of phosphoric acid on the copper absorption signal, the interferences of hydrochloric perchloric and nitric acid were minimized at high applied powers (115). Similar results were obtained for the interference effects of 12 foreign ions on the chromium absorption signal (114).

The tantalum strip has been used for the determination of Mg in control serum and in aluminum alloys (113), for the analysis of Cr in steel (114) and for the microdetermination of Pb in blood (116). From all of the atomizers made from metals, only the tantalum strip is commercially available (Instrumentation Laboratories, Lexington, Mass.). Compared to atomizers made from carbon or graphite the

tantalum strip atomizer has the advantage of avoiding carbide formation and the disadvantage of lower temperature. Other practical applications of this atomizer have been discussed elsewhere (117).

d. <u>The AA Microsampling System Involving Sampling Boats and</u> <u>the Delves Cup</u>. The AA microsampling system is often described as a "semi-nonflame" atomizer. After placing the sample in a cup or boat-shaped container and drying the sample, the vessel is introduced into a flame. The heat from the flame is sufficient to atomize volatile elements. The boat has a sample capacity ten times that of a cup which for some elements leads to a better detection limit. Both systems give much better detection limits than flames, but only for ten easily atomized elements. The origin of this work started when several attempts had been made to improve the atomization efficiency of total consumption nebilizer burners by using them with long-path absorption tubes of various materials and internal reflective coatings (118-120). The atomization efficiency of a premixed burner-nebulizer system has been improved by means of sample cups, boats and platinum loops.

Kahn et al. (121) used a tantalum boat technique for the analysis of lead in urine. White (122) employed a platinum wire loop to vaporize blood samples into a nickel absorption tube for lead determinations. By combining the two previous methods, Delves (123) vaporized blood samples from nickel cups into an absorption tube placed in a longpath length flame. Lead can be determined in a sample volume of 10 μ 2. As many as 30-50 samples can be analyzed per hour.

In all of the above techniques, a minimum of two peaks are seen in each determination, the first of which is from unashed organic

material and is variable in size, while the second one is the lead signal. A time delay circuit could be used to eliminate the recording of non-specific absorption signals (124). Although the method is easy to use, it has been shown that, it is prone to both positive and negative interferences for the determination of mercury (125) and tellurium (126). Because of the effects of the sample matrix and the cup quality on peak absorbance, integration of the signals has been recommended (127). These atomizers are commercially available (72).

e. Carbon and Graphite Filament Atomizers. Among all the filamenttype cells, the atomizers made from carbon or graphite appear to be highly applicable because of the high operating temperatures (2500-3000 °C) which can be achieved. West and Williams (128) have reported the construction and use of an atomic vapor cell made from a graphite filament 1-2 mm in diameter and about 20 mm in length, for AA and AF. The filament was supported by water cooled stainless-steel electrodes and heated to 2000-2500 °C within 5 seconds by applying a current of about 100 A at 5 V. Sample volumes of 1-5 μ L are placed on a depression **in** the filament, and the assembly is housed within a chamber which can be purged with argon. The original device was used for the detection of Ag and Mg by AA and AF, but a modified design did not incorporate a **cl**osed chamber assembly (129). Using these systems, West and coworkers have determined Cd (129), Mg, Ag (128, 130), Pb, Zn, Bi, Tl, Ga (130), Au (131), Sb, Cu, Co, Ni, Hg (132) and Mn (132,133) by atomic fluorescence spectrometry, while Ag, Mg (128,132), Au (131), Pb, Cu (132,134), Ni, Al (134), Mn (133,135), Ni (136), Cr (137), Fe (138), Zn . Mo (139), Cd (140), V (141) have been measured by atomic absorption.

Since, in contrast to furnaces, no further energy is available in the space above the filament-type atomizer, condensation of the atomic vapor occurs and results in a shorter lifetime of free atoms. In order to minimize interelement effects, it is necessary to view the atomic vapor close to the atomizer. It is possible to remove or reduce the severity of interferences by carrying out AF and AA measurements in such a way that an area extending only 0.5 mm above the filament is illuminated (131,132,134-136). This method of measurement is referred to as a "limited field of view" in the literature and can also be employed for the study of the decay of atomic populations both by AA and AF (131,132,134,138-140,142,143). The rate of decrease of the atom population above the atomizer is considerably less if the argon atmosphere is replaced by hydrogen. In operation, the glowing filament ignites the hydrogen, and a diffusion flame results. Using a modified form (144) of West's device and a hydrogen-diffusion flame, Amos et al. (146) observed considerably less serious spectral and chemical interferences from other ions. Winefordner and coworkers (143-**145**,147) have used similar techniques and noted the improvement of free atom lifetimes above the filament.

In comparing the West-type atomizer with furnaces, it should be **noted** that while the filament-type atomizer does not exhibit the **same** freedom from interferences and can be used for the analysis of **a smaller** number of elements, it has the advantages of compactness, **lower** power consumption, and ease of operation. In an effort to com **bine** the virtues of the West filament and the Massmann furnace, a **transverse** hole of 1.5 mm in diameter was drilled in a 5 mm diameter **rod** to produce a miniaturized furnace (148). Other versions, which

are basically similar to the miniature furnace, involve the use of a carbon cup or tube (149). The West-type atomizer, the carbon cup and the carbon tube are all commercially available from Varian Techtron (Walnut Creek, Cal.).

The various versions of graphite or carbon filament atomizers have had widespread clinical, environmental and industrial applications. They have been used for the determination of Mg (150), Zn (150), Cd (151), Cr (152), Pb (146,150), Fe (150,153), and Cu (150,154,155) in blood (146,150-152), plasma (150), serum (153-154) and tissue (155), for the determination of Cd in food and air (151) and for the analysis of Cd in sea-water, sugar and glycerine (152). Mini-Massmann type carbon rods have been employed for the measurement of Au and Ag (156) as well as Sb (157) in geological and metallurgical samples.

Alder and West made direct determinations of Ag and Cu in lubricating oil (158) and Hall et al. (159) evaluated the mini-Massmann carbon rod and the West-type filament for routine determinations of Ag, Cu, Fe, Ni and Fe in lubricating and crude oil. Winefordner and coworkers (160) have determined Ag and Cu in jet engine oil by atomic fluorescence and have analyzed for Ag, Cr, Cu, Fe, Ni, Pb, and Sn in used jet engine and reciprocating engine oil by atomic absorption (161). Finally, West and coworkers have determined Ni (162) and V (163) in crude and residual fuel oil, while Bratzel and Chakrabarti (164) and Robbins (165) have reported the determination of Pb in petroleum and petroleum products.

3. Cold Vapor Technique

A widely used method for the measurement of traces of Hg, As, Se and Sb is the cold vapor technique utilized for both AA and AF. For mercury compounds, the sample is introduced into a reduction cell, and the resulting mercury vapor is swept into a long path length absorption cell for measurement. For As, Se and Sb, the resulting gases are either introduced into an electrically heated absorption tube (166) or into an argon-hydrogen flame. The technique has been used for the determination of mercury in air samples (167), in fish, sediment, and wheat flour (168-170), in urine and plasma (171), in geological materials (169,172,173) and in clothing materials (170).

4. Nonflame Atomizers Using Electrical Discharges

a. <u>Cooled Hollow Cathodes</u>. In 1959 Russell and Walsh (174)
suggested that cathodic sputtering might be a means to obtain an
atomic vapor from solid samples for use in AA. Gatehouse and Walsh
(175) were the first to use a hollow cathode tube as an absorption
cell, and they determined Ag in metallic copper in the range of 0.0050.05%. It must be noted that the determination of Ag in Cu is one of
the most favorable since the sputtering yields are high. Later, Walsh
(176-177) reported that Sullivan, who used water-cooled cathodes and
a flow through gas system, had analyzed phosphorus and silver in copper,

With a similar system, Gobels and Brody (179) evaporated sample VOl umes onto the inner wall of an aluminum hollow cathode and detected lug of Na, Ca, Mg, Si, and Be, although considerable inter-elements effects were observed. Gobel (180,181) has also developed a technique

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for the determination of isotopic composition by using this device in atomic absorption spectrometry. Recently, Walsh and coworkers (177, 178) determined C, Si, P, Mn, Ni, Cr, Mo, V and Cu in iron-base alloys with a non-dispersive atomic fluorescence system which incorporates a sputtering chamber. The standard deviation at higher concentrations was reported to be $\sim 1\%$, and the analysis time was 3-4 minutes. Harrison and Daughtrey (182) have also used a demountable hollow-cathode lamp with a steel cathode for trace analysis of gold by atomic emission.

b. <u>Hot Hollow Cathodes</u>. Atomic absorption methods with hot hollow cathodes were first described by Ivanov et al. (183). The cathode cylinder was held in the optical path by a thin molybdenum foil. This configuration causes the conductive heat losses from the cathode to be smaller than radiation losses, and the cathode becomes red-hot during the discharge period. The sample, placed in the cathode as a solid or as a solution, is entirely evaporated in the discharge. A similar type of absorption cell incorporating a graphite cylinder was employed by Massmann (184). The discharge was operated at an argon pressure in the range of 1-10 torr and a power of up to 1 kW. It was noticed that the atomic vapor was produced by boiling the sample in the hot hollow **Cath**ode and only to a lesser extent by cathodic sputtering. This is a **d**efinite advantage of the hot hollow cathode over the cooled version.

If the hot hollow cathode is operated with a half-wave rectified ^{Cur}rent and the primary radiation source is activated only when the ^{abs} Orption cell is dark, then AA measurements can be made without ^{spectral} interference. Since the graphite cathode, heated by an electrical discharge at reduced pressure, cannot reach temperatures

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higher than 2000 °C, only volatile elements such as Zn, Pb and Al can be analyzed. Since the residence time of the atoms in the absorption tube is short, the method is not suitable to detect small amounts if sample size limitations exist. With this device, Massmann obtained detection limits for Ag, Sb, Zn, Cu, Cd, Mg, Mn and Cr in volatile matrices.

c. <u>Arc and Spark</u>. The use of an ac or dc arc for sample atomization in AA has been reported by several workers. Kantor and Erdey (185) employed an electronically controlled ac arc and made a timeresolved study of Cd, Na, Al, and Pb using Osram or tungsten filament lamps as primary radiation sources. It was noticed that for Na the amount of emission was negligible 2.4 msec after the discharge, and for Al and Pb absorption occurred only when the arc was operated in an argon atmosphere. Belyaev et al. (186) utilized an arc atomizer for the determination of silver in rocks and reported a sensitivity of 1.5×10^{-7} %. The standard deviation at the sensitivity threshold was 30%.

Marinkovic and Vickers (187) described a long-path stabilized dc arc for the determination of Al, B, Mg, V and W. The sample was introduced into the arc as a solution aerosol. The result showed that neither the analytical curves nor the sensitivities were appreciably different from those obtained with chemical combustion flames. The lack of improvement was due to the fact that the optimum region of the arc for AA measurements was far removed from the high temperature axial region.

Jones et al. (188) combined a direct current capillary arc operating in argon at atmospheric pressure and a device which produced fine

particles from the surface of a solid metal for use in atomic emission. The aerosol generator was a device in which the sample acts as the cathode of a dc arc discharge. A flowing argon gas stream carried the aerosol particles to the capillary arc discharge. The method was applied to the determination of 10 elements in stainless steel alloys. Winge et al. (189) used a similar aerosol generator, but employed a flame as the atomization device for the determination of Cr, Mn, and Ni in steel. Finally, Robinson (190) used a conventional nebulizer and a spark for AA measurements of aluminum.

d. <u>Plasmas</u>. Several types of electrically generated flames have been introduced for atomic emission and atomic absorption in recent years. The plasmas can generally be classified in terms of the frequency of the exciting field. The induction-coupled plasma and plasma torch were first employed for atomic emission analysis (191,194). The plasma generator usually had a frequency of 4-36 MHz and a power level of 500-5000 W. Wendt and Fassel (195) demonstrated the use of the induction-coupled plasma for the determination of nine elements by AA. Friend and Diefenderfer (196) also determined elements forming refractory oxides by AA.

With a similar plasma but a different sample introduction system, Veillon and Margoshes (197) reported pronounced inter-element effects. Dickinson and Fassel (198) reported the detection limits of 26 elements in AE and stated that the conclusions of Veillon and Margoshes were bas ed on observations made with particular experimental conditions and that their deduction does not appear to be generally applicable. Boumans and DeBoer (199) evaluated induction-coupled plasmas for simultaneous multielement analyses and determined 33 elements by AE. In many

instances detection limits lower than published previously (198) were established. Induction-coupled plasmas have been used for the determination of trace metals in microliter samples in oils, organic compounds and biological fluids (200,201).

Microwave plasmas, operated at a frequency of 2450 MHz, have also been used for spectrochemical analysis. Most of the work in this area is related to atomic emission. Mavrodineau and Hughes (202) excited the spectra of 75 elements, and Murayama et al. (203) reported the detection limits of 25 elements. Similar systems have been used for the detection of Cd, Ga, In, Hg, and Zn (204). West and coworkers utilized a 40 W microwave-induced plasma in conjunction with a sample introduction system such as a platinum or tungsten loop for the analysis of 12 elements in AE (205). Recently Busch and Vickers discussed the fundamental properties of a low-pressure, microwave-induced plasma as an excitation source for analytical spectroscopy (206).

e. <u>Radiation Heating</u>. Pulsed discharge lamps and pulsed lasers are two different types of radiation sources which have been employed to evaporate samples for atomic absorption by heating. In both techniques the solid samples can be evaporated by a pulse of short duration. For laser heating, the evaporation is done by a focused laser beam, while for the pulsed discharge lamp, no optical arrangement is used to focus the radiation onto the sample.

The pulse operation of a capacitor discharge flash lamp allows **Production of large amounts of light with relatively modest equipment. Kue bler and Nelson (207) estimated that the irradiance of such a lamp was as high as 60 KWcm⁻².** The same authors employed this system to **obtain spectra of gaseous species formed at flash-heated surfaces (208).**

Later absorption spectra of Au, Al, Ag, B, Ca, Cu, Dy, Eu, Fe, Mg, Pb, W, and Zn were produced directly from solid elements, chloride deposited on graphite strips, or from impurities in W (209). In these experiments, the duration of a flash was about 3 msec. A second flash lamp was used as the primary source. The source flash persisted for 20 µsec and could be ignited with variable delays of up to 6 msec. after the start of the heating pulse. A photographic emulsion was used as the detection system, but no quantitative data were reported. In some cases loss of sensitivity for an element may occur due to vaporization as a molecule. Intense absorption of AlCl was an indication of this effect.

Since the invention of a pulsed, high-power laser in 1960, there have been numerous publications regarding the utility of a laser for atomic spectroscopy (210). In order to achieve direct atomization of certain phosphors and photocathode materials for atomic absorption analysis, Atwill (211) vaporized analytical samples with the concentrated output of a gigawatt pulsed laser. This could provide pulses of 10¹⁰ kWcm⁻² at the surface of the substance under study and was **Capable of vaporizing a sizeable portion of any known material**.

Because of the initial cost and wear on optical elements, Mossotti et al. (212) used a laser pulse of medium power as a means of atomizing $0.1-10 \mu g$ of analytical material for atomic absorption. The atomic vapor produced by the Q-switched laser was excited by a Xenon flash lamp, and the atomic absorption due to the transient vapor cloud was displayed as a function of time on the screen of an oscilloscope. Since the standard deviations of measurements were high, the concentration limits for Ca, Ag and Cu were reported at 10 percent absorption

and were 0.0025, 0.0040 and 0.0035 percent respectively. It was also noticed that the laser atomization efficiency was critically dependent on the nature of the target material.

Piepmeier and Malmstadt (213) used a Q-switched laser and studied energy absorption in the plasma of an aluminum alloy. It was stated that matrix effects depend upon the atmosphere as well as the sample material and should be significant. A similar system was used in conjunction with pulsed hollow cathode lamps as primary radiation sources for AA measurements (214). Calibration curves were obtained for Cu (0.002-0.15%) in an aluminum alloy and Mn (0.013-0.124%) in graphite pellets.

5. Controlled Explosion Atomizer

A new, direct application of chemical energy for atomic absorption has been engineered by Venghiattis (215). The method consisted of controlled burning of a blend of a solid propellant (oxidizer and fuel mixture) and the solid material under study. The generated atomic vapor was introduced into the absorption light path of a conventional atomic absorption spectrometer. The technique has been applied to the determination of trace elements such as Au, Ag, Cu, Pb, and Zn in ores. Although some sample dilution was necessary, the method was sensitive to ppm concentrations of gold in ore. However, it may be difficult to achieve better than 5 percent precision because the method requires considerable sample preparation, especially for materials that are not easily pulverised. The technique may find considerable application in field analysis if transportation of gas cylinders, solutions and chemicals is inconvenient.

D. Radiation Sources for Atomic Absorption and Atomic Fluorescence Spectrometry

One of the most important components of atomic absorption and atomic fluorescence instrumentation is the radiation source. At least part of the remarkable success of atomic absorption as an analytical technique must be attributed to the successful manufacture of hollow cathode lamps and their commercial availability. On the other hand, the lack of suitable radiation sources for atomic fluorescence is a practical disadvantage at the present time. Various sources such as metal vapor discharge lamps, hollow cathode lamps (HCL's), high intensity HCL's, demountable and water-cool HCL's, modulated and pulsed HCL's, electrodeless discharge lamps (EDL's), modulated EDL's, temperature-controlled ELD's, continuous sources, induction-coupled plasmas, flames, arcs, sparks and lasers have been used for AA and AF spectrometry. A description of almost all of these sources has been given in literature (216,217) and reviewed recently (218). Since lasers and pulsed HCL's have not been reviewed in great detail, a review of the previous work on these sources is presented here.

1. Radiation Source Requirement in AA and AF Spectrometry

One of the most important characteristics of a radiation source for both AA and AF is the shape of spectral line emitted by the source. The six factors which govern the shape of spectral line are Natural, Doppler, Lorentz, Holtzmark, (or Resonance), Stark, and Self-absorption broadening. Lorentz and Holtzmark, broadening together are often called pressure broadening. In the conventional HCL used in atomic absorption, broadening effects that reduce sensitivity most are

Doppler and Self-absorption broadening. This situation may change, however, if the lamp is operated in the intermittent high current mode. Before getting to the discussion of pulsed HCL's, the general requirements of radiation sources are summarized. Because of the differences in the mechanisms of the AA and AF phenomena, there are some differences in the source requirements.

For Atomic Absorption:

a. The source should radiate light of the element of interest without interference from other spectral lines originating from other components of the source.

b. The resonance spectral line must be sharp and bright against a very low background.

c. Radiation intensity should be high for low lamp currents.

d. The source should have short and long term stability (low noise and drift).

e. Ignition and burning voltage should be low to permit pulsed or modulated operation.

f. The source should be commercially available, easy to operate, of low cost, small in size, capable of being operated continuously and safely, and should have a long shelf-life.

For atomic fluorescence the source requirements are similar to those for AA except that:

a. Since the atomic vapor produces essentially monochromatic fluorescence emission, the purity of the source spectrum is not as important as it is for AA. Scattering of light in the vapor cell, if present, may result in erroneous measurements of the fluorescence signal, however. b. The source need not radiate such narrow spectral lines.

c. The fluorescence radiation observed in an atomic fluorescence measurement is directly proportional to the radiance of the excitation source as is shown by Equation (9) in Chapter III. Thus, the main requirement is a high intensity of the resonance line at the absorption wavelength peak. In fact, if a radiation source such as a laser should provide a highly excited system which is near saturation, then the fluorescence emission shows relatively little dependence upon changes in laser intensity or changes in collisional quenching (219, 220). It should be noted, however, that under this condition, the fluorescence emission still retains a linear dependence (assuming dilute vapor) upon analyte atomic density in the atomizer.

2. Laser Sources

Most of the work done with lasers as excitation sources has been concerned with atomic fluorescence. However, a tunable dye laser has been used for sodium analysis (221) by atomic absorption. The limit of detection was reported to be 2 ng for sodium, and the calibration curve was linear from 2 to 500 ng/ml.

The first application of a tunable dye laser for atomic fluorescence was described by Denton and Malmstadt (222), who reported the analysis of barium. A stable, pulsed, tunable dye laser pumped with a N_2 laser has been employed in conjunction with a fast response multiplier phototube and a boxcar integrator by Winefordner and coworkers (223-225) to excite the atomic fluorescence of 27 elements in flames. The dye laser system has a peak power of greater than 10 kW from 360-650 nm, a pulse repetition rate of about 1-25 Hz, a pulse

half-width of about 2-8 msec, and a spectral half-width of about 0.1 -1 nm. The calibration curves were linear over 2-4 orders of magnitude, and detection limits were improved for some of the elements. Since strong ionic fluorescence has been observed for some of the rare earth elements, ionic as well as atomic fluorescence detection limits were reported. For the majority of the rare earths, atomic fluorescence detection limits were essentially the same as the best ones reported by flame atomic absorption, but inferior to flame atomic emission.

It should be noted, however, that laser excitation has several advantages over conventional continuously operated line or continuous sources. First, only one source is needed. Second, it is possible to eliminate noise due to scattering of exciting radiation from particles within the vapor cell if nonresonance fluorescence is used. Nonresonance fluorescence with conventional sources is not useful because of low quantum yields. However, the high spectral irradiance of the laser allows these lines to be readily observed. This has been shown for Al and some of the other elements (224). Third, in addition to resonance fluorescence, other types of fluorescence have been shown to be analytically useful. Fourth, since the saturation condition is approached with laser excitation, the proportional dependence of the fluorescence signal upon the quantum yield, Y, observed at low irradiances, is removed. This has been also shown theoretically and experimentally both for monochromatic and broad-band laser excitation (219, 220,226,227). In other words, assuming that the atomization efficiency does not change, the saturated fluorescence signal obtained with vapor cells of different quantum yields would be the same. For example, one could take full advantage of the greater reduction of chemical

interferences and/or the greater atomization efficiency of the C_2H_2/N_2O flame over the $O_2/Ar/H_2$ flame (226). Fifth, when a laser or another high irradiance source is used as an excitation source, the dynamic range is increased. For example, analytical curves for indium were linear from 50 to 10,000 ppm and for strontium from 100 to 50,000 at high irradiances (227). The calibration curve bent at lower concentrations when the laser irradiance was decreased.

Laser excitation has its disadvantages, however. First, for concentrations above the detection limit, one of the major sources of noise is laser pulse-to-pulse variation. One convenient way to minimize this effect is to assume that the long term average source radiance is constant and then integrate the output signal for a period of time. Furthermore, it has been shown that under saturation conditions the fluorescence signal is not greatly influenced by source stability (219.226). Second, the scattered light intensity continues to increase in direct proportion to the laser spectral output, while the excited atom population begins to level off as saturation is approached. It is possible, of course, to use a non-resonance line. Third, at the present time, the enormous consumption of electrical energy by a laser necessitates the focusing of the laser beam to a small region of the atomizer to achieve saturation. Furthermore, typical laser beams may not have uniform cross-section and a careful consideration of the entire optical system is required. Fourth, the lower wavelength range of the present dye laser is approximately 2500 Å, although it may be possible to extend the wavelength range down to 2000 Å, by frequency doubling. Fifth, the very high cost of the dye laser system and its maintenance is prohibitive at the present

time.

3. Pulsed Hollow Cathode Lamps

Because of the above disadvantages of the laser, the spectral source which appears to be highly suitable for atomic fluorescence with respect to cost, availability, wavelength coverage, selectivity and intensity is the hollow cathode lamp operated in a pulsed mode.

The first analytical application of pulsed hollow cathode lamps was discussed by Dawson and Ellis (228). By passing large currents (300-600 mA) of short duration (15-40 μ sec) repetitively through conventional hollow cathode lamps, such as Ca, Co, Cu, Mg, Mn and Sr lamps, an increase in intensity from fifty to several hundredfold was achieved. The enhancement obtained was greatest with the metals of lower melting points, and there was no corresponding increase in the intensity of the spectrum of the filler gas. The detection limits and calibration curves obtained were comparable to those reported in the literature with other sources. From these observations and from the fact that the mean current was about 2 mA, the authors concluded that the resonance lines were not significantly broadened in the pulsed mode.

Using a similar system in conjunction with a resonance monochromator, Willis (229) reported that the fluorescence signal from the resonance monochromator, excited by a pulsed copper hollow cathode lamp, was only about five times that obtained by operating the lamp in the dc mode at the same average current. In other words, the large increase in emission intensity was achieved at the expense of an increase in broadening of the emitted resonance lines. Since the resonance

monochromator has a spectral bandpass of about 0.01 Å, this experiment showed that the increase in intensity at the *center* of the line, obtained with pulsed operation, is not as large as found by Dawson and Ellis for the integrated intensity over the whole line.

The increase in broadening can be explained in terms of the excitation mechanism (216,230) in a hollow cathode lamp operated at high currents. Initially, the discharge filler gas is excited or ionized by electron impact. The discharge ions then collide with the cathode walls where they are neutralized or release a neutral atom of the cathode material. Then, neutral atoms are brought into the plasma where they can be excited by electron impact or by collisions of the second kind. At higher currents, a larger amount of the discharge gas is ionized and, hence, more neutral atoms are formed. These neutral atoms can either form a deposit at the cathode or leave the discharge by diffusion. The plasma inside the hollow cathode is emitting and partly absorbing the resonance emission. The slab (231,232) outside the electrode contains atomic vapor diffusing from the discharge and is only absorbing. If the concentration of these absorbing atoms between the emitting atoms and the lamp window is significant, additional broadening will be experienced by the resonance lines (233). Therefore, it is not unreasonable that high current pulsed hollow cathode lamps exhibit effects of broadening or self-reversal.

Despite the increase in emission line width, pulsed hollow cathode sources are still very useful for atomic fluorescence. Weide and Parsons (234), who use pulsed hollow cathodes in conjunction with a box-car integrator, reported that the limit of detection for zinc (0.003 ppm) with the pulsed system was nearly three orders of

magnitude lower than with a conventional system. Mitchell and Johansson (235-236) used the pulse-modulated technique for an elaborate multielement atomic fluorescence system. However, they gave no indication of any gain in detection limit using their own pulsing system.

Massmann (69) employed HCL's of his own design and manufacture to excite fluorescence for nine elements. Sufficient intensity was obtained by manually pulsing the HCL at a current of several hundred mA for periods of about 15 seconds during which fluorescence measurements were made. No information was given on the profiles of the resonance lines emitted by this source, but the author commented on the comparatively low intensity of such sources. Nevertheless, the detection limits obtained by AF for Zn and Cd were superior to those obtained by AA. For seven other elements investigated by both techniques, absorption was found to give superior results.

Several authors have used pulsed hollow cathode lamps for atomic absorption and atomic fluorescence measurements, and results obtained indicate little additional line broadening due to pulsing (214,237-241). Gains in light intensity due to pulsing were about one to two orders of magnitude (214,238-241). The exact intensity increase depends on the element and the filler gas and may vary from lamp to lamp. The lamp lifetime has been reported to be longer in the pulsed operation than in the dc mode (228,240). It has been shown that the ON time, the pulse width/period ratio, the number of periods, and the wait time between each series of ON-OFF periods were all important for providing reliable operation (240).

Various versions of pulsed hollow cathode systems have been used for the selective modulation of resonance lines, for the construction

of atomic absorption spectrometers with no monochromator, etc. (242-245). Pulsed hollow cathode sources were also used by Kielkopf (246) who operated them at peak currents between 30 and 1500 A. With this pulsed hollow cathode lamp, excitation of up to the third spectrum of iron and aluminum and parts of the fourth spectrum of the rare earths could be observed. The plasma within this source showed an ionization temperature of about 12,000 °K, electron densities of about 10^{15} cm⁻³, and electron temperatures of about 15,000 °K. This type of source has proven very useful in classifying lines in ionized rare earth spectra and in analyzing the processes which go on in pulsed discharges.

E. Multielement Analysis

The important role of minute amounts of elements in physical, chemical and biological systems has emerged as methods of analysis have increased in sensitivity. A wide variety of various instrumental techniques such as X-ray fluorescence spectrometry, spark and arc emission spectrometry, spark source mass spectrometry and thermal neutron activation, involving widely different principles and capabilities, have been introduced for simultaneous multielement analysis. Each of these techniques has its own advantages and disadvantages. While the detection power increases in the order the techniques have been arranged, there is a corresponding increase in the cost and complexity of the instrumentation. In general, it is desirable for any analytical system for simultaneous multielement analysis to meet certain general requirements. First, the system must be capable of handling small

sample sizes. Second, the techniques must be capable of determining accurately and precisely many elements at the 0.02-10 ng/ml concentration level. Third, absolutely no sample preparation should be needed. Fourth, a broad dynamic range is required. Fifth, the technique should be rapid, easy and safe to operate and inexpensive.

In a recent review article, Busch and Morrison (247) compared flame spectrometry and other multielement techniques with respect to some of the above requirements. It is an obvious fact that, at the present time, there is no analytical technique which can fulfill all of the above general requirements. However, flame and nonflame spectrometry can fill the gap among the more expensive techniques and are adequate and satisfactory alternatives.

There is no question that compared to AA and AF, flame emission is more adaptable to multielement analysis. The development of semiconductor photo-electronic detection devices (248) will provide a detection system other than the multiple slit-multiple detector system used in expensive emission spectrometric system. Experimental results for the nitrous oxide-acetylene flame (249) indicate that flame emission may cover some 40 elements with detection powers equivalent or superior to flame absorption. Thus, for complete coverage of the common group of some 70 "spectroscopic" elements, flame atomic absorption and/or flame atomic fluorescence must be used complementarily to flame emission (199). If an induction-coupled plasma similar to that described by Fassel and coworkers (198,201) is employed, the detection power of many elements would be in the range of 0.02-10 ng/ml and complementation by atomic absorption and/or atomic fluorescence is not required (199). In chosing a plasma system, however, the following

facts should be considered. First, the high excitation temperature necessitates the requirement of a medium or high resolution spectrometer. Second, matrix effects (199) do occur and must be studied systematically. Third, the economic factors, such as cost of equipment and large amounts of argon consumption must be carefully considered.

Another interesting technique of performing simultaneous multielement analysis is a completely nondispersive method. In contrast to energy dispersive X-ray fluorescence where the achievable detection limits are in the range of 10-50 ppm, the working range for a nondispersive atomic fluorescence system is ppb to ppm. The previous work on multielement atomic spectrometry has been reviewed (47,247), and it is the author's intention to briefly review the nondispersive systems.

The first nondispersive system for atomic fluorescence was proposed by Jenkins (250), who noted that a filter could replace the monochromator to isolate the resonance line of the element of interest. Larkins et al. (251) suggested the application of solar-blind photomultiplier detectors for atomic fluorescence flame measurements. Since most of the noise emitted by the flame appears at wavelengths longer than 3000 Å, it is possible to allow the fluorescence radiation to fall directly on the detector and still avoid flame background noise. Vickers and coworker used this system (252) and a similar system incorporating a chlorine cutoff filter, which responded to radiation of wavelengths shorter than 2800 Å (253). Larkins (48) used a solar-blind photomultiplier in conjunction with a sheathed flame and examined the fluorescence of 24 elements. He found that his system gave better detection limits for nine elements compared to atomic absorption flame spectrometry. Similar nondispersive systems have been
used by other investigators (254-256).

Nondispersive atomic fluorescence methods for multielement analysis were first described by Michell and Johansson (257,258). Their instrument was used for the determination of Ag, Cu, Fe and Mn using an airhydrogen flame, and their results were quite comparable with those obtained by others who used a conventional monochromator system. A sixchannel atomic fluorescence spectrometer based on this system was manufactured by Technicon Corp., Tarrytown, NY. The AFS-6 (now taken off the market) instrument has been used for the determination of metals in soil extracts (259) in aluminum alloys (260), and with preconcentration by an automated solvent extraction procedure (261). Using the same principle, Cordos and Malmstadt (241) described a similar dispersive system which incorporated a programmable monochromator for high speed wavelength isolation. Their instrument may be used to determine up to 12 elements sequentially.

III. THEORETICAL DESCRIPTION OF NONFLAME ATOMIZATION AND ANALYTICAL SIGNAL

The first section of this chapter discusses the various distribution laws for flame and nonflame atomizers and the influence of various processes on the atomizer temperatures. Section B presents the radiance expressions for atomic absorption and fluorescence spectrometry along with the expressions providing the peak atomic concentration in flame and nonflame devices. The atomization processes in nonflame atomizers are discussed in the third section, and the influence of natural and forced convection on nonflame atomization are discussed in the fourth section. In the final section, the time behavior of analytical signals with nonflame devices is described.

A. Distribution Laws

In deriving the radiance expression relating the concentration of an element in a sample to the readout, it is assumed, in both AA and AF, that the atomizer is in a state of "local" thermodynamic equilibrium. In thermodynamic equilibrium, the spectral distribution of radiation density and the distribution of energy over the various internal and translational degrees of freedom as well as the distribution of ionization and dissociation products are determined by T, the temperature of the system. If it is assumed that singly charged ions and free electrons are the only ionization products in a flame atomizer, there are five statistical distribution laws (35) for the various forms of energy which are summarized below:

1. Planck's Radiation Law

Planck's radiation law relates the spectral radiance B_{λ}^{b} of a black body to the temperature T and the wavelength λ by Equation 1

$$B_{\lambda}^{b} = \frac{2hc^{2}\lambda^{-5}}{\exp\{hc/\lambda kT\}-1}$$
(1)

where h is Planck's constant, c is the speed of light and k is the Boltzmann constant. The absorption factor $\alpha(\lambda)$ is defined as the ratio of the absorbed radiant power to the incident power and, by definition is equal to unity for a black body. The spectral radiance B_{λ} of an arbitrary radiating body with $\alpha(\lambda)$ <l is related to the spectral radiance of a black body at the same temperature by Kirchhoff's law given in Equation 2

$$B_{\lambda} = \varepsilon(\lambda)B_{\lambda}^{b} = \alpha(\lambda)B_{\lambda}^{b}$$
(2)

where $\varepsilon(\lambda)$ is the emission factor. Equation 2 is an approximation for open flames where radiative equilibrium may not exist.

2. The Boltzmann Law

The Boltzmann law describes the relative populations of the various discrete levels of internal energy of a particle. The fraction of particles $f(E_j)$ in the jth level with the statistical weight of g_j and with an energy E_j with respect to the ground level is given by Equation 3

$$f(E_j) = \frac{g_j \exp\{-E_j/kT\}}{\sum_{i=0}^{\infty} g_i \exp\{-E_i/kT\}}$$
(3)

3. The Maxwell Law

The Maxwell law describes the distribution of the velocity and provides the fraction $f(E_k)$ of particles with mass m that have a kinetic energy E_k with a spread dE_k

$$f(E_k)dE_k = \{2/(\pi)^{1/2}\}\{E_k/(kT)^3\}^{1/2}exp\{-E_k/kT\}dE_k \qquad (4)$$

where V_x , V_y and V_z are the velocity components along the X, Y and Z axes respectively, and $E_k = \frac{m}{2}(V_x^2 + V_y^2 + V_z^2)$.

4. The Saha Law

The Saha law relates the concentration of neutral species to those of the corresponding ionic species and free electrons.

5. The Mass Action Law

The Mass Action law relates the concentrations of reactants to reaction products in equilibrium.

It should be realized, however, that since actual flames are not truly adiabatic systems, local differences in temperature occur and a general thermodynamic state of equilibrium cannot exist. It may happen that for some forms of energy an equilibrium distribution has already been established, whereas for other forms it has not yet resulted. In other words, a situation may exist where various timevarying T parameters can be assigned to different forms of energy. For example, for a flame burning at 1 atm pressure, the relaxation time (35) for the achievement of the Maxwell velocity distribution may be on the order of 10^{-8} to 10^{-9} seconds. The relaxation time for the Boltzmann equilibrium over the molecular rotational degrees of freedom is 10^{-7} to 10^{-8} seconds, while equilibration of energy over the vibrational degree of freedom may require as long as 1-10 $\mu \text{sec.}$

Under these conditions we may speak of *Partial Equilibrium* for each form of energy. Furthermore, since a Maxwell velocity distribution of all atomic and molecular species is readily established, the temperature associated with velocity distribution can be defined as the "true" (local) flame temperature.

B. Radiance Expressions

It should be stressed again that the radiance expressions have been derived (263-265) for a region in a flame which is in local thermodynamic equilibrium. These expressions are useful for comparison of theoretical limits of detection and for determining the shapes of analytical curves in AA and AF. In the following radiance expressions, it is assumed that the analyte atomic vapor is excited by a line source in both AA and AF systems, that a monochromator is used to isolate the resonance line and that the source halfwidth, $\Delta\lambda_s$, is smaller than the absorption halfwidth, $\Delta\lambda_A$, in the flame.

1. Atomic Absorption Expressions

If the spectral bandpass of the monochromator isolates only the resonance line, the total radiance absorbed, B_{AAL} , is given by Equation 5

$$B_{AAL} = B_{L}[1 - exp(-\kappa_{o}nflo_{o})]$$
 (5)

where B_L is the total integrated radiance of the line source, n is the concentration of the atomic vapor in the ground state, f is the oscillator strength, κ_0 is the modified absorption coefficient, ℓ is the

atomizer path length and δ_0 is the Voigt profile factor. For low concentrations of analyte, B_{AAL} is directly proportional to n as shown in Equation 6

$$B_{AAL} = B_{L} \kappa_{o} nf \ell \delta_{o}$$
(6)

while for optically dense media the absorbed radiance is independent of atomic concentration.

In AA, the measured parameter is the fraction of radiance absorbed, $\ensuremath{\alpha}$

$$\alpha_{AAL} = \frac{B_{AAL}}{B_L}$$
(7)

which is related to absorbance $A = -Log(1-\alpha)$. Thus,

$$A = \frac{\kappa_0 n f \ell \delta_0}{2.303}$$
(8)

It can be seen from Equation 8 that the absorbance is linearly related to n. At high concentrations, the Voigt profile factor δ_0 decreases and the absorbance no longer increases linearly with n.

2. Atomic Fluorescence Expressions

The fluorescence radiance with a line source B_{AFL} is given by

$$B_{AFL} = B_{AAL}(\frac{\Omega}{4\pi})(\frac{L}{\ell})Yf_{s}$$
(9)

It is assumed in Equation 9 that right angle illumination is used, that the entire flame width L is illuminated by the excitation beam, and the fluorescence over the entire flame width ℓ is collected by the monochromator. The parameter Y is the quantum yield for resonance fluorescence and the factor $\Omega/4\pi$ is the fractional solid angle of radiation collected from the source which impinges upon the flame. For low values of n, the self-absorption factor, f_s , is unity while for high optical densities f_s is proportional to $1/\sqrt{n}$. Thus, a plot of log B_{AFL} against log n would yield a slope of unity for low nl values and a slope of -1/2 at high values of nl.

3. Relationship Between n and Solution Concentration

For the flame atomizers, the atomic concentration n in Equations 5 and 9 is related (35,263,265) to C, the concentration of the analyte in the solution by Equation 10

$$n = 6x10^{23} \left(\frac{F \epsilon \beta C}{Q e_f B(T)} \right)$$
(10)

where F is the transport rate of solution as determined by the nebulizer, ε is the efficiency of producing analyte molecules in the flame, β is the free atom fraction, C is solution concentration in moles of analyte/cm³, Q is the flow rate of unburnt gases into the flame, e_f is the flame gas expansion factor, and B(T) is the normalized partition function. Because of the variation of the degree of ionization, solute vaporization, aspirator yield and solution transport rate with C, the concentration n of the analyte in flames, may not be linear with C at all solution concentrations. The effect of all of these parameters have been the subject of many publications by various investigators and have been summarized and critically discussed (25).

With minor modifications, the above theoretical expressions are generally applicable to various versions of AA and AF systems which incorporate line radiation sources. For example, a nonflame atomizer such as a furnace containing hot gases can be approximated to exhibit a state of thermodynamic equilibrium. Thus, Equation (10) is also valid for a tubular furnace into which the sample is continuously nebulized. The situation is different, however, if discrete sampling is employed as is done with many furnace and filament-type atomizers.

C. Atomization Processes in Nonflame Atomizers

For the sake of simplicity, the whole process of transformation of the analytical sample into free atoms by a variety of mechanisms and the interaction of these free atoms with their environment is arbitrarily divided into three parts: the atomization period; the steady state period; and the de-atomization period. In the atomization period, the rate of free atom formation is much higher than the rate of the removal of the free atoms from the observation window; the net rate is positive. For the steady state period, the net rate is zero, while in the de-atomization period the net rate of free atom production is negative.

1. Atomization Rate

Under conditions of high vacuum and where the vapor pressure of the substance is less than about 1 torr, the vapor molecules can be assumed to leave the emitting surface relatively unimpeded. The mass of substance removed as vapor from unit area at a given temperature and in unit time will then be the same as that evaporating from the surface of the substance in equilibrium with its saturated vapor.

Under these conditions the following equation has been derived for the rate of evaporation R_F in a vacuum (266).

$$R_{E} = aP \sqrt{\frac{M}{2\pi RT}}$$
(11)

where P is the saturated vapor pressure at the temperature T, M is the molecular weight, and a is the condensation coefficient. Metals are monoatomic in the vapor phase with the exception of antimony which evaporates mainly in the form of diatomic molecules. The condensation coefficient a has been found to be equal to unity for most metals. Simplifying equation 11, we have

$$R_E = 5.85 \times 10^{-2} P \sqrt{\frac{M}{T}} g.cm.^2 sec.^1$$
 (12)

where P is in torr. At atmospheric pressure, it can be assumed (267, 268) that the evaporation rate is about one-sixtieth of the rate in vacuum, $R_{atm} = \frac{R_E}{60}$.

Using Equation 12, L'vov calculated the vapor pressure required for any element to be vaporized in less than 100 msec. (9). If an instantaneous temperature of 3500 °K can be achieved, it was found that in order to atomize 10^{-8} g of an element with an arbitrary atomic weight of 50, a vapor pressure of 0.1 torr or greater is required. Since for most elements, except the refractory metals, the saturated vapor pressure is greater than 0.1 torr, it can be assumed that most elements are atomized in less than 100 msec. It should be noted that L'vov's calculation assumes instantaneous achievement of temperature and does not incorporate the chemistry of free atom formation if the element is present in the form of a compound. For most furnace and filament atomizers, a finite time is required before a desired temperature is achieved. This dead time can vary with the design of the heating system, the atomizer, and the method of its regulation and is discussed in Chapter VI. Even if the atomization temperature can be reached instantaneously, if the sample is not a pure element, a certain amount of time is also required to convert the compound to the element. This time, the reaction time, is a function of the rate constant(s) of the chemical reaction(s) involved in free atom formation. Furthermore, the atomization of an element takes place throughout a certain range of temperature. To a first approximation, the atomization rate and the vapor pressure are exponentially related to the temperature. Increasing the temperature by 100-200 °C corresponds to increasing the atomization rate and the vapor pressure by an order of magnitude. Thus, the actual atomization time is a function of the dead time, the reaction time, and the calculated atomization The dead time is later referred to as the pre-steady state period. time.

If the temperature is the same throughout a furnace atomizer, the atomization efficiency, β , would also be uniform throughout the vapor cell. For a filament atomizer, however, β is a function of the distance between the observation window and the filament. Increasing this distance results in a decrease of the atomic population, which again to a first approximation is an exponential function. On the other hand, if a filament-type atomizer is not heated uniformly and/ or the heat is intentially confined to the center of the atomizer, then the atomization efficiency will be different at different axial locations of the atomizer, which can lead to a smaller AA and AF signal.

2. Atom Populations in Furnace-type Atomizers

The length of the steady state period is normally longer in a furnace compared to a filament atomizer. The atomic vapor in a furnace, may be lost by five different processes: 1) diffusion of atoms through the furnace walls; 2) diffusion of atoms through the open ports of the cell; 3) losses due to natural convection currents close to the heated surface of the furnace; 4) losses due to the forced flow of the inert gas; 5) escape of excess vapor if the volume of the vapor exceeds a certain fraction of the volume of the cell.

The atomic vapor losses for filament-type atomizers, which are open to the atmosphere, are controlled by processes 2, 3, and 4. For the furnace, the amount of vapor lost through the wall is more than that lost through the open ports. The former can be minimized by using pyrographite cells or coating a standard graphite cell with a layer of pyrolytic graphite. The expulsion of the excess atomic vapor is also negligible if the vapor volume is 10 percent of the volume of the furnace. The loss due to forced flow is zero, if the inert gas flow is stopped. For a horizontal tube and for a furnace of a large length-to-inner diameter ratio, the amount of vapor lost due to natural convection currents is negligible compared to loss by diffusion.

Under the steady state conditions, the mass of substance diffusing per unit time is given by

$$\frac{dm_{a}}{dt} = -D_{a} \frac{d\rho_{a}}{dx} S$$
(13)

where S is the cross sectional area of the open ports, $\frac{d\rho_a}{dx}$ is the density gradient of the vapor in the direction of diffusion, and D_a

is the analyte atom diffusion coefficient. D_a in a gas is related to the standard state diffusion coefficient D_o by

$$D_{a} = D_{o} \left(\frac{T}{273}\right)^{o} \left(\frac{760}{\rho_{a}}\right)$$
(14)

where o is about 1.5 to 2 for various gas mixtures and ρ_a is the analyte pressure at the temperature T. If it is assumed that ρ_a is maximum at the atomization location (furnace center) and linearly falls to zero at the furnace ends, we find

$$\frac{d\rho_a}{dx} = 2 \cdot \frac{\rho_a}{\ell/2} = \frac{8m_a}{\ell^2 S}$$
(15)

where V = SL is the furnace volume and L is the furnace length. Substituting $\frac{d\rho_a}{dx}$ into Equation (13), gives

$$\frac{dm_a}{m_a} = -\frac{8D_a}{\ell^2} \cdot dt$$
 (16)

where $m_a(t)$ and $m_a(o)$ are the masses of the vapor at time t and zero, respectively. The atomic concentration of analyte varies in the same manner as shown by Equation 18

$$n(t) = n(o)exp(-\frac{D_a t}{g^2})$$
 (18)

where n(t) is the concentration of atomic analyte at time t and n(o) is the peak atomic concentration before any loss occurs. The peak atomic population is approximately given by

$$n(o) \cong (6x10^{23}) \frac{\gamma_s C_0 V_0 \varepsilon \beta}{f_v V_f e_g M_a B(T)}$$
(19)

where γ_s is the weight fraction of the sample which is the analyte, C_o is the concentration of the analyte (g/ml), V_o is the volume of sample (ml), and $m_a = \gamma_s C_0 V_0$. The term ε is the efficiency of producing atoms, ions, and molecules from the solid sample, β is the free atom fraction, $f_V V_f$ is the volume of the analyte vapor, f_V is the fraction of the space occupied by analyte vapor, V_f is the furnace internal volume (cm³) e_g is the gas expansion factor (dimensionless) between the heated gas temperature and room temperature, M_a is the atomic weight of the analyte, and B(T) is the normalized partition function.

The mean time, τ spent by the atoms in the furnace is given by Equation (18)

$$\tau = \frac{\ell^2}{8D}$$
(20)

Although the residence time of the atom can be increased by increasing the length of the furnace, the power input increases with the length of the cell, and it is thus not practical to use very long furnaces. Thus, in order to increase the residence time of the atoms in the vapor cell, the diffusion coefficient should be minimized. Equation 14 shows that the diffusion coefficient is directly proportional to temperature, while an increase in the pressure decreases this parameter. The reduction in temperature is not practical for elements having low vapor pressures. The increase in the pressure, however, is very effective in reducing D. An increase in the pressure of the argon gas from 1 atm to 9 atm results in a five-fold increase in the steady state of Cd vapor (9). It should also be noted that increasing the pressure would also result in a more linear calibration curve. The absorption line profile is broadened and is almost entirely controlled by Lorentz broadening. Thus, the emission line from the radiation **source** "looks" more monochromatic. If such broadening is sufficient, **a** continuum source can also be used favorably as a radiation source.

It should be noted that the type of inert gas employed should also be considered. The diffusion coefficient D is the number of molecules per second crossing a unit area under a unit concentration gradient. For a mixture of two different gases

$$D = \frac{1}{3} b_1 \bar{c}_1 X_2 + \frac{1}{3} b_2 \bar{c}_2 X_1$$
 (21)

where X_1 and X_2 are the mole fractions of the two gases in the mixture and the parameters b and \overline{c} are the mean free path and the average speed of the particles. The parameters b and \overline{c} are given by Equations 22 and 23, respectively

$$b = \frac{1}{\sqrt{2}\pi Nd^2}$$
(22)

$$\bar{c} = \sqrt{8RT/\pi M}$$
 (23)

where N is the number of molecules, d is the molecular diameter, and M is the molecular weight. If Equations 22 and 23 are substituted in Equation 21, we find

$$D = \sqrt{\frac{2RT}{9\pi^3 N^2}} \left[\frac{1}{d_1^2 \sqrt{M_1}} X_2 + \frac{1}{d_2^2 \sqrt{M_2}} X_1 \right]$$
(24)

Equation 24 shows that because of its higher atomic weight, argon is More effective than helium in increasing the mean time, τ , spent in the cell or reducing the loss due to diffusion.

3. Atom Populations with Filament-type Atomizers

For the filament-type atomizer, whether they are enclosed in a chamber or they are open to the atmosphere, there are three different mechanisms responsible for vapor losses. For a static system, there is no inert gas flow and the atomic vapor loss from the observation window is controlled by diffusion into the atmosphere and by natural convection currents. The actual atomization period can be described similarly to the furnace atomization. In a dynamic system, the forced flow of inert gas transports the atomic vapor and this effect, which depends on the flow rate, adds to the previous losses.

The duration of the steady state period is usually shorter for filament atomizers even if there is no gas flow in the system. This is due to the fact that the filament atomizer does not have any boundary. Thus, there is a great temperature and concentration gradient between the atomizer and its close environment during the so called atomization period. The processes of natural and forced convection are discussed in the following section.

D. Natural and Forced Convection

The process of natural of free convection heat transfer happens whenever the atomizer is located in a fluid medium at a lower or higher temperature than that of the atomizer. Because of the temperature difference, heat flows between the atomizer and the gaseous environment and leads to a change in the density of the gas in the vicinity of the atomizer surface. Thus there is an upward flow of the less dense gas and a downward flow of the higher density gas. The only

force responsible for natural convection currents in the heated filament case is gravitational attraction. When the motion of particles is caused by some external agent, such as an inert gas flow, we have forced convection. For both natural and forced convection, the motion of the gaseous environment may be laminar or turbulent.

In laminar flow, the particles move in an orderly sequence without passing one another, while for the turbulent flow the particles move in a zig zag manner with irregular paths. The statistical averages of the motion of a large number of individual particles is regular and predictable, however.

Irrespective of whether the flow is laminar or turbulent, the concept of the boundary layer can be applied to describe the transformation of various processes. This concept, which was introduced first by Prandtl, divides the flow field around a body into two domains; a thin layer covering the surface of the body where the viscous forces are large and the velocity gradient is great, and a region outside this layer where the effects of viscosity are negligible and the velocity is nearly the same as the free-stream value.

1. Forced Convection

Here we consider the flow of inert gas around the filament atomizer. At the leading edge of the atomizer, only the gaseous molecules in immediate contact with the surface are slowed down, while the remaining particles continue at the undisturbed free-stream velocity. As the inert gas proceeds along the atomizer, the thickness of the boundary layer increases. The velocity profiles near the leading edge are representative of a laminar boundary flow. This laminar flow within

the boundary layer changes to a turbulent flow after a certain distance from the leading edge. This distance is related to a dimensionless quantity called the local critical Reynolds number. In general the point of transition depends on the surface contour, the surface roughness, the disturbance level and even the heat transfer. If the surface is rough, or if disturbances are introduced into the flow, as for example by a careless design of a gas sheath or atomizer holder, the flow may become turbulent at lower Reynolds numbers than when the flow is calm.

The boundary layer concept is of great importance to an understanding of convective heat transfer. The rate of convective heat transfer between the atomizer surface and gaseous environment is given by

$$q = A\bar{h}_{c}(T_{A} - T_{\infty})$$
(26)

where q is the rate of heat flow, A is the surface area of the atomizer, \bar{h}_{C} is the average convective heat transfer coefficient, T_{A} is the temperature of the atomizer and T_{∞} is the temperature of the inert gas away from the atomizer. The convective heat transfer coefficient is a complicated function of the gas flow, thermal properties of the fluid medium, and the geometry of the system. There are four (269) general methods available for the evaluation of \bar{h}_{C} with each method having its limitation which restricts its scope of application. These are:

- 1. Dimensional analysis combined with experiments.
- 2. Exact mathematical solution of the boundary-layer equations.
- 3. Approximate analysis of the boundary layer by integral methods.

4. The analogy between heat, mass, and momentum transfer. It should be noted that no single method can solve all the problems. The limitation and the scope of each technique have been described (269), and we are only concerned here with the first method, which has found the widest range of application.

2. Dimensional Analysis for Forced Flow in a Furnace

Dimensional analysis is mathematically simple and facilitates the interpretation of the experimental data by correlating the data in terms of dimensionless groups such as the Reynolds number. The principle disadvantage of the technique is that it contributes little to our understanding of the transfer process and at least a preliminary theory is required before dimensional analysis can be performed. The algebraic theory of dimensional analysis will not be developed here. A rigorous treatment of the mathematical background has been given by Langhaar (269).

The procedure in dimensional analysis is simply as follows. First, an arbitrary system of primary dimensions is chosen so that all variables can be expressed in terms of them. We shall employ the primary dimensions of length L, time θ , temperature T, and mass M. The dimensional formulae of velocity and mass flow rates would be L/ θ and M/ θ respectively. Second, the Buckingham II-theorem (270) is used to determine the number of independent dimensionless groups needed to express the relation describing a phenomenon. Third, experimental data are correlated by plotting the dimensionless numbers against each other. Fourth, the Principle of Similarity is employed to describe the behavior of two systems if they have the same

dimensionless number(s) and vice versa.

3. Buckingham II-Theorem

The required number of independent dimensionless groups, Idiml is given by

$$Idim\ell = P_q - P_d$$
(27)

where P_q is the total number of physical quantities (such as density, specific heat, heat transfer coefficient) and P_d is the number of primary dimensions required to express the dimensional formulae of the P_q physical quantities. If these dimensionless groups are designated as Π_1 , Π_2 , etc., the equation describing the relationship among the variables has a solution of the form

$$F(\Pi_1, \Pi_2, \Pi_3, ...) = 0$$
 (28)

The above theorem can be applied in correlating the experimental convective heat transfer data for an inert gas flow through a heated tube or a filament atomizer. Although we shall consider the heated tube here, the treatment of other systems such as wire loops and other filament atomizers is quite similar. The physical quantities for a heated tube are listed in Table 1.

Since there are seven physical quantities and four primary dimensions, we need three dimensionless groups to correlate the data. In order to find these groups, we write Π as a product of the variables,

Physical Quantities	Symbol	Dimensional Equation
Heat transfer coefficient	Б _с	M∕θ ³ T
Tube diameter	D	L
Density of the inert gas	ρ	M/L ³
Viscosity of the inert gas	μ	M/L0
Velocity of the inert gas	v	L/0
Thermal conductivity of the inert gas	k	ML/0 ³ T
Specific heat at constant pressure	C _P	L ² /θ ² T

Table 1. Physical Quantities and the Dimensional Equations for a Heated Tube

each raised to an unknown power

$$\Pi = D^{a}k^{b}V^{c}\rho^{d}\mu^{e}Cf_{p}\bar{h}_{c}^{g}$$
(29)

Substituting the dimensional formulae into Equation (29), we get

$$\pi = [L]^{a} [ML/\theta^{3}T]^{b} [L/\theta]^{c} [M/L^{3}]^{d} [M/L\theta]^{e} [L^{2}/\theta^{2}T]^{f} [M/\theta^{3}T]^{g}$$
(30)

The exponents of each primary dimension must separately add up to zero if Π is to be dimensionless. Since there are four equations containing seven unknowns, we choose values for three of the exponents in such a way that each exponent is independent of the others. By solving the four equations simultaneously, the value of the exponents are obtained and we get the following groups

$$\Pi_{1} = \frac{\overline{h}_{c}D}{k}$$
(31)

$$\Pi_2 = \frac{VD\rho}{\mu}$$
(32)

$$\pi_3 = \frac{C_p \mu}{k} \tag{33}$$

 II_1 is called the Nusselt number, N_u , and can be physically interpreted as the ratio of the temperature gradient in the fluid immediately in contact with the atomizer surface to a reference temperature gradient. Once its value is known, the convective heat transfer coefficient \overline{h}_c can be calculated

67

$$h_{c} = N_{u} \frac{k}{D}$$
(34)

It can be seen that for a given Nusselt number, \bar{h}_{c} increases as the thermal conductivity of the inert gas increases. It is also obvious that an increase in the significant length D, causes \bar{h}_{c} to decrease. In general the parameter D specifies the geometry of the object from which heat flows. For the heated tube, D represents the diameter. Thus, as far as the convective heat transfer is concerned, it is desirable to minimize the diameter of the atomizer.

The second group, Π_2 , is called the Reynolds number, R_e . Its magnitude represents the extent of turbulence in a system. The higher the number, the more turbulence is found in the system. It can be seen from Equation (32) that the Reynolds number increases with the inert gas velocity and with the significant length of the atomizer. Since the atmosphere above a filament atomizer is cold, it is desirable to have minimum mixing of the generated atomic vapor with the inert gas. This would decrease the number of collisions of the analyte atoms with the cold inert gas molecules and minimize condensation of the vapor or chemical reactions with impurities in the inert gas environment. In atomic fluorescence, the number of quenching collisions would also be lower in a laminar flow than a turbulent flow.

The dimensionless group Π_3 is known as the Prandtl number, P_r , and relates the temperature distribution to the velocity distribution. It is the ratio of two molecular transport properties, the kinematic viscosity $v=\mu/\rho$, which affects the velocity distribution, and the thermal diffusivity $k/\rho C_p$ which affects the temperature profile. It indicates the steepness of the temperature gradients in the flow field. For monoatomic and diatomic molecules the value of P_r ranges from 0.67 to 0.74.

It can be seen that the seven original variables involved in the **Problem** of the heated tube are combined into three dimensionless groups, **and** the experimental data can now be correlated in terms of three **rath**er than seven variables.

Using Equation (28), we can write

$$N_{\mu} = f(R_{\rho}, P_{r})$$
(35)

It is now possible to apply the result of only one set of experiments to a variety of other problems. This can be performed by plotting the Nusselt number $\bar{h}_c D/k$ (or some product of N_u and P_r) versus the Reynolds number. This correlation of the data permits the evaluation of the heat transfer coefficient for a system using any size filament-type atomizer as long as the Reynolds number of the system falls within the range covered in the first set of experiments. This is called the Principal of Similarity.

According to this principle, the behavior of two systems will

be similar if the ratios of their linear dimensions, forces, velocities, etc. are the same. Therefore, in geometrically similar systems having the same P_r and R_e numbers, the temperature distribution will be similar. These considerations are generally true for furnaces and filament-type atomizers where there is a forced flow of inert gas in the system. The following section considers the effects of natural convection.

4 Natural Convection in Nonflame Atomizers

For a static system with no forced flow, the Reynolds number is superfluous and another dimensionless group is required to describe the natural convection. This parameter, the Grashof number, G_r , is a measure of induced flow in the system. It is analogous to the Reynolds number for forced flow and is a criterion for the transition from laminar to turbulent processes in natural convection. For low Grashof numbers, the flow is very weak and thick, while for high G_r values, the flow is thin and vigorous, which leads to laminar instability. The latter is more or less characteristic of the production of the Plume of atoms in a heated filament.

The Grashof number is given by

$$G_{r} = \frac{\rho^2 g_{\beta} (T_{A} - T_{\omega}) D^3}{\mu^2}$$
 (36)

where g is the gravitational acceleration and the rest of the terms have been defined previously. It is interesting to compare Equations (32) and (36). For natural convection, the significant length of the atomizer is introduced as D^3 . Thus, the effect of the dimensions of the atomizer is much more important than the corresponding effect in

forced convection. It can also be observed, as expected, that as the **temperature** of the atomizer is increased, more turbulence is introduced in the system.

For similarity of the temperature field in forced convection, it was stated that the Prandtl numbers should be equal. This applies also for free convection. Thus, when geometrically similar bodies are cooled or heated by free convection, both the temperature and velocity fields are similar if the G_r and the P_r numbers are equal at corresponding points. Similarly, when the G_r and P_r numbers are equal, the Nusselt numbers for the bodies are the same.

The product of $G_r P_r = R_a$, is called the Rayleigh number. The **experimental** data for natural convection are correlated by plotting **the** Nusselt number against the Rayleigh number.

$$N_{\mu} = f(G_{r}P_{r}) \tag{37}$$

Figure 1 shows the correlation (271) of the experimental data from **various** sources for free convection from horizontal wires and tubes **which** have been obtained by employing an equation similar to Equation 37. It can be seen that data for fluids as different as air, glycerin, **and** water are correlated for G_r numbers from 10^{-5} to 10^7 for cylinders **rang**ing from small wires to large tubes.

5. Forced and Natural Convection Combined in Nonflame Atomizers

In the two preceeding sections the effects of forced and natural COnvection were treated individually. In most of the present nonflame atomizers, the two effects exist simultaneously and a combined or "mixed" Convection process exists. In the region where both natural and forced

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Figure 1. Correlation of data for free convection heat transfer from horizontal cylinders in gases and liquids (271).

convection effects are of the same order of magnitude, heat transfer is increased if natural convection effects act in the direction of flow and decreased if natural convection acts in the opposite direction.

The question that arises is under what circumstances can either natural or forced convection be ignored and under what conditions are the two effects of comparable magnitude. An indication of the relative magnitudes of natural and forced convection may be obtained from the Novier-Stokes boundary - layer differential equation, which describes the flow process. Careful examination of the various terms in the Novier-Stokes equation (272) indicates that the ratio G_r/R_e^2 can provide a good qualitative indication of the buoyancy on forced convection. If the Grashof number is of the same order of magnitude or larger than R_e^2 , natural convection effects cannot be ignored compared to forced convection. Small values of $R_e/\sqrt{G_r}$ result in small forced convection effects.

Several investigators have reported empirical equations to predict the extent of either forced or natural convection in mixed processes. Most of the results, however, are reported for low temperatures where the effects of radiation and conduction losses are minimal. Even at low temperatures, these criteria depend on the geometry of the system as well as on a variety of the other factors (272). Collis and Williams have studied long horizontal cylinders in air (273). It was suggested that for long fine wires the condition for negligible natural convection in forced flow was $R_e \ge 0(G_r^{1/3})$. The condition for the two effects to be of an equal order of magnitude is reported as $R_p = 0(G_r^{1/2})$. It should be noted that since filament atomizers have a finite length, both the length l and diameter d are significant lengths so that the ratio l/d must be incorporated in the dimensionless group. It has been shown (270) that for three dimensional shapes such as short cylinders the characteristic length is given by

$$\frac{1}{D} = \frac{1}{D_{h}} + \frac{1}{D_{v}}$$
 (39)

where D_v is the height and D_h the average horizontal dimension.

From Equations 32 and 36, the G_r , R_e and G_r/R_e^2 numbers were calculated for a filament, 3 cm in length and 3 mm in diameter, at three different temperatures and for four different gases. All the physical properties were calculated at $T_m = T_A + T_{\infty}/2$, where the temperature of the free-stream gas T_{∞} was assumed to be 28 °C, and the diameter of the atomizer was used as the significant length. No significant change in the significant length results if both length and diameter are introduced in Equation 39. The flow rate was assumed to be 1 1/min and was distributed over an *average* area of 1 in². The atomizer was located in a chamber with a cross-sectional area of 2x2 in². The results are shown in Tables 2-4 and plotted in Figures 2-4.

Table 2. Influences of Atomization Temperature and Sheath Gas Type on Natural Convection

Atomizer	Ai	r	N ₂	<u></u>	H	e	H	2
Temp °C	Gr	GrPr	Gr	Gr ^P r	^G r	PrPr	Gr	^G r ^P r
1000	43.5	31	45.4	31.3	0.81	0.56	0.969	0.68
1500	18	13.3	20	13.6	0.321	0.225	0.4	0.264
2250	10.5	7.91					0.218	0.157

Atomizer	A	ir		N2	-	Te Te	T	2
Temp. °C	æ	RePr	້	RePr	Å	RePr	Å	RePr
1000	6.2x10 ⁻⁷	4.4×10 ⁻⁷	6.4×10 ⁻⁷	4.41×10 ⁻⁷	8.5x10 ⁻⁸	5.95×10 ⁻⁸	9.2×10 ⁻⁸	6.48×10 ⁻⁸
1500	3.87×10 ⁻⁷	2.48×10 ⁻⁷	4×10 ⁻⁷	2.7×10 ⁻⁷	5x10 ⁻⁸	3.5x10 ⁻⁸	5.6x10 ⁻⁸	3.7×10 ⁻⁸
2250	2.66x10 ⁻⁷	2x10 ⁻⁷					3.96x10 ⁻⁸	2.85×10 ⁻⁸

Forced Convection
n
Type
Gas
Sheath
and
Temperature
Atomization
of
Influences
Table 3.

Influences of Atomization Temperature and Sheath Gas Type on the Relative Magnitude of Natural and Forced Convection Table 4.

A tomi tox	Air	N2	He	H2
Temp. °C	Gr/Re ²	G _r /R _e ²	Gr/Re ²	Prre ²
1000	1.13×10 ⁺¹⁴	1.11×10 ⁺¹⁴	1.12×10 ⁺¹⁴	1.14×10 ⁺¹⁴
1500	1.2x10 ⁺¹⁴	1.25×10 ⁺¹⁴	1.28×10 ⁺¹⁴	1.27×10 ⁺¹⁴
2250	1.48×10 ⁺¹⁴			1.39×10 ⁺¹⁴



Figure 2. Influence of atomizer temperature and sheath gas type on natural convection.



Figure 3. Influence of atomizer temperature and sheath gas type on forced convection.

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Figure 4. Influence of atomizer temperature and sheath gas type on the relative magnitude of natural and forced convection.

The following conclusion can be drawn. First, for both forced and natural flow, gases with smaller atomic or molecular weights produce more laminar than turbulent flow. Second, the flow becomes more laminar with an increase in temperature. Third, the ratio of G_r/R_e^2 increases, as expected, with temperature, which means that at higher temperatures natural convection becomes more dominant. Furthermore, since this ratio is very high, the effect of forced flow is negligible.

It should be noted that these calculations are only true for steady-state conditions and not for a transient type situation which actually is present with most nonflame atomizers. Transient convection and conduction have been treated for bodies of different geometry at relatively low temperatures (272). Although investigations in this area can be very helpful in understanding the various heat transfer processes, they will not be treated here.

Although the above calculations can provide an indication of the general behavior of the system, they do not specifically describe the behavior of the generated atomic vapor. Since the problem is of a very complicated nature, only the effects of the various heat transfer processes on the time dependence of the atomic vapor are discussed here.

E. Analytical Signal in Nonflame AA and AF Spectrometry

The analytical signal may be defined as the response of the measurement device to the presence of the analyte. This indicates that the information provided by the measurement device is a result of a

convolution of its response characteristics and the physical property being measured. Time is the important factor in considerations of the analytical signal. Steady-state signals are produced when the analyte is continuously introduced in the system, while transient signals are encountered when discrete sampling is employed.

Peak height and peak area measurement techniques are normally utilized in recording the analytical signal. The merits of each technique are influenced by the time dependence of the analytical signal which itself is a function of atomizer temperature. In this section the relationship between the heating rate and various heat losses and gains will be developed for electrically heated nonflame atomizers. The temperature-time dependence will serve to indicate the time dependence of atom formation as well as the advantages and disadvantages of peak height and peak area as measurement techniques.

1. Temperature-Time Dependence

The temperature-time dependence is a function of a variety of factors such as the heating techniques, the input power, the heat losses by convection, conduction, and radiation. The influence of the heating technique is discussed in Chapter VI. For the following treatment it is assumed that the atomizer is heated by a constant current i and that the physiochemical properties of the atomizer are not influenced from one experiment to another. Furthermore, it is also assumed that the work done on the system by pressure-volume variations is negligible compared to the magnitude of the internal energy and various heat losses and gains.

In general, we have U=Q where Q is the net heat transfer and U

is the internal energy, or

$$q_{internal energy} = q_{electrical} + q_{Thomson heating} - q_{radiation}$$

$$q_{conduction} - q_{convection} - q_{sample}$$
(40)

For a filament-type atomizer of perimeter P, diameter D, and surface area s, Equation (40) can be expanded into the following equation

$$\rho C_{p} s \frac{\partial T}{\partial t} = i^{2} R_{o} (1 + \alpha T) + \frac{i f(T)}{\rho C_{p} s} \cdot \frac{\partial T}{\partial x} - P_{\sigma \varepsilon} (T^{4} - T_{o}^{4})$$
$$- k_{o} (1 + \beta T) s \frac{\partial^{2} T}{\partial x^{2}} - P(T - T_{o})h(T) - Pm\Delta H \qquad (41)$$

where ρ and C_p are the density and specific heat of the atomizer respectively, R_0 is the atomizer electrical resistance at room temperature, α is the temperature coefficient of resistance, σ is the Stefan-Boltzmann constant, ε is the total emissivity of the atomizer, T_0 is the sheath gas temperature away from the atomizer, k_0 is the atomizer thermal conductivity, β is the coefficient of thermal conductivity, x is the distance from the center of the atomizer, h is the combined convective heat transfer coefficient due to forced and natural convection, m is the amount of analyte deposited on the atomizer, ΔH is the amount of energy required to atomize the compound, f is the Thomson coefficient and may be of either sign. The heat due to the Thomson effect disappears if ac heating is used.

Rearranging Equation (41), we get
$$\frac{\partial T}{\partial t} = -\frac{P\sigma\epsilon}{\rho C_{p}s}T^{4} + \left(\frac{i^{2}R_{0}\alpha}{\rho C_{p}s} - \frac{Ph(T)}{\rho C_{p}s}\right)T + \left(\frac{i^{2}R_{0}}{\rho C_{p}s} + \frac{Ph(T)T_{0}}{\rho C_{p}s} - \frac{Pm\Delta H}{\rho C_{p}s} + \frac{P\sigma\epsilon T_{0}}{\rho C_{p}s}\right) + \frac{if(T)}{\rho C_{p}s} \cdot \frac{\partial T}{\partial x} - \frac{k_{0}}{\rho C_{p}}(1+\beta T) \frac{\partial^{2}T}{\partial x^{2}}$$
(42)

It should also be noted that parameters such as f and h are functions of temperature. An exact solution of the above equation is certainly difficult. Numerical integration was attempted for the platinum loop and graphite braid atomizers, but these calculations are not conclusive thus far due to a lack of experimental data over the entire range of temperature.

For an approximate solution of the above equation, certain gross assumptions can be made. For a nonflame atomizer such as the graphite braid, which is discussed in Chapter VI, the temperature is uniform throughout the atomizer. The parameters $\frac{\partial T}{\partial x}$ and $\frac{\partial^2 T}{\partial_x^2}$ are practically zero over the entire length of the atomizer. However, a steep temperature gradient may exist at the contact points of the atomizer and its holder, and the heat lost by conduction and by the Thomson effect cannot be neglected. The same is also true for the carbon and graphite filament atomizers used normally for nonflame atomization. However, since the sample is deposited at the center of the atomizer, the information desired is the rate of temperature variation in the center and not at the atomizer contact points with its holder. The magnitude of the error introduced by this assumption depends on the length-todiameter ratio of the atomizer. This ratio is about 10 for the graphite braid atomizer and about 100 for the platinum loop atomizer. In order to neglect the conduction effect the ℓ/D ratio should be greater than 20,000 for a temperature of about 300 °C (274). This indicates the grossness of the above assumption. For the following equation it is further assumed that the convective heat transfer and the Thomson coefficients do not change significantly with temperature. We can then write

$$\frac{dt}{dT} = \frac{A}{T^4} + \frac{B}{T} + C$$
(43)

where

$$A^{-1} = \frac{P\sigma\varepsilon}{\rho C_{p}s}$$
$$B^{-1} = \frac{i^{2}R_{o}\alpha}{\rho C_{p}s} - \frac{Ph}{\rho C_{p}s}$$
$$C^{-1} = \frac{i^{2}R_{o}}{\rho C_{p}s} + \frac{PhT_{o}}{\rho C_{p}s} - \frac{Pm\Delta H}{\rho C_{p}s} + \frac{P\sigma\varepsilon T_{o}}{\rho C_{p}s}$$

Integration of Equation (43) yields

$$t = \frac{A}{3} \cdot T^{-3} + B \cdot \log T + C \cdot T + D$$
 (44)

where D is the integration constant. It can be seen that temperature is a complicated function of time. The contribution of each term depends on the magnitude of the constants in Equation 44.

2. Time Dependence of the Atom Population

The rate of introduction of atoms by an electrically heated atomizer follows the rate of temperature growth in the system. The first treatment of transient signals in nonflame atomizers was initiated by L'vov (9) who assumed that the rate of introduction of atoms into a cell was a linear function of the evaporation temperature which can be approximated to be a linear function of time. L'vov, however, *provided no justification* for his assumption. The justification can be seen from Equation 44 when either coefficients A and B or A and C are set to zero.

Using this assumption, we can then write the equation for the balance between the atoms entering and leaving the cell as follows (9)

$$\frac{dN}{dt} = n_1(t) - n_2(t)$$
 (45)

For a nonflame atomizer

$$n_{l}(t) = Et$$
 (46)

where E is a proportionallity constant. Since the analyte atoms, N_0 , in the sample are transferred into the cell in τ_1 seconds, then

$$\int_{0}^{\tau_{1}} n_{1}(t) dt = N_{0}$$
 (47)

Therefore

$$n_1(t) = 2N_0 t \tau_1^{-2}$$
 (48)

Since the analyte atom spends an average time, $\boldsymbol{\tau}_2,$ in the cell, we have

$$n_2(t) = \frac{N}{\tau_2}$$
 (49)

and

$$\frac{dN}{dt} = \frac{2N_0 t}{\tau_1^2} - \frac{N}{\tau_2}$$
(50)

If Equation (50) is solved for N(t), we obtain

$$N(t) = \frac{N_0^2 \tau_2^2}{\tau_1^2} (\frac{t}{\tau_2} - 1 + \exp\{-t/\tau_2\})$$

for $t \le \tau_1$ (51a)

and

$$N(t) = \frac{N_0^2 \tau_2^2}{\tau_1} (\frac{\tau_1}{\tau_2} - 1 + \exp\{-\frac{\tau_1}{\tau_2}\}) \exp\{-(t - \tau_1)/\tau_2\}$$

for $t \ge \tau_1$ (51b)

If it is assumed that the measurement device has an impulse response of unity, the ratio $\frac{N}{N_0}$ is a function of τ_1/τ_2 . The smaller the τ_1/τ_2 ratio, the larger the N/N₀ ratio. The peak height measurement can provide its best results if atomization occurs instantaneously. The sensitivity is decreased if τ_1 is greater than zero. Integration of N(t) provides information which is independent of the atomization time as shown by Equation (52)

$$\int_{0}^{\tau_{1}} N(t) + \int_{\tau_{1}}^{\infty} N(t) = N_{0} \tau_{2}$$
 (52)

Integration of the signal thus provides a more linear working curve and better precision.

IV. INSTRUMENTATION

A. Introduction

The instrumentation used in nonflame atomic absorption and atomic fluorescence spectrometry is similar to that used in conventional flame spectrometry except for the atomization and the detection systems. The instrumentation employed throughout this work varied from a completely non-automated system to a system in which the operational functions were performed by a logic sequencing system and finally to a system in which the entire operation, data treatment, and optimization were performed under computer control with no operator intervention. This transition was dictated by the rigorous analysis of experimental results during the various stages of this investigation and not by a simple desire to have an automated system. Since the experimental data obtained with the non-automated system have all been repeated with the computer-controlled system, only the data obtained with the latter are presented. Furthermore, no detailed descriptions of either the non-automated or the sequencer-controlled system is given here. The latter has been published (275), and the interested reader can refer to that article. However, the experimental results obtained with the non-automated system provided valuable information which helped us in the design of both the sequencer-controlled and the computer-controlled system and some of these conclusions will be summarized here.

First, in order to employ nonflame atomizers for routine analysis, the sample delivery step should be automated. In all nonflame atomizers used so far, this has not been considered, and samples are usually transported to the atomizer manually by means of a microsyringe. Since the sample volume required by many of the atomizers is extremely small (1-10 μ), sampling imprecision can be a limiting factor in the overall measurement. Second, there are many interdependent parameters which can influence the free atom concentration in nonflame atomizers. For example, the temperature of the atomizer is a complicated function of the power applied to the atomizer, the sheath gas flow rate, and several other parameters. The sheath gas can similarly influence the residence time of the atomic vapor in front of the observation window and, in the case of atomic fluorescence, can also influence the quenching of the excited atoms. Thus, optimization of experimental parameters for high signal-to-noise ratios can be a critical factor. Although this can be performed by a non-automated system, it is time consuming and tedious, and the treatment of the experimental data is subject to operator malfunction or at least bias. It is, therefore, essential to have a computer-controlled system. Third, because of the interdependence of the experimental parameters, it is desirable to simplify the atomization process either by decreasing the number of variables and/or decreasing the dependence of these parameters on each other. For instance, it was shown during our primary investigation, that it was practically impossible to prevent the simultaneous vaporization of solvent and solute from the atomizer when some of the gas sheath designs were employed to transport

the atomic vapor. Furthermore, if the sample is present in a complicated matrix, it is desirable to reduce matrix effects by removing some of the interfering species before the atomization step. This requires a multistep programming system for the electrical heating of nonflame atomizers.

In this chapter, the design of the various components of the computer-controlled spectrometer is described. In the first section, a general description of the apparatus is given along with a description of the atomization system and the optical system. The design and operation of a hardware and a software multistep programming system for electrical heating of nonflame atomizers are discussed in the second section. Two different automatic samplers are described in the third section. With one of the samplers it is possible to have computer control over the size and type of the sample. Finally, the various integration methods employed for the measurement of transient signals are described and the various functions of the computercontrolled spectrometer are discussed.

B. Nonflame Atomic Absorption/Fluorescence Spectrometer

1. General Description

Figure 5 shows a block diagram of the AF spectrometer. The system functions as an AA spectrometer if the positions of the sampler and the light source are interchanged. The AA/AF spectrometer is controlled by a minicomputer, which directs the sampler, the hardware temperature programmer or the current regulator, the optimization, the data processing and the readout. Under computer control, the





sampler delivers a desired amount of a desired solution onto the atomizer. The computer then commands the hardware temperature programmer or the current regulator to provide the atomizer with appropriate currents and time delays for the desolvation, ashing, and atomization steps. The atomic vapor, which is transported by an inert gas, is excited by the light source, and the transmitted/emitted light is received by the monochromator and photomultiplier transducer. The resulting signal is amplified, digitized and sent to the computer. After the digitized signal is stored by the computer, the atomizer is shut-off, and the integrated signal is printed out on a teletype. The remaining operations depend on operator decisions and are described in a later section.

2. Atomization System

a. <u>Nonflame Atomizer Assembly</u>. Figure 6 shows the atomization chamber with a wire loop atomizer located on top of an adjustable gas sheath. This arrangement was used for AF investigations. The whole system is fixed on a 9.5 x 5 in. plate and can be mounted in optical alignment with the monochromator in a matter of a few seconds. This type of arrangement was not subject to air drafts, and a change in the position of one component did not affect the other components. The wire loop holder was mounted on the plexiglass walls of the chamber. The two L-shaped holders were made from either brass or stainless steel and had two slots at the lower ends. The wire loop was inserted in the slots and was held in place by a spring clip arrangement as can be seen in Figure 6. The horizontal and vertical positions of the atomizer could be changed by means of a set of screws.



Figure 6. Schematic Diagram of the atomization chamber with a wire loop atomizer located on top of an adjustable gas sheath.

A lens holder was mounted on one of the plexiglass walls. The lens holder had an angle of 90° with respect to the monochromator entrance slit. The lens was used to form a cylinder of primary radiation at the top of the atomizer. No lens was used to focus the fluoresced radiation on the monochromator. For AA work a similar lens holder was employed at an angle of 180° with respect to the monochromator entrance slit.

The plexiglass walls were supported by a stainless steel base. One of the plexiglass walls can be removed to allow replacement of the atomizer. In a later modification, the atomizer was held by a holder from below rather than from the top. This decreases light scattering by the atomizer holder. Light scattering was also reduced by introducing suitable light traps and painting all components with optical black paint. For multielement analysis, the plexiglass walls were removed from the assembly.

b. <u>Gas Sheath Designs</u>. The atomizer was positioned over an adjustable inert gas sheath which transports the atomic vapor plume to the optical axis, minimizes oxide formation, and reduces quenching of the fluorescence radiation in AF. Numerous of gas sheaths were designed and constructed from stainless steel. One such sheath can be seen in Figures 6 and 19. The gas sheath could be supplied with an inert gas through suitable hose nipples. In all designs, the height of the sheath was variable over a two inch range starting from just below the entrance slit of the monochromator. The design of only two different gas sheaths are described here.

The first design consisted of inner and outer clusters of holes drilled on a circular piece of stainless steel. The distance between

the inner and outer cluster was 0.32 in. The holes in the inner cluster had a diameter of 0.018 in. each and were located on four rings of 0.04, 0.08, 0.12, and 0.16 in. radii. The central ring had nine holes, but the rest of the rings had seventeen holes each. The outer cluster had four rings of holes located on 0.62, 0.66, 0.7 and 0.74 in. radii. The holes, which were staggered to improve the sheathing efficiency, had diameters of 0.032 in. each. The sheathing gas was supplied through the inner and outer hose nipples.

The second design consisted of a square piece of 2 x 2 in. stainless steel with inner, middle and outer clusters of holes. The distances between the inner-middle and middle-outer cluster were 0.125 and 0.25 in., respectively. The middle and outer cluster each consisted of three square matrices of holes. The holes in these two clusters had diameters of 0.032 in. and were 0.048 in. apart. The inner cluster consisted of a square matrix of holes with five parallel rows of holes, which had diameters of 0.018 in. and were 0.032 in. apart. In contrast to the first design, the holes were not staggered in the second design.

c. <u>The Wire Loop Atomizers</u>. A variety of wire loop atomizers, such as wires from gold and tungsten, wires from alloys of nickel and chromium, and wires from alloys of platinum were investigated as atomization devices. In the nickel-chromium alloys, the Cr content makes the alloys resistant under oxidizing conditions, and the Ni content enables them to retain resistance under reducing conditions and in strongly alkaline solutions. The best alloy from an electrical standpoint was the 80% Ni - 20% Cr alloy. However, because of its chemical reactions with various analytes, this atomizer was discarded.

Although gold wire was very resistant to chemical reactions and to oxidation, the melting point of this element is about $1060 \, ^{\circ}C_{*}$ and gold cannot be used for the atomization of high boiling point elements. Platinum has a melting point of about 1770 °C and is only attacked by aqua regia and somewhat slowly by hydrochloric acid and other oxidizing agents. Alloying with iridium and ruthenium reduces the rate of corrosion. Iridium and rhodium have a boiling point of about 2400 and 1970 °C respectively, but they undergo oxidation to a greater extent than platinum, and they are moderately hard. In general, Pt-Rh alloys were found most useful, and an alloy of 90% Pt and 10% Rh was chosen. This particular alloy was selected because of its stiffness and overall strength, higher operating temperatures than pure platinum and low susceptibility to oxidation. Although fatigue is commonly exhibited in pure metals under repeated heating and cooling, the Pt-Rh alloy exhibited this effect to a lesser extent than pure platinum. For high atomization temperatures, tungsten wire loops were also used. The melting point of this element is about 3390 °C, but it undergoes oxidation.

Thus, the metal wire loop atomizers used throughout this investigation were made of Pt and W metals, and 90% Pt - 10% Rh. The diameters of wires used ranged from 0.032 to 0.008 in. for Pt and its alloys and from 0.01 to 0.02 in. for tungsten. The physiochemical properties of these atomizers are discussed in Chapter V.

3. Optical System

The optical system used was similar to that used in conventional AA/AF spectrometers. The radiation from a metal vapor discharge lamp

(George W. Gates & Co., Inc., Franklin Square, NY) or a hollow cathode lamp (Fisher Scientific, Waltham, MA) was focused above, and slightly beyond the loop atomizer by a 2 inch focal length quartz lens (f/1.3), which was only employed for AF work.

The rest of the spectrometer consisted of a grating monochromator (EU-700, f/6.8, Heath Co., Benton Harbor, MI), a photomultiplier module (EU-701-30, Heath Co.) a current-to-voltage converter (Model 427, Keithley Instruments, Inc., Cleveland, OH), a digital voltmeter (EU-805, Heath Co.), an oscilloscope (Type 564, Tektronix Inc., Portland, Oregon), a recorder (EU-205-11, Heath Co.), and a PDP Lab 8/e minicomputer (Digital Equipment Corp., Maynard, MA).

C. Multistep Current Programming Systems for Electrical Heating of Nonflame Atomizers

1. Introduction

Nonflame atomizers for atomic absorption (AA) and atomic fluorescence (AF) spectrometry have been shown to be of considerable value for the detection and analysis of trace amounts of metals in a variety of matrices. In order to reduce matrix effects and to allow some control over the atomization process, most nonflame atomizers utilize a two or three stage electrical current program for heating the atomization element. In the first step, a small current is applied to the atomizer to vaporize the solvent. If organic material is present, a second larger current step is applied to ash the material, and in the final step, a high current (often > 100 A) is applied to atomize the sample.

For most efficient use of such a current programming system for nonflame atomizers, it is desirable to have precise control over the current applied during each stage, the length of time for which each current step is applied, and the times for various other operations such as data acquisition and sample delivery. In this section two different programming methods are described for multistage electrical heating of nonflame atomizers, such as carbon filaments, tantalum strips and hot-wire loops. The operation of the first system is controlled by a logic system, while the second programmer is controlled entirely by a minicomputer.

2. <u>Hardware Programming System for Electrical Heating of Nonflame</u> Atomizers

A digital programming system is described for multistage electrical heating of nonflame atomizers. The integral parts of the programmer consist of a logic system, a serial D-to-A converter, and a current-regulated power supply. The design and characteristics of the system are presented and discussed.

a. <u>Principles of Operation</u>. A block diagram of the entire multistep current programmer is shown in Figure 7. Before the experiment begins, the operator presets the digital sequencer by entering binary numbers from switch registers in order to select the following:

1. An initial time delay for the sample delivery to the atomizer.

2. The desolvation time and current.

3. The ashing time and current if an ashing step is necessary.

4. The atomization time and current.

The sequence begins when the sequencer receives a logic 1+0 transition



Figure 7. Block diagram of the multistep current programmer.

either from a manual switch or from an automatic sampler. This start pulse opens a gate and allows clock pulses to enter preset binary counters, which are the heart of the programmer. After the initial time delay, a count-serial digital signal (a number of standard sized pulses) is sent to a count-serial digital-to-analog converter (SDAC) where an analog output voltage is produced corresponding to the desired desolvation current. The SDAC output is applied to a current-regulated programmable DC power supply which controls the current in the atomizer. When the preselected desolvation time is over, the ashing current is applied, if an ashing step is desired. When the ashing step is complete, the atomization current is applied for a preselected time. During the atomization step, the sequencer signals the data acquisition system to start the data collection process, and the AA or AF data are then acquired. In the final step the current through the atomizer is shut off, and the entire logic system is cleared and prepared for the next start pulse. Details of each of the functional blocks shown in Figure 7 are given below.

b. <u>Sequencing System</u>. The operating cycle of the programmer is under the complete control of the sequencing system which provides the appropriate time delays and pulses for the different steps. Since a binary counter stores the maximum possible amount of information, the system was constructed from 4-bit binary counters. The logic system is described for a two step program of desolvation and atomization. An ashing step can be implemented by the addition of a third similar circuit. All components were mounted on circuit cards and inserted into an Analog-Digital Designer (Model EU-801A, Heath Co., Benton Harbor, MI), which supplied the necessary power to operate the

1-1

sequencing system.

Figure 8 shows a general block diagram of the entire sequencing system along with its connections to the SDAC. The initial time delay (ITD), the desolvation time unit (DTU), the desolvation current unit (DCU), the atomization current unit (ACU), and the atomization time unit (ATU) are preset independently by means of parallel switch registers. Figure 8 also shows that two different clock rates are utilized for the time controlling and current controlling units. The clock rates were normally 0.1-1 Hz and 1 kHz for the time and current controlling units, respectively. The different clock rates were obtained from a 1 MHz crystal oscillator and frequency dividers, which are not shown in the figure.

Figure 9 shows the circuit diagram of the initial time delay (ITD) step. The four Exclusive-NOR gates and NAND gate 1 form a digital comparator. The comparator output, known as the final count detector (F.C.D. 0), and the reset signal operate the clock gate. The gated clock output is sent to the binary counter input. Signals A_1 , B_1 , C_1 , and D_1 are switch outputs which can provide logic 0 or 1 levels to the Exclusive-NOR gate inputs. These switches are used to preset the desired number of counts.

After the desired number of counts is selected, the rest of the operation is as follows. A logic 1 at "reset" results in clearing all flip-flop outputs to zero, while a logic 0 allows the clock pulses to enter the counter. The comparator matches the desired count with the counter output and undergoes a 1+0 transition as soon as the balance is reached. This transition prevents NAND gate 2 (gated clock) from passing more clock pulses and starts the operation of the





Figure 9. Circuit diagram of the initial time delay (ITD) step.

desolvation time unit (DTU) and desolvation current unit (DCU) simultaneously. If the clock has, for example, a frequency of 1 Hz and switches A_1 and D_1 are set at logic 1 levels, the initial time delay is 9 seconds. The flip-flops are not reset until all stages of the program are completed.

The logic diagram of the DCU is essentially the same as the ITD circuit except that the gated clock output is connected both to the counter input and to the SDAC. The pulses applied to the SDAC are converted to a proportional voltage, which controls the application of the electrical current to the atomizer. In contrast to the ITD unit, the final count detector of the DCU circuit (F.C.D. 1) only operates the clock gate.

The next three stages of the logic system are basically similar to the two previous steps. The counter and digital comparator of the DTU, shown in Figure 10, are twice the size (8-bits) of the ITD unit. The inverted final count detector output ($\overline{F.C.D.}$ 0) gates the output of NAND gate 2 (gated clock) in the DTU through another NAND gate to ensure that the count starts at the end of the first step.

The atomization time unit and the "reset and clear" systems are shown in Figure 11. The circuit of the atomization time unit, shown on the left hand side of the illustration, is quite similar to that of the ITD circuit of Figure 9. However, the clock pulses are gated in a slightly different manner as illustrated in Figure 11. Because of its resemblance to Figures 9 and 11, no circuit diagram is given here for the atomization current unit (ACU). The counter and comparator are the same size as the DTU. The clock is gated as shown in Figure 11, and the gated clock output is sent both to the



Figure 10. Circuit diagram of the desolvation time unit (DTU).





counter and to the SDAC.

The right hand side of Figure 11 shows the circuit diagram of the "clear and reset" system. The final count detector output of the ATU (F.C.D. 4) is used to reset automatically all flip-flop outputs to logical 0's at the end of the cycle. If it is desired to stop the process in the middle of a cycle, the reset switch can be used to reset all the flip-flops and discharge the capacitor in the SDAC.

c. <u>D-to-A Converter (SDAC)</u>. An operational amplifier integrator (OA1) and a diode pump network form a simple count-serial DAC which is shown in Figure 7. The FET switch across the capacitor C_2 is open during the operation cycle. This allows the capacitor to store a charge which is proportional to the number of pulses applied to the DAC input. At the end of the operation, the switch closes and capacitor C_2 is discharged.

d. <u>Current Regulator</u>. The current regulator shown in Figure 7 consists of a 28V DC, 25A power supply (catalog No. 2475-2, Lambda Electronics Corp., Long Island, NY), power transistors, and an operational amplifier feedback system for current regulations. During operation, the power supply is on at all times. However, the transistors prevent current from reaching the atomizer until a command is received from the logic system. The resistor R_{CS} senses the current through the atomizer and a corresponding voltage is produced at the input of the control operational amplifier (OA2). The OA compares this voltage with the SDAC output and supplies a current, i, to the atomizer, such that iR_{CS} equals the SDAC output voltage.

Thirteen power transistors are mounted on a water-cooled heat sink. Connected to the emitter of each transistor is a resistor of

0.51 Ω to distribute the same load over all power transistors. Two additional transistors are used to drive the power transistors. These transistors are in turn driven by the control operational amplifier (0A2) output. The SDAC output passes through two thermal microswitches which are mounted on the two terminals of the heat sink. The switches are normally closed, but if the operator forgets to water cool the heat sink, the thermal switches open and prevent current from reaching the power transistors and the atomizer. The SDAC output is also connected to a l0k Ω potentiometer which can provide a continuous control over the maximum available current. Since each power transistor can handle 115 W, the maximum power capability of the present system is limited to 1.5 kW.

e. <u>Procedure</u>. After the operator selects the proper parameters for the programmer, $2 - 10 \mu$ l samples are placed on the atomizer by an automatic sampler, to be described later, or a 10 μ l syringe (Hamilton Co., Inc., Whittier, CA). The operation is initiated by a signal from the sampler or from a push button switch depressed by the operator. At the start of the atomization step, a trigger signal (Tl in Figure 7) is produced by the sequencer, and the readout system begins data acquisition at a specified rate. At the end of the atomization step the sequencer produces a second trigger signal (T2), which stops data acquisition. Integration of the peak-shape signals are performed by a digital integrator, and the analytical results are printed on a teletype. The digital integration method is discussed in a later section.

f. <u>Linearity and Reproducibility of the Hardware Programmer</u>. The electrical current applied to the atomizer is controlled by the SDAC

output voltage, which for a two step program is given by

$$v_{o} = N v_{in} \frac{C_{1}}{C_{2}}$$
(55)

where C_1 and C_2 are the capacitances of the capacitors in Figure 7, N is defined as $N = N_{DC} + N_{AC}$, v_{in} is the amplitude of the preset number of pulses N, and $\rm N_{\rm DC}$ and $\rm N_{\rm AC}$ are the number of pulses for the desolvation and atomization currents, respectively. Moreover, the output voltage is a function of the clock rate and decreases as the rate increases. The linearity of the programmer was checked at the SDAC output, and v_o was found to be a linear function of the preselected number of pulses. The reproducibility of the applied current depends on the clock rate and the values of the capacitors C_1 and C_2 used in the SDAC. The reproducibility of the generated waveform was checked at the SDAC output and, for C_1 = 0.1 μF , C_2 = 1 μF and a clock rate of 1 kHz, the relative standard deviation (RSD) was found to be less than 1%. Higher clock rates increased the %RSD. For a clock rate of 10 kHz, the %RSD increased to 5 - 10%. The effects of clock rate on the magnitude of the SDAC output and its reproducibility is shown in Figure 12. Below 1 kHz the programmer is still reproducible, but the low clock rate results in a smaller AA or AF signal for the sample. In fact, the sample is lost gradually by evaporation from the atomizer and only a fraction of the original sample remains for atomization.

As was previously described, pulse trains are shunted through the system continuously, and a waveform is generated when the various gates in the system close or open. It is obvious that any gate might



CLOCK RATE, Hz

Figure 12. The effects of clock rate on the magnitude of the SDAC output and its reproducibility.

open at any time during any one pulse. Thus, even though the pulse is counted, the SDAC does not "see" the entire pulse, which results in a small loss in the output. The same is also true about the various time delays in the system. In order to decrease the relative error due to this effect, one pulse should contribute a very small amount to the value of any parameter (time, current). Therefore, a large number of counts should be accumulated during each current and time step. With the present system sufficient pulses were counted to achieve errors of less than 1%. In order to reduce the error even further, higher resolution counters and comparators are required. However, since the SDAC is a serial converter, the conversion time will increase and this may result in a gradual evaporation of the sample in the atomization process. This problem can be solved if a parallel DAC replaces the serial DAC. For our purposes, the effect of this error was very small and could be neglected.

Although the above programmer has only desolvation and atomization steps, the system can be expanded to have an ashing step. The electronic circuit is similar to the other steps and is not discussed here. The analytical results obtained with this programmer compare favorably with results obtained with most nonflame AA and AF techniques and are discussed in Chapter V and VI.

3. Computer-Controlled Heating of Nonflame Atomizers

The hardware programming system described previously has a number of disadvantages which can be best taken care of through software control over the electrical parameters which govern the atomizer temperature. First, iterative optimization of parameters such as

desolvation, ashing, and atomization time or current, if not practically impossible, is extremely tedious. This prevents a fundamental investigation of the chemical problems in a routine manner. Second, multielement analysis and samples of complicated matrices require additional heating steps which necessitates the expansion of the sequencing system. Third, the logic system is subject to various transients and should be protected by suitable isolation devices.

The computer-controlled heating system employs the same current regulator described in the previous section. The serial DAC and the sequencing system are replaced by a parallel DAC and a minicomputer, respectively. The minicomputer was a PDP Lab 8/e system (Digital Equipment Corp., Maynard, MA). For all the interfacing designs, a minicomputer interface system (EU-801E, Heath Co., Benton Harbor, MI) with appropriate circuit cards was used. Figure 13 shows the interface which was designed for the computer-controlled system. The parameters which control the temperature of the atomizer and the various time delays are stored in the computer through an initial dialog between the operator and the teletype. The stored digital information relating to the amount of current for each heating step, is transferred to the computer interface buffer (CIB) under computer control. The Data Bus card directs the digital signal to a 10-bit DAC card, which produces a corresponding analog voltage between 0 to -10 V when it is properly addressed. The DAC output is sent through a unity gain inverter to provide appropriate polarity for the current regulator circuit. This output voltage is compared at the OA input terminal (OA2) with the voltage drop across a current sensing resistor in series with the atomizer.





In order to be addressed unambiguously, the DAC also needs a Strobe and a Device Select signal from the computer. The Data Bus card provides these different Input/Output signals (IOP1, 2, and 4), and IOP1 was used as the Strobe signal. The Octal Decoder card was also employed to provide the Device Select Code (11).

In operation the system functions as follows. Under program control a small current from the programmable current supply is applied to the atomizer to desolvate the sample for a preselected length of time. After the desolvation step is complete, a larger current is applied to ash the sample if the operator has indicated in the initial dialog that an ashing step is necessary. This is done by commanding the DAC to provide a larger voltage at the OA2 input terminals. Again, the ashing current and ashing time are under computer control. Finally, a third high-current step is applied to atomize the sample. During the atomization time, the computer enters a data acquisition routine to obtain quantitative absorption or fluorescence information. The data acquisition system is described in a later section.

D. Automatic Samplers for Nonflame Atomizers

1. Introduction

In many types of chemical experiments, the "hang up" to complete automation comes in the steps of sample preparation and sample handling which occur prior to the instrumental measurement. The automation of these steps along with the more conventional steps of data acquisition, data processing and real-time control over instrumental variables would then allow computer feedback in a "closed-loop" type system.

The effects of the sample delivery process are more pronounced in nonflame spectrometry compared to most other chemical experimentation. This is due to the fact that the required sample volumes range between $1 - 10 \mu$ l, and it is essential to deliver reproducible volumes of sample solution to the same location on the nonflame atomizer. In those filament-type atomizers, such as a wire loop or West-type carbon filament, where the heat is confined to the center of the atomizer and there is a larger temperature gradient throughout the atomizer, the sample must be delivered to exactly the same point every time to provide reproducible free atom populations.

The first automatic sampler for a wire loop nonflame atomizer was reported by S. R. Goode (276) in these laboratories. The sampling system consisted of a pump, similar to a peristaltic pump, and a delivery capillary. A motor-driven "wiper" compresses tygon tubing lying between an adjustable stage and the wiper, and this compression forces a certain amount of sample through the tubing. The sample is delivered to the wire loop by a quartz capillary tube, which is positioned directly below the wire loop. The droplet attaches itself to the loop in preference to the quartz.

This type of automatic sampler has a certain number of disadvantages, however. First, the sampler is only suitable to the loop type atomizer and it is not possible to employ the sampler with furnace and filament atomizers. Second, since the quartz capillary tube is close to atomizer at all times, it might clog or break because of solvent evaporation and high temperatures. The solvent evaporation introduces a systematic error in the overall measurement. Third, the presence of the quartz capillary tube disturbs the inert gas flow in the atomization chamber.

Fourth, the solution level in the solution container should be closely monitored to prevent erroneous results. Fifth, the pump-capillary system suffers from the siphoning effect. Sixth, there is sample adsorption onto the tygon tubing and this makes trace analysis impossible. Finally, with this type of arrangement, computer control over the size and type of the sample cannot be exercised.

In sample-limited situations such as in the analysis of trace elements in biological fluids it is desirable to use only a few microliters of the sample. This is not possible if the sampler has a large dead volume. Furthermore, although it is possible to employ this sampler as a component of an automated spectrometer for fundamental chemical studies, its capabilities are practically and fundamentally limited.

In order to eliminate all of the above drawbacks, the author designed and evaluated a variety of sampling systems. In this section the designs, characteristics, and the computer interfaces for two sampling systems are discussed. In both cases the sampler is not present in the atomizer environment during the atomization process, and sample delivery is made from above the atomizer. In one design, it is possible to have software control over six different sample types with a software-selected volume ranging between 0.05 μ l to 200 μ l. The operation of each system is discussed separately.

2. Automatic Sampler - Design I

With this design, the desired amount of sample is selected by the operator. The amount of sample can be continuously varied from 0 to 5.6 μ l. The principles of operation, sequencing system and

analytical results are reported in this section.

a. <u>Principles of Operation and Design Consideration</u>. The sampler consisted basically of two parts; a pump and a moveable syringe. A schematic diagram of the pump is shown in Figure 14. Three spring loaded stainless steel pistons (0.5 in. diameter) sequentially press a piece of tygon tubing. The movement of the pistons is governed by a cam attached to a small motor. The amount of delivered solution, which is continuously variable and covers an overall range from 0 to 5.6 μ l, can be set by a circular plate (c) attached to a set screw (a). The amount of solution delivered on each operation cycle depends on the pressure applied on the tubing by the set screw (a). A locking device (a') is provided to maintain each setting during operation.

The operational cycle of the sampler as a function of the position of the cam and piston is shown in Figure 15. At the start of the operation piston 3 is closed and pistons 1 and 2 are open. This situation prevents the flow of solution. As the motor starts to rotate the cam, piston 2 and then piston 1 press the tygon tubing, and the solution is pushed out. After a 120° rotation of the cam, piston 3 and then piston 2 open, and the solution comes through. Finally, the pistons return to their initial positions.

The second part of the automatic sampler consisted of a moveable handle connected to a miniature air cylinder. The piston of the cylinder was actuated by a 4-way, solenoid-operated valve. The other side of the moveable handle holds a 5 in. long stainless steel tube, which was sharpened on one end. The tube is electrically insulated from the rest of the system. The tygon tubing was clamped to the handle and attached to the stainless steel syringe. The X, Y, Z









Figure 15. Operational cycle of the sampler design I as a function of position of the cam and pistons.
positions of the syringe could be changed by three screws on the moveable handle. In operation the delivery syringe is initially in a position out of the optical path of the spectrometer. On command of the computer or operator the solenoid - actuated air piston moves the syringe into position over the atomizer, a preselected amount of solution is delivered to the atomizer by the pump, and the syringe is moved back out of the light path by the release of air pressure.

b. Sequencing System. The circuit diagram of the sequencing system is shown in Figure 16. The entire operating cycle of the sampler was controlled by a simple electronic circuit which consisted of three relay switches RS1. RS2 and RS3 and two microswitches MS1. and MS2. The MS1 switch was mounted below the cam, and its moveable contact was normally held closed by the pump cam. The sampler starts its cycle when the manual switch is pushed momentarily by an operator or when a +5V dc signal is applied to the RS3 coil by another instrument. This closes switch RS1, actuates the solenoid and moves the syringe to the atomization chamber. As soon as the syringe "sits" on the top of the atomizer, the moveable contact of switch MS2 is pressed by the moveable handle, switch MS2 closes, and the motor is activated. When the motor turns, the cam rotates and releases the MS1 contact, which results in closing switch RS2. Because of the new contacts, the solenoid remains "actuated", and the motor continues its operation to deliver the sample.

When the sample is left on the atomizer, the cam presses the contact of MS1 again, which deactivates switch RS2 and the solenoid. The solenoid valve is then opened to release the air pressure and, as a result, the syringe leaves the atomization chamber.





The system has the capability of purging itself. This is done when the purge switch is left at the "2" position. It can be seen from the circuit diagram, that the solenoid is deactivated in this case, and the sampler runs continuously to remove the solution from the tygon tubing. The time required for cleaning the sampler depends on a variety of parameters such as the size of tubing, sample type and concentration. This sample delivery system has the drawback of possible adsorption onto the tygon tubing. This problem was eliminated by the automatic sampler described in the next section.

c. <u>Computer Interface</u>. The function of the computer interface was only to command the sampler to move to the atomization chamber. The remaining operations were performed by the sampler itself. In order to perform this function, the computer was programmed to provide a +5V signal for an operator selected length of time. This can be done by a variety of software and hardware combinations, and one possible method is as follows. The computer was programmed to provide a variable time delay between two input-output instructions, 6411 and 6421. The device select signal 41 was connected to the Latch card input, and the corresponding Latch card output was sent to the sampler. In order to transfer the signal from the computer to the sampler, the Latch card should be addressed with a minimum of two gating signals. Device select signals 41 and 42 were taken from the Octal Decoder card and connected to an OR gate. The OR gate output and IOP1 were sent to the Select and Strobe inputs of the Latch card, respectively.

With the first instruction, 6411, the Latch card is gated and transfers a +5V signal to the sampler. After a preselected time delay, the computer performs the 6421 instruction, which results in the

elimination of the +5V signal.

d. <u>Precision and Accuracy</u>. The sampling system delivers samples with a precision of 2 to 3% relative standard deviation. The precision was found to be a function of the sample volume delivered. The precision increases initially with sample volume and passes through a maximum for a sample volume of 1 to 2 μ l. The accuracy of the sampler was determined for only a sample volume of 2 μ l and was found to be ±3 percent. The precision and accuracy were determined by weighing droplets and also by measuring the absorbances of solutions produced when the sampling system injected a dye into a spectrophotometer cell. Even though the precision in dispensing a sample was better for a manual syringe (1 to 2% relative standard deviation) the overall precision of absorption and fluorescence measurements was increased with the automatic sampling system because of the excellent reproducibility in positioning samples on the atomizer.

3. Automatic Sampler - Design II

a. <u>Principle of Operation</u>. The sampler described previously could be used for optimization studies involving a fixed volume of sample. For studies which involved variation of the sample size or automatic selection of the sample, the sample handling system pictured in Figures 17 through 19 was designed. This sampling system consists of a sample turntable, a stepping motor driven micrometer syringe, and a pneumatic system for moving the syringe. The moveable arm to which the syringe is attached has 3 positions. In the position shown in Figure 17, the syringe is tilted backward so that it is out of the optical path. Figure 18 shows the syringe in the second position,







where it is moved to the sample turntable for sample pickup. In the third position shown in Figure 19, the syringe is positioned directly over the atomization element for sample delivery.

All operations of the sampler are controlled by means of five small motors and two miniature air cylinders. The sample turntable employs one motor, and the micrometer syringe is driven by a stepping motor. The remaining three motors perform three basic operations called the Purge, the Fill, and the Deposit functions. The miniature air cylinders are responsible for transporting the moveable arm to the atomization chamber or the sample turntable. A brief description of the various functions and the computer interfaces is given here.

b. <u>Sample Turntable</u>. The sample turntable has provisions for six sample cups and suitable height control adjustment with respect to the micrometer syringe. The turntable is moved by a small motor, and any of the six sample cups can be moved into position under the syringe for sample pickup. The sample handling system has provision for flushing. One cup is normally kept filled with deionized water and a second one, the waste cup, is kept empty for the sampler to dump its content if so commanded. The movement of the turntable can be controlled by the computer or a sample selector switch mounted on the front panel.

c. <u>Stepping Motor Driven Micrometer Syringe</u>. The basic component of this system consisted of a stepping motor, a micrometer syringe and a stepping motor driver circuit. The stepping motor was connected to the micrometer syringe by means of flexible mechanical linkages, and the combination was attached to the moveable arm. The X, Y and Z positions of the micrometer syringe - stepping motor combination could be changed by means of a set of screws. Two small microswitches were mounted on this combination to indicate when the micrometer syringe had reached its upper and lower limits. As soon as the syringe is filled with a solution the upper microswitch opens and stops the stepping motor. The same function is performed at the lower limit when the syringe is empty. Since in most of our investigations the computer keeps track of the amount of solution in the syringe, these microswitches were not employed as limit indicators. They are utilized, however, if the computer is replaced by a hardware sequencer.

The stepping motor (Model 20-2215 D 200-F1.5, Sigma Instruments, Inc., Braintree, Mass.) was an inductor-type motor with 200 steps per revolution. The angular accuracy reported by the manufacturer was ± 3 percent and was non-cumulative. The accuracy of the 200 µl micrometer syringe (Catalog No. 7840, Cole-Parmer, Chicago, IL) was 0.5 percent. The luer joint of the syringe allowed the attachment of a hypodermic needle. Each division in the sleeve corresponds to 0.2 µl, and each revolution of the micrometer head dispenses 10 µl of the sample. Thus each step of the stepping motor delivers 0.05 µl of sample solution. Delivery is accomplished at a maximum rate of 10 µl/sec.

The stepping motor driver circuit (Type A202, Sigma Instrument), rated at 28V dc and 2A, was used to convert pulses at either forward or reverse input terminals into four current patterns for proper bidirectional rotation of the stepping motor. The required pulse was a negative six volt transition with a minimum pulse width of 20 μ sec. By decoding in this manner, it was possible to use only two bits of information to drive the stepping motor. Setting up the proper current

sequence within the computer was discarded on the grounds that this required four bits of information, more programming, and was more expensive.

The stepping motor driver was powered from a 28V dc, 8A power supply. For the maximum possible speed, the stepping motor was connected to the driver card by the arrangement shown in Figure 20. The resistors are required because the nominal motor voltage based on the rated coil resistance and current, is less than the power supply voltage. A large difference between these voltages results in a high stepping rate. For an inductor-type stepping motor, the rate of rise of current is determined by the motor winding time constant L/R, where L is the coil inductance and R is the total circuit resistance. It is, therefore, desirable to have low values for the ratio, L/R.

The forward or reverse pulses for the drive circuit were obtained either from a hardware sequencing circuit or from the computer. The detailed description of the hardware system design will not be given here. It basically consisted of a counter for sample size selection. The same counter in conjunction with the two microswitch limit indicators could also be utilized for filling or emptying the syringe. The description of the computer interface will be given later in this section.

d. <u>The Purge Function</u>. In this function, the moveable arm to which the micrometer syringe and the stepping motor is attached, is carried to the sample turntable by means of two miniature air cylinders. The pistons of the air cylinders were actuated by two 4-way single solenoid-operated valves. The first cylinder transports the arm from its initial position towards the sample turntable. This process





changes the position of the arm in only the horizontal direction. The second air cylinder then transports the arm in the vertical direction and positions it on top of the sample turntable with the tip of the syringe in the waste sample cup. A pulse train is then delivered at the forward input terminal of the stepping motor system which causes the syringe to dump its contents into the waste cup. The air pressure on the second air cylinder is then released, and the syringe leaves the sample turntable. The sample turntable is automatically actuated and moves to the deionized water cup. The syringe then moves to the sample turntable, is filled with deionized water, and leaves the sample turntable. The sample turntable and dumps its contents into the waste cup.

The syringe leaves the sample turntable by releasing the air pressure on the second piston and finally moves to its initial position as soon as the air pressure on the first piston is also released.

The computer responsibility for this operation is to provide an initial pulse to actuate the Purge function as well as to control the stepping motor driven micrometer syringe. The rest of the operations, such as the transport of the moveable arm to the sample turntable and the selection of deionized and waste cups are performed automatically by a small motor and a number of cams attached to the motor shaft. Each cam is in a form of circular plate with the motor shaft passing through the center of the plate. Thus all cams are parallel, and the movement of the motor shaft rotates all the cams simultaneously. The circular movement of these cams results in the opening or closing of a number of microswitches, which are in contact with the circumferences

of the circular plates. This provides a programming system for the various operations of the Purge function. The cycle time for the operation of this function is shown in Figure 21.

e. <u>Fill Function</u>. The operation of this function is similar to the Purge function described in the previous section. The cycle time of the Fill function is shown in Figure 22. The sample type is either selected by means of a computer command signal or manually by the sample selector switch mounted on the front panel. The syringe moves to the sample turntable, and a pulse train is then applied to the reverse input terminal of the stepping motor system by the computer, which causes the syringe to be filled with the desired solution. The moveable arm then leaves the sample turntable and returns to its initial position.

The computer has the responsibility for providing an initial pulse to actuate the Fill function, a second pulse to supply the proper sample cup for the syringe, and a pulse train for the stepping motor driven micrometer syringe. The remaining operations are performed by a motor-cam system similar to that described in the previous section.

f. <u>Deposit Function</u>. In this function, the moveable arm transports the stepping motor driven micrometer syringe to the atomizer by means of only one air cylinder. After the syringe is positioned at the top of the atomizer, a software-selected amount of sample is delivered to the atomizer, and the syringe returns to its initial position. The computer is only responsible for sample size selection and delivery and for providing an initial pulse to activate the Deposit function. The rest of the operations are performed by a motor-cam mechanism similar to that described for the Purge function. The





- 1 PURGE ACTIVATION SIGNAL.
- 2 SYRINGE MOVES TO SAMPLE TURNTABLE, FROM ITS INITIAL POSITION.
- 3 SYRINGE DUMPS OUT SOLUTION, INTO THE WASTE CUP.
- **4** SYRINGE LEAVES THE SAMPLE TURNTABLE.
- 5 SYRINGE RETURNS TO SAMPLE TURNTABLE, AND IS FILLED WITH THE SOLVENT.
- 6 SYRINGE LEAVES THE SAMPLE TURNTABLE.
- 7 SYRINGE DUMPS OUT SOLVENT INTO THE WASTE CUP.
- 8 SYRINGE RETURN TO ITS INITIAL POSITION.
- Figure 21. Cycle time of the Purge function in automatic sampler design II.



- 1 FILL ACTIVATION SIGNAL
- 2 SYRINGE MOVES TO SAMPLE TURNTABLE FROM ITS INITIAL POSITION.
- 3 SYRINGE IS FILLED WITH THE DESIRED SOLUTION
- 4 SYRINGE RETURNS TO ITS INITIAL POSITION.
- Figure 22. Cycle time of the Fill function in automatic sampler design II.

cycle time of the Deposit function is shown in Figure 23.

At the conclusion of the Purge, Fill, and Deposit functions, the sampler can provide a pulse to indicate that its operation has concluded. These pulses are only utilized when a hardware sequencer controls the automated spectrometer. When a computer-controlled system is used, the proper time delay patterns are generated by the computer, and the above signals are not employed. Figures 21 and 23 show that the duration of the Purge, Fill, and Deposit functions are 185, 65, and 35 seconds, respectively. The time durations of these functions can be decreased by a factor of three if the stepping motor provides 50 steps per revolution instead of 200 steps, if the three motors employed for the above functions are three times faster and have three times the torque of the present motors. It should also be noted that in order to operate the sampler independent of a computer, front panel switches were available.

g. <u>Computer Interface</u>. In order to operate the sampler, the sample turntable, the Purge, the Fill and the Deposit functions, 110V ac were required. Since there were six sample cups and three functions, the computer should switch ON and OFF 110 V ac for nine different devices. A combination of optoelectronic switching devices and triacs was employed in order to isolate the logic system from the line voltage.

The circuit diagram for remote activation of one device is shown in Figure 24. This circuit is repeated nine times for the above nine devices. All circuits, however, are powered by the same 9 V dc power supply.

In order to control the atomizer and the various components of the sampler, a minimum of 12 different devices should be under computer



1 DEPOSIT ACTIVATION SIGNAL.

- 2 SYRINGE IS POSITIONED ON THE TOP OF ATOMIZER.
- 3 SYRINGE DEPOSITS THE SAMPLE.
- 4 SYRINGE RETURNS TO INITIAL POSITION.
- Figure 23. Cycle time of the Deposit function in automatic sampler design II.









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Figure 26. Computer interface for the control of automatic sampler design II.

control. A variety of software and hardware combinations was employed to perform these functions. One such interface is shown in Figures 25 and 26. The computer provides +5V logic level signals to the components through the computer interface. The Device Select Signals in both figures are provided by the same Octal Decoder card. Figure 25 shows that the same DAC is employed for the operation of the atomizer and for supplying pulse trains to the forward and reverse input terminals of the stepping motor driver circuit. The DAC output is, however, gated by means of the Latch card and FET switches to prevent simultaneous activation of different devices. Figure 26 shows the interface for the sampler. It should be noted that the same Data Latch card is used in both circuits shown in Figures 25 and 26. The +5V output signals from this card are connected to the optoelectronic switching circuit shown in Figure 24. The computer does not provide a signal for the Fill function. However, since the sample turntable should be activated before the filling process, the same signals which command the sample cups are employed to control the Fill function simultaneously.

E. Integration Methods

Early in this work a system for the integration of the peakshaped photocurrent signals was found necessary. Analytical curves constructed using peak height data were nonlinear at high concentration. Both fixed and variable time analog and digital integration have been employed throughout this work. Analog integration generally suffered from long term drifts, and almost all data have been obtained with digital integration.

1. Variable-Time Analog Integration

Figure 27 shows the circuit diagram for analog integration. The circuit consisted of an OA (Model PP25 AU, Philbrick/Nexus Research A Teledyne Co., Dedham, Mass.), connected as an integrator, a comparator (Comparator/V-F card, EU-800-HB, Heath Co.) and a digital voltmeter. A buffer was introduced between the i-v converter and comparator to prevent loading of the signal by the comparator. The photomultiplier output was converted to a proportional voltage by a current amplifier whose transfer function could be varied from 10^3 to 10^{11} V/A. The resulting signal was connected to both the comparator and the integrator input.

As soon as the voltage crosses a preselected level, the comparator output changes its state and closes the switch Sl. Integration is then performed if switch S2 is open. In fact, switch Sl provides a variable time window which is the function of signal. The integrated signal is then displayed on the digital voltmeter. The integrator output voltage e_0 is related to the input voltage e_{in} by

$$-e_0 = \frac{1}{RC} \int_0^t e_{in} dt$$

where t is the integration time and R and C are the values of the resistor and capacitor in Figure 27. The integrator is reset by closing switch S2, which discharges the capacitor.

2. Fixed-Time Digital Integration

In this method a computer functions as a digital integrator and the readout system. During the atomization period, the analog signal is continuously digitized at regular intervals by an analog-to-digital





converter (ADC) and stored in the computer core memory. The integration is then performed by summing all the stored digital information. The result of the integration is printed on a teletype and is also stored in the computer for statistical treatment. The stored digital signal is also available for visual observation by activating a display routine. Integration of the baseline is performed prior to a fluorescence or absorption measurement and is automatically subtracted from each integrated signal value. After a preselected number of experiments have been performed, the mean, the standard deviation, and the percent relative standard deviation are reported on the teletype.

3. Fixed-Variable Time Digital Integration

This method is basically a combination of the two previously described integration techniques. A computer was used as a digital comparator, integrator and readout system. The analog signal is continuously digitized and stored by the computer during the entire atomization time, which is normally a fixed period. After the data acquisition is over and the atomizer is shut off, the computer functions as a digital comparator by utilizing a peak recognition routine. The computer first searches through the stored digital information for only the largest stored number, the peak maximum, and also finds the average of the first five A-to-D conversions. The leading edge of a peak is defined as those points that have a value equal to or greater than twice this average and less than the peak maximum, with the condition that the values of successive points are continuously increasing. The same condition is also applied for the trailing edge except that the values of successive points should continuously decrease. After the leading and trailing edges are recognized, the computer functions

as an integrator by summing all the data points between the start of the leading edge and the end of the trailing edge. The rest of the operation is similar to that described for the fixed-time integration technique. The programs for both integration techniques have been written in assembly language. The fixed-variable time technique should only be employed when the behavior of the signal can be predicted. If a double peak is present in the system, erroneous results are obtained. This situation does not normally exist in nonflame atomizers, however. Furthermore, double or multiple peaks can also be handled by additional software.

F. General Description of the Program

Since two types of automatic samplers have been used in this work, two different types of programs were written using assembly languages. Only a description of the program employing sampler Design II is given here. A simpler version of this program was employed when the fixed-volume sampler was used.

Before the experiment begins, the operator communicates through the teletype with the computer and provides responses to seventeen questions listed in Table 5. Except for questions C, D, and N, the meaning of the rest of the questions is obvious. For the sample size in question C, a number 20 times larger than that required should be typed. For example, the number 20 means $1 \ \mu$ 1 while 40 means $2 \ \mu$ 1, etc. This number actually represents the number of pulses which are applied to the forward input terminal of the stepping motor driver card. In question D, the sample type should be specified by a number

Table 5. Initialization and Optimization Questions

```
A. No. of Experiments?
B. Amplifier Gain?
C. Sample Size = ?
D.
   Sample No. = ?
E. First Time Delay = ?
F. Desolvation Time = ?
    Desolvation Power = ?
G.
   Ashing Time = ?
Η.
I. Ashing Power = ?
J. Atomization Time = ?
K. Atomization Power = ?
L. Cooling Time = ?
   Type "1" for AF and "2" for AA mode.
Μ.
N. Type "1" for optimization submode and "2" for normal submode.
0. Type "1" to generate & "2" to delete paper tape copy of the
    data.
P. Type "1" to display & "2" to delete the display of data on
    the scope.
Q. Type "R" if Ready to start the experiment.
```

between 1 to 6. These numbers represent the different sample cups. The program can provide two submodes of operation in both AA and AF. The operator has to select these submodes by answering question N.

In the optimization submode, after each experiment or sets of experiments has been executed, the operator is asked if variations in the parameters or experimental functions are desired. The operator can ask for variation of any parameter or function by typing the characters A through Q, which refer to the questions listed in Table 5. After the parameter is changed, the computer prints the message "what else", which asks if any other variable or function is to be changed. This process continues until the operator types "Q", which indicates that optimization is completed.

In the Normal submode, it is assumed that optimization has been performed, and the computer provides a closed-loop operation. After each experiment, there will be a preselected time delay for cooling the atomizer, and the computer starts its new cycle. When a preselectednumber of experiments has been performed, the mean, the standard deviation and the percent relative standard deviation are printed on the teletype. In this mode of operation the computer can automatically vary atomization parameters to a *limited* extent after a preselected number of experiments has been completed. Programming this type of operation for all experimental variables requires mass storage or a computer memory of more than 8K. Iterative optimization in real time is, however, possible if the operator provides proper experimental parameters in a logical manner.

After initialization, the computer asks if the operator is willing to start the experiment. The operator can respond by typing "R" and

the computer starts its control operation. A general flow chart of the program is shown in Figure 28. Under computer command, the automatic sampler syringe is first rinsed and then filled with the desired sample solution. The sampler moves to the top of the atomizer and provides a preselected sample volume. Since the syringe volume is 200 μ], the sampler has enough samples for 100 experiments if a 2 μ l sample is employed in each experiment. Thus, the Purge and Fill operations are not required for every experiment. The operating cycle of one experiment can be best understood with the aid of Figure 29. When the sample delivery is completed, the sampler moves out of the optical path of the spectrometer. A fixed time delay ensures that the sampler has moved out of position. The computer then begins to control electrical heating of the atomizer. A two or three step current program is normally employed to desolvate, ash, and atomize the sample. During the atomization step, a stream of inert gas carries the atomic vapor to the level of the monochromator entrance slit where AA or AF occurs. The fluorescence or absorption signal is converted to a proportional voltage by the photomultiplier tube and the i-v converter. The analog signal is continuously digitized at a specified rate by the computer's 10-bit ADC, and the result is stored in core memory. The atomizer is then shut off, and the signal is integrated and printed on the teletype. The atomizer is allowed to cool for a preselected amount of time. The program has the capability of providing a punched paper tape of the stored integrated signals and a display of the signals on an oscilloscope if these routines are requested in the initial dialog.



Figure 28. General flow chart of the computer program.



V. FUNDAMENTAL INVESTIGATION OF NONFLAME ATOMIZATION FROM Pt and W WIRE LOOPS

A. Introduction

The computer-controlled nonflame atomic spectrometer described in Chapter IV is capable of handling any electrically heated nonflame atomizer such as a carbon rod, a tantalum strip, and a platinum or tungsten wire loop. Since we were interested in the investigation of the parameters influencing nonflame atomization, all the experimental results reported in this chapter have been obtained with the platinum or tungsten wire loop atomizer. Although a wire loop made of platinum or its alloys suffers from a low melting point (1700 °C) and can only be utilized for atomization of low boiling point elements, it has several advantages when used for fundamental investigations. First, the atomizer has a long lifetime. Approximately 5000 determinations can be performed with one platinum loop. Second, in contrast to carbon rods or furnaces, there is practically no gas evolution from the atomizer. Third, it requires less than 10 W of electrical power to provide an atomization temperature of about 1600 °C. Fourth, it is possible to monitor preatomization processes such as desolvation of the sample solution on the atomizer. This is not possible when a porous atomizer such as some versions of carbon rods or furnaces are employed as atomization devices.

In the first section of this chapter, the influences of the sheath gas flow rate on atomic populations, atomic fluorescence signals and

the precision of measurements are discussed. The second section discusses the complication of the optimization of experimental parameters in programmed and non-programmed heating systems and presents the optimized parameters obtained with the former system. The analytical data obtained with Pt and W loops are presented in the third section. The last section describes the physiochemical properties of W and Pt atomizers.

B. Effect of Sheath Gas Flow Rates

The experimental results reported in this section were all obtained under the conditions shown in Table 6. All measurements were performed in the atomic fluorescence mode with a two step current program to desolvate and to atomize the aqueous sample. Thus, before atomization occurs, the sample is present on the atomizer as a solid.

Figure 30 shows the effect of inner and outer sheath gas flow rates on the cadmium fluorescence signal. Argon was employed for both the inner and the outer sheaths. The inner flow rate (IFR) was kept at 1 1/min, when the outer flow rate (OFR) was varied between 0 and 6 1/min of argon. The same is true for IFR variations. It can be seen in Figure 30 that the AF signal decreases with an increase in the flow rates above 1 1/min. The signal-to-noise ratio (1/relative standard deviation) normally follows the AF signal variation with both the IFR and OFR. The change in AF signal is small between flow rates of 1 to 2 1/min but becomes larger as the flow rate increases. The decrease in integrated AF signal with increasing flow rate can be attributed to the smaller residence time of free atoms in front of

Elements	Cd	Zn	Hg			
	1. Atomization Parameters					
Type of Atomizer	Pt	Pt	W			
Diameter of the wire, in.	0.0126	0.0126	0.01			
Diameter of the loop, in.	0.0625	0.0625	0.0625			
Sample Size, µl	3	3	2			
Sample concentration, ppm	.1	.2	10			
Desolvation current, A	2	2	2			
Desolvation time, sec.	33	33	45			
Atomization Temperature, °C	1200	1200	900			
Atomization time, sec.	4	4	4			
Atomizer Location	Bottom of slit					
Gas Sheath	Design II					
Distance between gas						
Sheath and Atomizer, in.	1	1	1			
	2. Instrumental Parameters					
Metal Vapor Lamp current, A	1.2	1.2	1.2			
Monochromator slit width, mm	1.5	1.5	1.5			
Analysis wavelength, nm	228.8	213.86	253.65			
Photomultiplier supply voltage, V	800	800	800			
i-v converter rise time, msec	1	1	1			

Table 6.	Experimental	Conditions	in	the	Investigation	of	Nonflame
	Atomization				-		



Figure 30. Influence of inner and outer flow rate on the cadmium fluorescence (arbitrary unit) signal.

the observation window, to a lower atomization efficiency, or to both. It is also possible that increased quenching effects occur at high flow rates.

1. Atomization Efficiency

In order to examine the effect of flow rate on the atomization efficiency, the atomizer temperature as a function of flow rate was monitored. The results, shown in Figure 31, demonstrate that the integrated AF signal follows the atomization temperature very closely. Furthermore, an increase in the inner sheath gas flow rate causes the atomizer temperature and consequently the atomization efficiency to decrease. On the other hand, the outer sheath gas flow rate has, within a 95% confidence internal, no influence on the wire loop temperature. However, the integrated AF signal decreases with an increase in the outer sheath gas flow rate. This indicates that although the atomization efficiency decreases with flow rate, the influence of atom residence time is also guite significant.

2. Atom Residence Time

The effect of atom residence time on the AF signal was confirmed by two sets of AF experiments with Cd as the test element. The results are shown in Figure 32. In the first set, similar to the previous experiments, the electrical current through the wire loop was kept constant and therefore, the atomizer temperature varied with the flow rate. In the second case, the computer was programmed to provide different currents at different flow rates so that the loop temperature was kept constant. It can be seen that for both sets, whether the temperature is constant or not, the integrated AF signal decreases



Figure 31. Influences of flow rate on the integrated AF signal (arbitrary unit) and atomization temperature.



Figure 32. Influence of atom residence time on the cadmium AF (arbitrary unit) signal.

with increasing flow rate, but in all cases the signal is greater in the experiments with constant temperature. The same phenomenon was observed for other elements such as Hg and Zn.

The results for Zn are illustrated in Figure 33. Again, the OFR was kept at 1 1/min when the inner flow rate was varied and vice versa. The integrated AF signal decreases with both the IFR and OFR. The system was then programmed to change the atomization current between 3.5 to 4.3 A when both the inner and outer flow rates were kept constant at 5 and 1 1/min respectively. Currents higher than those shown resulted in loop melting. It can be seen that although the integrated signal has increased by a factor of more than fifty, the signal is about twenty times smaller than when both the IFR and OFR were at 1 1/min. The effect of OFR on temperature for Zn was similar to that observed with cadmium.

3. Quenching Effect

In atomic fluorescence, collisions of the radiationally excited atoms with free electrons, or with atomic and molecular particles present in the vapor cell may deactivate the excited atoms with no radiation being produced. The quenching effect in flames has been reviewed in detail by Alkemade and Zeegers (35). From a classical point of view, the number of binary collisions per second and per unit volume, $Z_{A,B}$ is given by

$$Z_{A,B} = [A][B]\pi(r_A + r_B)^2 \bar{\nu}_{rel}.$$
 (56)

where $\bar{\nu}_{rel}$ is the average relative velocity of the colliding particles, and r_A and r_B are the radii of two particles A and B as hard spheres,


Figure 33. Influences of flow rate and atomization current on the Zn AF (arbitrary unit) signal.

and [A] and [B] are the concentrations of A and B, respectively. The number of quenching collisions then is proportional to the concentration of the colliding species, their cross sections and their relative velocity.

The variation of AF signal with the flow rate should also be influenced by the quenching effect. The quenching cross section for noble gases such as He, Ne, and Ar, is small compared to molecular species like N_2 , O_2 , and CO_2 . However, because atmospheric gases can become entrained in the Ar flow, the quenching effect is present when argon is employed as the sheath gas and should vary with Ar flow In order to demonstrate the quenching effect, four sets of rate. experiments were performed. The computer was programmed to provide nearly the same temperature at various flow rates and for two different sheath gases. Thus, the variation of the AF signal with the flow rate can be accounted for in terms of the residence time of the atoms and the quenching effect. In the first two sets, nitrogen and argon were employed for the inner and outer sheath gases, respectively. For the second two sets, argon was used for the inner and nitrogen as the outer sheath gas. In all four cases, the flow for one gas sheath was kept constant when the second one was varied.

The variation of the cadmium AF signal with flow rate is shown in Figures 34 and 35. Comparison of these results with those given in Figure 30 to 32 indicates that the presence of N_2 in the system decreases the AF signal. Furthermore, N_2 has also caused a shift in the optimum argon flow rate from about 2 to 3 l/min. The influence of the flow rate on the quenching effect cannot be evaluated from these results, however. This is due to the fact that the loop temperature



Figure 34. Influences of the quenching effects and flow rate on the integrated AF (arbitrary unit) signal.



Figure 35. Influences of the quenching effects and flow rate on the integrated AF (arbitrary unit) signal.

was measured with an optical pyrometer and had an uncertainty of ±50 °K. Moreover, although the number of quenching collisions is proportional to the relative velocity of the colliding particles, the effective quenching cross section decreases as the velocity increases.

From these experimental results, the following conclusions may be reached. First, an increase in sheath gas flow rate results in a decrease of the atomization efficiency and of the residence time of the atom and influences quenching. Second, when atomization occurs, the atomic vapor will be uniformly distributed around the atomizer if there is no forced flow in the system. If the atomizer is located at the bottom of the observation window, as was the case in these experiments, the atomic plume covers the entire area of the slit. Because of natural convection, however, the atomic vapor expands and gradually leaves the observation window. If the production of atomic vapor results in a laminar plume, the integrated AF signal would be expected to be at its maximum and would be very reproducible. On the other hand, a turbulent plume would result in a lower signal-to-noise ratio (higher relative standard deviation). The inner gas sheath confines the atomic vapor and causes an improvement in the signal-to-noise ratio. However, as the inner flow rate increases the volume of the atomic plume in front of the slit shrinks and becomes more cylindrical in shape. In the extreme situation, for large flow rates, the cross-sectional area of the cylinder becomes smaller or comparable to the area of the slit. Because of turbulence, the atomic vapor does not pass in front of the observation window in a reproducible manner and the signal-to-noise ratio deteriorates. Third, the decrease of AF signal with an increase in the OFR can also be explained similarly. The atomic

vapor should occupy a volume with a cross-sectional area greater than the size of the inner gas sheath. Increasing the outer flow results in a shorter residence time, but the decrease in the signal-to-noise ratio should be less than that expected for increases in the inner flow rate. Thus, even though the AF signal decreases because of a decrease in atomization efficiency and a decrease in residence time, the OFR would not be able to reduce the atomic vapor volume to the same extent as the IFR. It was experimentally observed that the relative standard deviation changes by more than one order of magnitude for variations of the IFR, but the same variation in the OFR produces a less pronounced effect.

When helium gas was employed as the sheath gas instead of argon in the study of Hg atomic fluorescence, it was observed that although the AF signal was decreased, the signal-to-noise ratio was improved by at least a factor of two to three. The improvement can be explained in terms of the thermal conductivity of He, which is about 8 times that of Ar. Helium also has a smaller quenching cross-section than argon. Furthermore, our calculations in Chapter II show that low atomic or molecular weight gases like N_2 can provide a more laminar flow than the high atomic or molecular weight gases like N_2 .

C. Optimization of Experimental Parameters 1. <u>Introduction</u>

In order to obtain the maximum signal and minimum relative standard deviation, a large number of measurements was performed to find the optimum experimental parameters. Critical optimization was only performed for the analysis of Cd, Zn and Hg in the atomic fluorescence

mode. No rigorous optimization was done for the detection of other elements. Although a set of optimum parameters in AF are not generally optimum for AA measurements, the same set of optimum parameters was employed for AA measurements. Furthermore, it was found that, except for the atomization period, the optimum conditions were approximately the same when programmed or non-programmed heating of the atomizer was employed. The detection limits and the signal-to-noise ratios were drastically different, however. Therefore, the optimum parameters for programmed heating are reported here.

Under optimum conditions, the AA and AF signals were approximately Gaussian in shape and had a time duration which varied from 100 msec at low concentrations to 4 sec at high concentrations when aqueous samples were used. Prior to optimization of the atomizer parameters, all the optical and electrical parameters of the spectrometer were adjusted for the highest signal-to-noise ratio. These adjustments included the position and electrical parameters of the excitation sources, the position of the nonflame cell with respect to the source, the monochromator spectral handpass, and the photomultiplier anodeto-cathode supply voltage. In the optimization of the atomizer parameters, the atomization temperature was kept constant for the variation of the flow rate as well as other parameters. The optimum parameters were found to be independent of the type of the wire loop atomizer provided that the wire diameter and the loop size were identical. Unless otherwise stated, all optimum parameters have been obtained with gas sheath design II. The results of the optimization study are summarized later in this section.

2. Atomization Processes Without Programmed Heating

The experimental results presented in the previous section were all obtained with a two step current program to desolvate and to atomize the sample. In other words, it was assumed that the sample is present as a solid just prior to atomization. Because the analysis time can be reduced and sample loss can be prevented during the desolvation and ashing steps, it is desirable to atomize the sample in one step. This method of atomization, however, may complicate the optimization of experimental parameters as well as the atom formation processes and the detection processes. A discussion of some of these complications is presented here.

As was previously stated, the limits of detections and the relative standard deviations obtained under optimum conditions, with a multistep programming system were superior to those obtained when atomization was performed in a single step. Another important characteristic of the non-programmed system is that the signal behavior may vary significantly when the system is not operated under optimum conditions. Figure 36 shows two atomic fluorescence signals for 10 ppm Hg when the atomizer was not optimized and gas sheath design I was employed. The long leading edge of the signal is due to sample explosion on the wire loop. In other words, as a result of a change in the mechanism of heat transfer, the solvent and solute are not separated in time and there is some light scattering by the sample. Thus, the fluorescence signal is seen on top of the scattering signal.

When gas sheath design II was tried, it was realized that the optimum parameters obtained with the previous gas sheath could not be duplicated. A variety of parameters such as the inner and outer flow



Figure 36. Two atomic fluorescence signals of 10 ppm Hg under Non-optimized conditions.

rates, the distance between the atomizer and the gas sheath, and the atomizer temperature were varied to find the optimum parameters. In contrast to design I, it was practically impossible to prevent the simultaneous vaporization of the solvent and solute. The detection limits and relative standard deviations increased drastically. In all cases, the signal-to-blank ratio was maximum at a flow rate of 2 l/min., however.

It is obvious that the changes in the behavior of the system are due to the different designs and constructions of the gas sheaths. Thus, optimization, if not impossible, can be extremely tedious. This originates from the fact that most of the parameters are dependent variables. In order to simplify the system, the number of parameters and their interdependence should be decreased. Programmed heating of the atomizer not only separates the vaporization of the solvent and solute in time, it makes the function of the carrier gas simpler, the effect of the gas sheath design less critical and the sources of light scattering and quenching (AF) more evident.

3. Optimization of parameters for Programmed Heated Wire Loop Atomizers

a. <u>Introduction</u>. Among the parameters unique to electrically heated filament atomizers are the diameter and size of the filament, the sample size, the sample type, the gas sheath designs, the inner and outer sheath gas flow rate, the distance between the atomizer and the gas sheath, the vertical distance between the observation window and the atomizer, the desolvation, ashing, and atomization times and temperatures. All the optimized parameters reported here have been obtained with aqueous solutions. Therefore, a two step current

programming technique was employed. The optimized parameters for the atomization step are reported in terms of temperature instead of current or power. The latter are a function of loop dimensions and other parameters in the system. The temperature was measured by an optical pyrometer and was reproduced for different flow rates by making relative emission measurements at 6500 Å. For the desolvation period, where there is no visible emission from the atomizer, the electrical current through the atomizer was optimized instead of temperature.

b. <u>Preliminary Optimization</u>. Wire loops with diameters larger than the maximum monochromator slit width were not employed in the work. The best loop size had a diameter of 2 mm. The best wire diameter was found to be 0.0126 in. Larger diameter wires could not normally provide a uniform temperature at the loop center. Wires with diameters less than 0.0126 in. were hard to fabricate. With this type of a loop, a sample size of 3 μ l was found to provide the best precision. Since the desolvation current for a Hg sample should be very small to prevent the covaporization of Hg, a sample size of 2 μ l was employed to prevent long desolvation times.

All optimized parameters have been obtained with gas sheath design II. The distance between the atomizer and the gas sheath was *selected* as 1 in. The atomizer was located slightly below the monochromator slit with the primary source focused 1 mm above the wire loop. This arrangement allows AF measurement before condensation of the atomic vapor occurs.

c. <u>Optimization Procedure</u>. After the preliminary optimization, the following procedure for optimization of other parameters was

normally followed. First, the desolvation time and current were adjusted so that the water vaporizes smoothly and leaves the solute on the atomizer. Second, an atomization temperature well above the boiling point of the element and an atomization period about twice the actual atomization time were also selected as initial estimates. Third, using these parameters, the inner and outer sheath gas flow rates were optimized for maximum signal-to-noise ratios. Fourth, since the outer flow rate did not change the atomizer temperature appreciably, the variation of inner flow rate with atomization temperature was monitored at the optimum outer flow rate. Both the AF signal and the signal-to-noise ratio were measured. Fifth, the desolvation current and time were optimized at the optimum atomization temperature and optimum inner and outer flow rates.

d. <u>Inner-Outer Sheath Gas Flow Rates</u>. Using the above procedure, the parameters were optimized for Cd, Zn, and Hg. The desolvation time and current for both Cd and Zn were chosen to be 33 sec and 2 A respectively. The atomization period was started immediately after water vaporization was visibly complete. The desolvation parameters for Hg were 45 sec and 0.6 A, and atomization was initiated before complete vaporization of water. This prevents possible vaporization of Hg during desolvation. In all cases, an atomization temperature and period of 1200 °C and 4 sec were employed as initial estimates.

Figure 37 shows a diagram of the influence of flow rate upon the relative standard deviation (RSD) of Cd AF signals. For the center contour line, the RSD of AF measurements was 5 percent or less, while for the next to the center line, the RSD varied between 5 to 10 percent. The optimum sheath gas flow rates were chosen to be inside





the 5 percent RSD contour.

e. <u>Inner Flow Rate - Atomization Temperatures</u>. In order to optimize the atomization temperature, the OFR was kept at 2 1/min, and the IFR and the atomization temperature were varied. Figure 38 shows the influence of these variations on signal-to-noise ratios and the magnitude of the Cd AF signal. The center AF signal contour represents all measurements which differ from the maximum integrated area by a maximum factor of 2 while this difference for the outer AF contour is within a factor of 5. Thus, the optimum temperature can vary between 1100 to 1350 °C and the optimum inner sheath gas flow rate may vary between 1 to 2.5 1/min.

f. <u>Desolvation Time - Desolvation Current</u>. For optimization of the desolvation step, the optimized parameters for atomization temperature, IFR, and OFR were taken as 1250 °C, 2 1/min, and 2 1/min. respectively. The influence of the desolvation current and time on the relative standard deviation and AF signal for Cd is shown in Figure 39. The AF signal contour line incorporates all measurements which are different from the maximum integrated area by as much as 10 percent. At high currents and long desolvation periods, evaporation of the sample occurs and the signal-to-noise decreases. At low currents and short desolvation periods, water vaporization is not complete before the start of atomization, which again results in a deterioration of the signal-to-noise ratio.

g. <u>Optimized Parameters for Cd, Zn, and Hg</u>. The above procedure was also employed to obtain the optimum parameters for Zn, and Hg. An extensive description of the behavior of these systems will not be given here. However, Table 7 shows a summary of the optimum









Element	IFR l/min	OFR l/min	Desolvation time time, sec.	Desolvation Current, A	Atomization Temperature, °C
Hg	1	1	40	0.8	1000
Cd	2	2	34	2	1250
Zn	2	2	34	2	1300

Table 7. Optimum Platinum Loop Atomizer Parameters Using Programmed Heating

parameters for these elements. These parameters were employed to obtain the analytical results presented in the next section for these elements. As can be seen from Figures 37 to 39, the optimum parameters for any system can vary within a certain range. For example, Hg can be analyzed between 1000 to 1300 °C with practically identical results. The optimum parameters for Cd are almost the same as for Zn because these elements have almost the same boiling points.

D. Analytical Results

After optimum parameters were chosen for the analysis of Cd, Zn and Hg, a study of the long term stability of the AF system was made, and analytical data were obtained. A comparison of the detection limits obtained with a programmed and a non-programmed heated platinum loop was also performed. The optimum parameters obtained by AF were also employed for the determination of Cd, Zn, Hg and other elements by AA.

1. System Stability

In all cases, the overall stability of the system with multistep programmed heating was found to be superior to cases when a one step atomization was used. Figure 40 demonstrates the long term stability of the system for 100 consecutive samples each of which contained 150 pg of cadmium. A 10 sec. cooling period was allowed between successive analyses. The system was operated in the AF mode with a programmed heated Pt loop and with the fixed-volume sampler. No operator adjustments were made during the total analysis time of 100 min. The largest deviation from the mean was approximately 15%, and the relative standard deviation of 100 samples was 6.5 percent. In a similar study for the AF analysis of Zn, and Hg, the relative standard deviations of 100 samples were 6.3 and 7 percent, respectively.

When a one step atomization was employed the relative standard deviation ranged between 8 and 10 percent under the same operating conditions. Both the short and long term reproducibility of the system are influenced by, among other factors, the physiochemical properties of the atomizer. This is discussed in a later section.

2. Analytical Working Curves

AF calibration curves under optimum conditions were obtained for Cd, Zn and Hg with programmed heating. All the working curves showed a sigmoid shape. In all cases the monochromator was flushed with argon and triply distilled deionized water was used in making all solutions. The analytical curves, Figure 41, for Cd, and Zn have a linear range of 5 orders of magnitude, while the linear range for



Figure 40. Long term stability of the computer-controlled AF spectrometer.



Figure 41. AF analytical working curves for Cd, Zn, and Hg obtained under optimized conditions.

Hg is about 3 orders of magnitude. The vertical markings around each experimental point indicate the relative standard deviation of 10 samples. All working curves show a slope of unity in the linear region. For extremely low concentrations, the slope differs from unity, although the precision of measurements is about 15 percent relative standard deviation. In this area, the blank concentration of the elements becomes comparable to the concentration of the analyte in solution.

3. Detection Limits

a. <u>Results</u>. The lowest concentration in the unity slope calibration curve was defined as the detection limit. It should be noted that this definition gives conservative detection limits compared to the most common definition (S/N=2). Table 8 shows a comparison of the

0
0
0

Table 8. Comparison of AF Detection Limits (ng/ml) With and Without Programmed Heating of Platinum Loop

detection limits for Cd, Zn, and Hg with and without the programmed heating of the Pt loop. The same optimum parameters were also employed to obtain the detection limits of the same elements by the AA technique. Detection limits were also obtained for Tl, Mg, Mn, Ni and Pb in atomic absorption with a W loop atomizer. Table 9 summarizes the detection limits of the elements obtained in AA.

b. <u>Discussion</u>. There are many factors responsible for the lower detection limits with the programmed heated system. Some of these factors are evident if one refers to some of the advantages of nonflame atomizers over flame atomization, which are described in Chapter II. In general there is: 1) more precise control over the spectral and chemical environment; 2) no flame gas expansion on combustion; 3) higher efficiency of free atom production; 4) less scattering of light and far less quenching of excited atoms (AF). In other words, in any nonflame method the increase in S/N is not only due to increases in the signal, but also to a decrease in noise. If the nonflame system is not programmed heated, the signal decreases because points 1, 2, and 3 are not present, and the noise increases due to the opposite effect of points 1, 2, and 4. Even in the simplest case of an aqueous solvent, the non-programmed system is complicated by the nature of the boiling process, which is not yet fully understood.

In order to describe the different processes which occur during solvent evaporation, we first simplify the system by assuming that a hypothetical high melting point wire loop is heated electrically in a pool of deionized water at atmospheric pressure and at the saturation temperature of 100 °C. We further assume that the wire is heated uniformly and define the difference between the wire and the solvent temperature as ΔT_E or the *excess* temperature. A plot of heat flux $(\frac{\Delta T_E}{A}; h = heat$ transfer coefficient, A = surface area) against excess temperature (277) indicates, that there are five distinct rates of

Elements	Analysis Wavelength A	Detection Limit	Atomizer
Hg	2536.5	0.2	Pt
Cd	2288	0.0005	Pt
Zn	2138.6	0.0005	Pt
TI	2767.9	0.06	Pt, W
Mg	2852.1	0.02	W
Mn	2794.8	0.08	W
Ni	2320	0.7	W
РЬ	2170	0.08	W

Table 9.	Atomic Absorption Detection Limits (μ g/ml) With Programmed
	Heated Platinum and Tungsten Loop Atomizers

The following parameters were kept constant for all elements.

PMT voltage, V	800
Monochromator Slit Width, mm	0.1
Sample size, µl	3
Flow Rate, l/min	2
For W Atomizer	
Desolvation time, sec	25
Desolvation current, A	3
Atomizer temperature, °C	2000



HEAT FLUX

Figure 42. Typical boiling curve for a wire in a pool of water at atmospheric pressure (heat flux has arbitrary unit).

heat flux variation. These five regions are shown in Figure 42 and are as follows. In the first region ($0 < \Delta T_F < 10$ °F), the convective flow circulates water, and evaporation occurs at the free surface of water. Since only water is in contact with the free loop, it can be assumed that the process is free convection. The process in regions 2 and 3 is called *nucleate* boiling (10 °F> ΔT_F <100 °F), and the heat flux changes rapidly with increasing wire temperature. Visual observations indicate that in the second region, individual bubbles form at certain places on the wire. They grow and push hot water from the proximity of the wire into the colder bulk of water. In the third region, one sees many rising streams of bubbles as $\Delta T_{\rm F}$ increases. These columns cause a considerable stirring action in the water and the heat transfer coefficient increases. It is obvious that the transfer rate is greater from wire to water than from wire to vapor. Thus, as ΔT_E increases more, a greater percentage of the wire surface is blanketed by bubbles. Eventually, this increased blanketing begins to counteract the tendency of higher $\Delta T^{}_{E}$ values to produce higher flux, and the two effect balance at some point. This maximum heat flux occurs at a temperature called the "burnout" point. Beyond this point an increase in the heater temperature results in a decrease in the heat flux. This region is called the transition boiling region. Finally, in the stable film boiling regions, a vapor film covers the entire wire surface. An event similar to this process can be observed when droplets are sprayed on a red hotplate. Because of the formation of a vapor film between the plate and water, the droplets dance on the plate and do not evaporate immediately. Moreover, the effect of radiation from the wire in this region becomes quite high, and this results in an

increase in the heat flux with respect to $\ensuremath{\Delta T_{E}}\xspace$.

In the transition boiling region, stable film and nucleate boiling take place alternatively, and this results in a very violent process. However, in the case of an electrically heated wire, transition boiling is not usually observed. The reason is that if at the maximum heat flux, the rate of energy generation is increased, the wire temperature rise provides a boiling process which cannot remove heat as rapidly as at the maximum heat flux. The difference between the generation and the dissipation rate produces a higher wire temperature with a consequent jump to the stable film boiling region.

We believe that the mechanism of solvent evaporation in the nonprogrammed system is similar to the boiling processes described above. The problem is, however, more complicated because of the presence of the solute and increased surface roughness, which tend to increase the heat transfer coefficient. Moreover, the sample is not at the saturation temperature initially, the instantaneous amount of both solvent and solute is a strong function of wire temperature, and the free and the forced convection which exist because of gas flow in the system complicate the processes.

Due to the limited amount of the sample, we believe the boiling process from a heated wire filament involves only the first three regions. When the current is turned on, the wire temperature increases gradually (not instantaneously). Even if the bulk temperature is below the saturation temperature, the boundary layer is superheated and bubbles form next to the wire. However, because of the temperature gradient the process would be more violent and much higher heat fluxes can be obtained in this case. The extreme agitation is responsible for

partial evaporation of the solute. Some of the solute is also lost when the cold sample splashes against the hot wire. Furthermore, as the amount of solvent is decreased by evaporation, the solute would be left behind on the loop. Since the final part of solvent evaporation is usually located on only one part of the atomizer (276), some solute evaporation results in this manner. A combination of these effects results in light scattering. Moreover the presence of water as well as other molecular species result in the quenching of excited atoms in AFS.

In a programmed heated system, on the other hand, the excess temperature can be kept low (<10 °F), which results in having a low heat transfer coefficient. The process is a conventional free convection. Although it is true that in a programmed heated system, the amount of heat for each of the steps and the time duration for each step should be optimized, the estimation of these quantities, because of the simpler heat transfer process, provides less of a problem.

E. The Physiochemical Properties of W and Pt Atomizers

The % RSD for the optimum parameters ranges between 2.7 to 7% for both Pt and W wire loops. The long term reproducibility of the W atomizer was not as good as for the Pt atomizer. This can be accounted for by the oxidation of the W loop, by its evaporation, and by chemical reactions between tungsten and the solute. These effects are discussed below.

1. Evaporation of the Atomizer

It has been shown that ac heating results in a higher evaporation rate than the dc method (278). The rate of evaporation of tungsten in a vacuum is given by (279)

$$Log m = 7.5 - \frac{40500}{T}$$
 (57)

where m is in g/cm^2 . sec and T is °K. It can be seen that if the temperature is increased from 2000 °C to 3000 °C the evaporation rate is increased by a factor of 2 x 10^5 . Although the evaporation rate is reduced in an inert atmosphere, it cannot be neglected. This effect is more or less present in the case of any nonflame atomizer and results in an increase in the electrical resistivity of the atomizer.

2. Chemical Reactions

A study of the chemical reactions of tungsten shows that although the metal is very inert, it is dissolved by strong oxidizing agents, and it is slightly attacked by phosphoric, sulfuric and nitric acids between 100 - 110 °C. Moreover, even for simple sample matrices, it can react with oxygen, water vapor, hydrocarbons, nitrogen, and other species between 500 - 1500 °C.

According to our experience, oxidation of tungsten was one of the major factors responsible for the poor long term reproducibility. It was possible to differentiate different tungsten oxides by their colors. At 500 °C tungsten oxidizes and forms a black protective film $W_{18}O_{49}$ or WO_2 (280). The gain in weight of tungsten follows a parabolic law (281).

$$G_W^2 = D.k.t$$
 (58)

where G_W is weight gain, D is a diffusion constant, k is a constant and t is time. With additional oxidation, the black oxidized layer changes to a green (at 600 - 950 °C) or a yellow (at 1000 - 1100 °C) layer which is no longer protective. This new trioxide layer changes the parabolic law into a linear law (281).

$$W = k' \cdot t$$
 (59)

The yellow trioxide layer, which is also an electrical insulator, vaporizes rapidly above 1000 °C, and this opposes the gain in weight. Although the above laws depend on the amount of oxygen in the system, we had no success in preventing the loop oxidation by the use of outer gas sheaths. In fact, it has been shown that tungsten is oxidized even when the partial pressure of oxygen is 10^{-13} atms (282).

It should be realized that since heat is localized in the center of the atomizer, different forms of oxides exist at different parts of the W loop. The two ends are black and this gradually changes to green and yellow toward the loop center. Finally, the atomizer is usually ruptured at the yellow trioxide layer.

Even if it is assumed that evaporation of the W loop is minimal in the presence of argon gas and oxide layers and it can be neglected in the discussion of long term reproducibility, formation of oxides and chemical reactions lead to an increase in the electrical and thermal resistance of the atomizer. Moreover, at temperatures of 2600 - 3200 °C, the loop may deform by shearing along the boundaries of recrystallized grains or creeping in the wire, which results in lowering the electrical efficiency of the wire. This means that the required power to atomize the sample is a function of at least time

and the number of experiments. If the power is kept constant, then the long term reproducibility deteriorates. The same explanation also holds true for the platinum loop. The better long term reproducibility of Pt is due to its low chemical affinity. It forms a monoxide at 510 - 560 °C when heated in oxygen, but the oxide decomposes above this temperature. Thus, the loop remains bright. The rate of volatilization is smaller in an inert gas than in oxygen or air, yet there is a loss in weight.

The gradual evaporation of the nonflame atomizer material is a fundamental disadvantage of these vapor cells. It results in a drift of atomization temperature and determines the lifetime of the atomizers. However, several methods can be employed to compensate for the variation of temperature and to extend the lifetime of the atomizer. These techniques will be discussed in Chapter VI.

VI. THE GRAPHITE BRAID, A NEW NONFLAME ATOMIZER

A. Introduction

The Pt loop atomizer, as stated in the previous chapter, is of considerable value in the investigation of the general behavior of filament-type atomizers. The atomizer, however, is of no significant value for the analysis of elements with boiling points greater than 1500 °C. Although a tungsten loop atomizer can provide high operating temperatures, the metal is subject to oxidation and extreme control of the atomization chamber is necessary. The lifetime of the atomizer at a temperature of 900 °C is about 250 samples, while increasing the temperature to 2000 °C reduces this figure to a maximum of 40-50 samples under the best conditions. Furthermore, since the mechanism of atom formation may be quite different from the mechanism of atomization from carbon or graphite, higher operating temperatures may be required to provide the same atom population. This increases the background emission from the atomizer and deteriorates the signal-tonoise ratio. For a tantalum loop or strip atomizer, the temperature is limited to a maximum of 2600 °C by the characteristics of tantalum metal.

The atomizers made from carbon or graphite appear to be highly applicable for analytical purposes because of the high operating temperatures (2500-3000 °C) which can be achieved. These atomizers, however, exhibit several practical limitations. Graphite or carbon

tubes and furnaces, for example, may require several kilowatts of electrical power to achieve atomization temperatures in the range of 2500 to 3000 °C (9,67,146). The different versions of graphite and carbon rods and cuvettes provide similar temperatures with a power of 500 - 1500 W, which depends on the size and design of the atomizer (128,146). Since the transfer of electrical energy into thermal energy is not perfectly efficient, a fraction of the electrical energy will be dissipated as electromagnetic radiation. Extensive shielding and/or careful circuit design must be employed to minimize these electromagnetic interferences. The sheer bulk of a system which requires kilowatts of power also prevents its application as a portable field analyzer.

The power requirements of carbon rods or filaments can be reduced by narrowing the central part of the atomizer. This intentional confinement of heat to the central region of the rod type atomizers also results in prolonged filament lifetime and reduction of background radiation (131), but it can cause some loss of sensitivity due to sample diffusion in the rod. The problem is more serious when larger volumes of the sample are used to increase sensitivity. A pyrolitic graphite coating makes the atomizer impervious to most gases and liquids, yet it is desirable to have a porous filament to minimize creeping of the sample, as in the analysis of fuel oil (162). Thus, it would be advantageous to have a uniform temperature throughout the atomizer. Furthermore, since in atomic absorption, absorbance is proportional to the optical path length, a uniform temperature throughout the atomizer can be helpful in increasing the absorbance.

In an effort to combine the virtues of Pt and W loop atomizers

(compactness, low power consumption, speed of operation) with the West rod (compactness, speed of operation, range of elements) and the L'vov furnace (range of elements, freedom from interference), a new filamenttype nonflame atomizer, the graphite braid atomizer (GBA), has been developed and investigated. The electrically heated GBA is capable of providing temperatures similar to other carbon or graphite atomizers, but with lower applied powers. The porous nature of the atomizer provides a furnace-type environment with a uniform temperature throughout the GBA. The new atomizer has been found to give high atomization efficiencies and low detection limits in the AA and AF determinations of several elements. In contrast to other carbon or graphite filaments or furnaces where a cooling system is required for the atomizer holder, no cooling system was needed for the GBA during this work.

In the first part of this chapter, the characteristics of the GBA are discussed. The various heating methods of nonflame atomizers are presented in the second section along with the application of these techniques, to the graphite braid and wire loop atomizers. Finally, the AA and AF analytical applications of the GBA are demonstrated in the last section.

B. Characteristics of the GBA

1. <u>Physical and Chemical Properties</u>

The graphite braid (Union Carbide Corp., Parma, OH) contains high strength, flexible, continuous filaments of graphite which are woven to form a thread of 1.5-2 mm in diameter. The physical properties of the GBA are summarized in Table 10. The type of gases evolved from

Unit	Magnitude
g/cc	1.5
°F	does not melt
°F	6600
BTU/(1b)(°F)	0.17
°F	0.4
ohm – in	0.0013
	0.0010
	0.0006
Yard/pound	412
\$/pound	85
	Unit g/cc °F °F BTU/(1b)(°F) °F ohm - in Yard/pound \$/pound

Table 10. Physical Properties of the Graphite Braid Atomizer

Table 11. A typical List of Major Elements in the Graphite Braid

Element	Concentration PPM	Melting Point °C	Boiling Point °C
Fe	35-50	1535	3000
Ca	20	850	1487
Mg	20	651	1109
Si	>5	1427	2290
Ti	>5	1800	5100
Cu	5	1083	2595
A1	3	660	2057
Na	>1	98	892

this material has been determined (283) in the presence of a vacuum and at a temperature of 1500 °C. Although the exact quantities are not known, some small quantities of sulfur, nitrogen, oxygen and hydrogen are evolved. Sulfur has been measured at 0.003 percent. The results of an emission spectroscopic analysis of the braid, shown in Table 11, suggest that the total impurity content does not exceed 150 ppm. Braids used in this work were outgassed by resistive heating to about 2500 °C for a period of 2-3 sec. The cleaning procedure was repeated until the AA or AF baseline was constant. This usually required two or three repetitions of the cleaning cycle.

2. Braid Temperature

Figure 43 shows the influence of applied power and applied current on the atomizer temperature. The temperature of the braid was found to be variable up to 2600 °C. The temperature dependence on power for a GBA 3 cm long, was approximately linear over the range 1000 °C to 2500 °C and had a slope of about 5 °C/W in this range, with only 350 W needed to heat the atomizer to 2500 °C. When the length of the braid is shortened, the required power needed to reach a given temperature is considerably less than the power needed for the longer braid as expected. Furthermore, when the diameter of the braid is decreased, the braid resistance increases and allows less current through the GBA. The relationship between the atomizer temperature, the voltage applied across the atomizer, and the applied power for a GBA of about 0.5 mm diameter is shown in Figure 44. The power requirement has decreased by a factor of about 3 and only 125 W are



Figure 43. Influence of applied power and applied current on the GBA temperature.


Figure 44. Influence of applied power and voltage across the atomizer on the temperature of a 0.5 mm diameter GBA.

atomizer, however, increases approximately linearly with temperature and about 28 V are required to reach a temperature of 2500 °C. The time required to reach a given temperature with this diameter GBA is shorter than when larger diameter braids are employed. Moreover, the background emission of the atomizer is smaller, because of the smaller dimensions of the atomizer. This type of braid is not commercially available, but because of the lower power requirement, lower background emission, and fast response, it should be investigated in detail. Throughout this work, the GBA had a diameter of 1-2 mm and was 3 cm long.

3. Braid Emission Spectra

Figure 45 shows the spectral emittance of the graphite braid as a function of wavelength and atomization temperature. For these experiments, the GBA was mounted in the optical path of the spectrometer, about 5 mm above the bottom of the monochromator slit, by an arrangement similar to that described for the Pt loop atomizer. The spectrometer was operated in the emission mode and the spectral emittance was monitored as a function of the wavelength at three different temperatures. The maximum spectral emittance moves towards lower wavelengths as the temperature is increased. In order to improve the signal-tonoise ratio, a R166 photomultiplier tube was employed instead of the 1P28 tube. The R166 phototube spectral response extends from 1600 to 3200 °A. Figure 46 compares the spectral emittance of the GBA obtained with the two phototubes. Note that the photocurrent from the R166 tube is amplified by three orders of magnitude. When the GBA is mounted below the optical path of the spectrometer, as is the case in AA and







Figure 46. Comparison of the spectral emittance (arbitrary unit) of GBA with two phototubes.

AF measurements, the braid emission would be negligible below 3200 Å. For the determination of high boiling point (b.p. >3000 °C) elements such as platinum, the atomizer is employed at its maximum operating temperature, and the atomic vapor should be observed as close to the braid surface as possible. For these determinations the GBA emission may cause some interference at concentrations close to the detection limits. This problem can be eliminated, however, if a suitable baffle is utilized to limit the braid emission reaching the observation window or if an ac detection system is employed in conjunction with a modulated radiation source instead of a dc system. Such systems were not found necessary throughout this work.

4. AA and AF signal Characteristics

During the atomization step, the atomic vapor above the atomizer gives rise to an AA or AF signal with a time duration which depends on a variety of factors such as the sample size, matrix, and atomization temperature. Typical signals were approximately Gaussian in shape with half-widths on the order of 0.5-1 sec. Integration of the absorption and fluorescence peaks was used to improve the accuracy and to extend the linearity of the working curves. The photometric signal was integrated for the duration of the atomization step.

After an aqueous sample is placed on top of the braid, it soaks down between the graphite fibers. Heating the fibers produces a furnace-like environment. The heating processes are very efficient because a high surface area is kept in contact with the sample. The possibility of sample explosion is minimized, again due to the furnacetype environment around the sample. An explosion and a concurrent

loss of sample could be observed if the sample were too viscous to soak into the braid and the desolvation temperature were set well above the boiling point of the solvent.

The effects of varying the length of time which the sample remained on the atomizer prior to desolvation were studied. For soaking times of up to 20 seconds, the mean AF signal for a l μ g/ml aqueous zinc solution remained constant, within a 95% confidence interval. The standard deviations of replicate trials were also unaffected by the soaking time, probably because the entire length of the braid is heated to a uniform temperature. Soaking of the sample into the braid may be a problem with a different sample matrices, however. When programmed heating was not employed, the mean AF signal increased initially with the soaking time, reached a maximum and finally decreased. In contrast to the platinum loop, no covaporization of the solvent and solute was observed with the GBA.

5. <u>Mechanisms of Atom Formation</u>

The process of atom formation in flames can either be thermal or chemical in nature. For many easily atomized elements one needs to elevate the temperature to a sufficient extent in order to liberate free atoms. For other elements, which form refractory monoxides, molecules with dissociation energies on the order of 7 eV or more this should not be the case. The efficiency of free atom formation is higher in fuel-rich flames, although stoichiometric flames can provide higher temperatures. The determination of B, Si, and W in the nitrous oxide - acetylene flame is one of the best examples of the effect of chemical formation of free atoms. The mechanism of free

atom formation in this flame is still unclear, but because of the presence of the reducing environment, the following mechanisms have been suggested.

$$MO + C \stackrel{\neq}{\leftarrow} M + CO$$
$$MO + NH \stackrel{\neq}{\leftarrow} M + NO + H$$
$$MO + CN \stackrel{\neq}{\leftarrow} M + CO + N$$

The mechanism of atom formation in nonflame atomizers depends on the type of nonflame device, the element, the chemical compound being analyzed, and the amount of oxygen in the system. For those atomizers made from metals such as Pt, W, and Ta, the process should be thermal in nature. If a sheath gas such as H₂ is employed, a hydrogen diffusion flame is produced during the atomization period. This reducing environment should minimize interferences, remove the oxide layer on the atomizer, and extend the range of determinable elements. For atomizers made from carbon or graphite, the hot carbon may assist in the atom formation process as well as the high temperature. The presence of carbon or graphite, however, presents a difficulty in analyzing for elements such as Al, Si, W, and B that form notoriously stable carbides. Although it has been possible to dissociate such carbides by thermal means in the case of Al and Si, such is not the case for W and B with carbon or graphite devices not coated with pyrolitic graphite.

The less reactive nature of the pyrolitic graphite also reduces the role of hot carbon in assisting the atom formation process. The nature of the process is questionable, however. Whatever the mechanism

of atom formation, thermal or chemical, the GBA should be superior or *at least* equivalent to the graphite or carbon filament devices in free atom formation. This is due to the porous nature of the atomizer and the large surface area which is in contact with the sample. Whether the atom formation is thermal, chemical or a combination of the two, the higher surface area of the GBA should provide higher free atom populations at the same temperature than other metals, carbon, or graphite filament devices.

6. Braid Lifetime

The lifetime of any nonflame atomizer depends on a variety of parameters such as the sheath gas flow, the sheath gas type, the sample size, the matrix, the method of programmed heating of the atomizer, the desolvation, ashing and atomization temperatures and the duration of each heating step. The following discussion is applicable to all electrically heated nonflame atomizers.

a. <u>Sheath Gas Flow - Sheath Gas Type</u>. The rate of vaporization of any material in a vacuum depends on its vapor pressure and temperature. The rate of evaporation in an inert gas atmosphere at atmospheric pressure is about 60 times slower than the rate in vacuum. Using Equation 12, the evaporation rate for a carbon atomizer was calculated and plotted as a function of atomization temperatures as shown in Figure 47. It can be seen that when the atomizer temperature is varied from 2100 to 3200 °C, the evaporation rate changes by five orders of magnitude. If the sheath gas or the impurities in the sheath gas react with the atomizer, the evaporation rate is still higher. The evaporation rate is also higher in a dynamic system compared to



Figure 47. Influence of the atomization temperature on the atomizer evaporation rate.

a static system. As the flow rate is increased, the vaporized material is swept out of the atomization chamber and the atomizer consequently produces more vapor. In addition to the above effects, for a GBA of very small diameter, the sheath gas applies a pressure on the braid which can cause the deformation or rupture of the braid fibers at higher flow rates.

b. <u>Sample Size - Sample Matrix</u>. The effect of sample size on atomizer lifetime is evident. The larger the sample, the more energy is required to atomize it, and this decreases the atomizer lifetime. This indicates that the duration of each heating step should be extended to completely desolvate, ash, and atomize the compound.

The sample matrix not only influences the magnitude and the duration of each heating step, but it can react with the atomizer and alter its physiochemical properties. The types of corrosive agents which both carbon and graphite do not resist are the strong oxidizing agents. Even in some cases of this kind, however, they may be found to be more serviceable than other atomizers.

c. <u>Influences of Heating Stages - Methods of Programmed Heating</u>. In order to reduce the matrix effects and to allow some control over the atomization process, most nonflame atomizers utilize a two or three stage electrical current program for heating the atomization elements. These steps are utilized to desolvate, ash, and atomize the sample. The lifetime of the atomizer decreases as the current through the atomizer and the duration of each stage increases. The effect of current during the atomization step on the number of determinations with the GBA is shown later in Figure 51. For atomizers made from carbon or graphite, vaporization of the atomization element

is the major factor responsible for the decreased lifetime of the atomizer. Vaporization results in increased electrical resistance. If the current through the atomizer is constant, as is the case with all programming systems reported so far, the atomizer temperature increases gradually and this can influence the long range reproducibility in the system. It is practically impossible to prevent the vaporization of atomization elements. However, other methods of programmed heating can be employed to compensate for the vaporization problem. Since these methods are shown to influence other parameters in the system as well as the atomizer lifetime, they are discussed in the next section.

C. New Methods for Programmed Heating of Nonflame Atomizers

1. Introduction

There are actually 5 different methods of programmed heating of nonflame atomizers, depending upon the electrical or physical parameters which are controlled during the heating steps. Most nonflame atomizers utilize a two or three stage electrical *current* program for heating the atomization elements. However, programmed heating can be accomplished by controlling the voltage across the atomizer, the power dissipated in the atomizer, the radiation emitted by the atomizer, and the actual atomizer temperature. The instrumentation employed for various heating methods is similar in that all techniques use a sensing device and a feedback system for heating regulation. In this section the instrumentation required for the various techniques is discussed along with the advantages and disadvantages of each method. The method of programmed heating is shown to influence the atomizer

lifetime, the time required for the atomizer to reach a steady state temperature and the separation and optimization of atomization parameters.

2. Current and Voltage Programming

In current-programmed heating, the power supply provides the atomizer with the preselected amount of current during the various heating stages. The current is monitored by a sensing resistor, R_{cs} , and current regulation is performed by the feedback circuit described in Chapter IV. In voltage programming, the voltage across the atomizer is preselected and kept constant during each heating stage. The magnitude of the voltage, therefore, would be different for the 3 heating stages. The instrumentation for voltage programmed heating is trivial and will not be discussed here.

In all programming operations reported here, a dc rather than an ac power supply was utilized for heating the atomizer. The ac evaporation rate of the atomizer material has been shown (278) to be greater than the dc evaporation rate under the constraint of either equal effective current or voltage. Both current and voltage methods of programmed heating result in atomization temperature drift. This can be easily observed from Equation 60, which has been obtained assuming ohmic heating.

$$i^{2}R(T) = C(T)\rho s \frac{dT}{dt}$$

 $T = \frac{k_{1}}{s}(i^{2}R) = \frac{k_{1}}{s}(iv) = \frac{k_{1}}{s}(W)$ (60)

where both the atomizer resistance R(T), and specific heat C(T) are functions of temperature, and ρ and s are the atomizer density and cross

sectional area.

If current programming is employed as the heating method, gradual vaporization results in higher electrical resistance and smaller crosssectional area for the atomizer. Thus, the atomization temperature will increase from run to run. For voltage - controlled heating, the increase in the resistance allows less current through the atomizer and the temperature decreases. The rate of atomizer evaporation, however, would be smaller than with current programming. These variations can be multiplied if the atomizer or its holder do not have the same temperature at the start of successive experiments. Depending on the magnitude and the sign of the coefficient of electrical resistance, different changes may result as shown by Equation 61.

$$R = R_{0}(1+\alpha T)$$
(61)

If the atomizer and its holder are made of the same material, a positive value of α results in the intensification of temperature variations, while a negative value may operate in the opposite direction. If the atomizer and the holder are made of materials with different α values, as is normally the case, other temperature variations can be expected. Therefore, the atomizer holder should be water cooled or a cooling period should be allowed between successive analysis.

The variation of the GBA temperature as a function of number of the experiments was monitored by measuring the emission intensity of the GBA for atomization currents of 9 to 21 A. An increase in the emission intensity of the GBA indicates higher atomizer temperatures. A two step current program was employed for all the data presented in this section. Figure 48 shows the variation of emission intensity

ATOMIZATION CURRENT, 15A





Table 12.	Experimental	Conditions	for	the	Investigation	of	Various
	Heating Tech	niques with	GBA		-		

Analysis Wavelength, Å	6500	
Gas Sheath Design	II	
Inner Flow Rate, 1/min, argon	2	
Outer Flow Rate, 1/min. argon	2	
Desolvation Current, A	1.5	
Desolvation time, sec	11	
Atomization Time, sec.	1.6	
Cooling Period, sec.	10	

as a function of the number of experiments and atomization current. Other experimental conditions, summarized in Table 12, were kept constant and no operator adjustments were made during the set of experiments. It can be seen that the atomizer temperature increases gradually. Furthermore, higher atomization currents (temperatures) shorten the atomizer lifetime. This type of temperature variation should be expected for other current-programmed heated nonflame atomizers.

Assuming that the atom population is observed in an area where the atomizer background emission variation does not influence the measurement process, the temperature variation can alter the optimized parameters in the system. The distribution of free atoms and the sheath gas flow pattern are influenced by temperature variations. The atom residence time would be shorter, which may require a faster data acquisition system. If the analyte is a volatile sample, gradual vaporization may occur during desolvation and/or ashing with a consequent decrease in the AA or AF signal.

3. Power Programming

In both current and voltage programmed heating, variations in temperature occur because only one electrical variable, either current or voltage, is being regulated during the various heating stages. Since it is practically impossible to prevent the physiochemical transformation of the atomizer, it is desirable to both monitor the current and voltage simultaneously. The product of the two parameters is the electrical power.

The instrumentation for power programming, shown in Figure 49,



The circuit diagram of the instrumentation for power programmed heating of nonflame atomizers. Figure 49.

consisted of two sensing devices for monitoring the current and the voltage, an analog multiplier (MC 1594, Schweber Electronics, Westbury, NY), a control operational amplifier, a power supply and power transistors. The current through the atomizer is sensed by the resistor R_{cs} and a corresponding voltage is produced at one multiplier input. The voltage across the atomizer is monitored by the instrumentation amplifier (EU-900-DA, Heath Co.) and its output is connected to the other multiplier input. The 1/10 voltage divider network provides a proper voltage level for the instrumentation amplifier. The control OA compares the multiplier output voltage with the reference voltage (power) and allows a current through the atomizer such that the multiplier output equals the reference voltage (power). As the atomizer resistance is increased because of the influence of factors such as vaporization, the voltage drop across the atomizer increases and the feedback loop allows less current through the atomizer. Consequently, the product iv, power, remains constant despite the fact that current and voltage vary from one experiment to another. As can be seen from Equation 60, the atomizer temperature is also proportional to the power dissipated in the atomizer. It is, therefore, expected that powerprogrammed heating should yield superior results in terms of reproducibility of atomization temperatures, atomizer lifetimes, and optimization of experimental parameters compared to either voltage or current regulation techniques.

The variation of the GBA temperature as a function of number of experiments, shown in Figure 50, was monitored by measuring the emission intensity of the GBA as described previously for the current programmed heating and under the same experimental conditions. Comparison of





Figures 48 and 50 indicates that the lifetime of the GBA has improved substantially with power programming. Furthermore, the rate of temperature increase is much lower than when the atomizer heating is current-programmed.

A more comprehensive comparison of the two techniques in terms of atomizer lifetime and variation of emission intensity is shown in Figure 51. The X axis is linear in terms of *current*. The corresponding atomization power and temperature are also shown on the same axis. The left hand Y axis represents the number of experiments performed with the same GBA. The right hand Y axis represents the ratio of the GBA emission intensity for the last and the first experiments in each set. Each data point is the average of three sets of experiments, and all data have been obtained under the experimental condition shown in Table 12. It can be seen that with power programming an average of 678 determinations can be performed at about 1485 °C before the braid deteriorates. This decreases to 162 determinations at 2250 °C. When current programming is utilized under the same conditions, the number of determinations decreases to 490 and 86, respectively. Furthermore, the emission intensity or the temperature variation is higher with the latter technique in all cases. With power programming, the ratio of the emission intensity does not change significantly from unity at higher temperatures. It should be noted that the emission intensity ratios shown in Figure 51 represent the ratio of the GBA emission in the last experiment of each set to the GBA emission in the first experiments of the same set. The ratio, therefore, indicates the maximum deviation from the initial temperature.

In practice, the GBA is replaced with a new braid as soon as braid

NUMBER OF EXPERIMENTS

Å

Å Å

ł



Figure 51. Influence of different heating methods and atomization parameters on the lifetime of the GBA and the GBA emission intensity variation.

deterioration begins by forming a hot spot. The hot spot usually forms at a point which is either located between the inner and the outer sheath gas flow or at the contact points of the atomizer and its holder.

4. Radiation Programming

According to Stefan's Law, the total rate of radiation emitted by a body increases with the 4th power of the Kelvin temperature. The radiation emitted by any electrically heated atomizer can be utilized for programmed heating. A radiation transducer such as a phototransistor can function as a radiation sensing device. In contrast to the current and power methods, where the atomizer temperature is a function of its dimensions as shown by Equation 60, the radiation technique does not suffer from this disadvantage as long as the radiation transducer monitors a fraction of the total emitted radiation. Furthermore, the variation of sheath gas flow rate and sheath gas type should not influence the atomizer temperature in the radiation technique. This is an important step in the separation of parameters in nonflame atomization.

When the current programming technique is employed for the carbon rod atomizer, it has been shown (284) that the rate of cooling water flow in the carbon rod holder influences the AA signal. Increasing the water flow has been shown to improve the sensitivity. This enhancement at higher water flow rates has been attributed to an improvement in the atomizer contact with its holder. When radiation programming is employed, these physical changes should not affect either the atomizer temperature or the AA and AF signals.

Since the nonflame atomizers emit visible radiation only during

the ashing and atomization periods, other programming methods should be utilized for heating the atomizers during the desolvation period where there is no visible radiation. One possible instrumentation system for multistep heating of filament atomizer is shown in Figure 52. The power control technique is used for the desolvation period and the radiation control method is employed during the ashing and atomization periods. A two channel analog switch (DG 152 AP, Siliconix **Incorporated**, Santa Clara, CA) provides the proper heating method during the various heating stages. One analog channel is active at all times. As soon as the desolvation period is complete, the computer supplies a +5V signal to the analog switch logic input for the entire length of the ashing and atomization stages. The analog switch disconnects the power sensing circuit from the control operational amplifier and simultaneously connects the radiation sensing circuit. The phototransistor (type TIL 64, Texas Instrument, Inc., Dallas, TX) monitors the atomizer radiation and produces a corresponding voltage, which is amplified and applied to the control operational amplifier input. The OA compares this voltage with the reference voltage (radiation) and allows a current through the atomizer such that the radiation circuit output voltage equals the reference output voltage.

When a furnace atomizer is used, the desolvation period is not often required because of the confined environment of the furnace. A two stage programmed heating technique is sufficient for the furnace atomizer to ash and atomize the sample. For furnaces, therefore, the radiation method can be employed alone. The required instrumentation is the same as that shown in Figure 25 if the instrumentation amplifier, the analog multiplier, and the analog switch are deleted from the





circuit.

In order to test the radiation method with filament atomizers such as the GBA and hot wire loops, the phototransistor was mounted in a holder which could be assembled in the lens holder. The X, Y, and Z positions of the phototransistor with respect to the atomizer could be changed by means of suitable adjustments. These controls could also function as an analog control over the radiation level (temperature). Because of the intense braid emission, light filters were employed to provide the proper emission intensity for the phototransistor.

The influence of radiation-programmed heating on the reproducibility of atomization temperature and the lifetime of the GBA was investigated using a procedure similar to that described previously for other heating techniques. The ratio of the emission intensities was about 1.3 at 1485 °C, but the ratio was unity at higher temperatures. Compared to other programmed heating methods, it can be argued that when the GBA is heated by the radiation method, excellent temperature reproducibility can be achieved.

With the radiation method, the GBA lifetime was found to be shorter than when it is heated by either the current or the power technique. The ratio of the average number of determinations using the power method to the average number of determinations performed with the radiation method varied between 2 to 4. This ratio decays as the atomizer temperature varies between 1485° to 2250 °C.

The shorter GBA lifetime when the radiation method is employed for heating can be explained in terms of the larger fraction of time that the atomizer spends in the final steady state temperature.

Figure 53 demonstrates the rate of radiation (temperature) increase for the three heating techniques. The atomization period is 1.56 sec. and the final GBA temperature is about 1650 °C. It can be noted that the steady state period is considerably longer in the radiation method. It is also interesting to examine the regulation of radiation (temperature) in the radiation technique. The duration of the steady state atomization period, t_s , as a function of atomization current is shown in Figure 54 for the three heating methods. It can be seen that t_s increases with increasing temperature in the current and power techniques, while for the radiation method the steady state periods decreases with increasing temperature.

Figure 55 shows the time duration, pre-steady state period, required before the GBA can achieve its final temperature. It can be noted from both Figures 54 and 55 that as far as the vaporization of the atomizer is concerned, the current and the power techniques should cause nearly the same amount of vaporization in a *single* experiment. When radiation programming is utilized, however, the atomizer spends a considerably longer time at its final temperature and a greater amount of vaporization should be expected. The atomizer lifetime will, therefore, be shorter compared to other techniques.

It should be noted that the length of the pre-steady state period is a function of maximum possible amount of current that a power supply can deliver. The larger the current, the shorter the pre-steady state period. Furthermore, since in the radiation methods, the atomizer achieves its final temperature at a higher rate, atomization of the analyte should be complete in a shorter atomization period. The



Figure 53. Intensity of GBA as a function of time and as a function of three programmed heating methods



Figure 54. Duration of the steady state period as a function of the atomization parameters for three programmed heating methods.

PRE-STEADY STATE PERIOD, t_{ps},msec.

> 410) 410) 410)

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life is t 5. p.j. 700. Can The Çe! re]0 ſ in ۴ę lifetime of the atomizer can be improved, if the atomization period is terminated shortly after the sample is completely atomized.

5. Temperature Programming

In all the heating methods discussed so far, an electrical or a physical parameter proportional to the atomizer temperature was monitored in the programmed heating. Direct temperature regulation can be performed if a thermocouple is employed as a sensing device. Thermocouples lend themselves conveniently to the measurement of temperature profiles in flame and nonflame atomizers, but empirical correction factors must be utilized to allow for radiation and conductance losses, and in any case they can only be used for low temperature flames. Catalytic heating on the wire surface may also cause errors in temperature measurements. For nonflame atomizers, where a violent reaction zone does not exist, a tungsten-rhenium thermocouple system may be used for temperatures from 1600 to 3000 °C. This thermocouple system has not been used in either flame or nonflame atomizers thus far, but it has been evaluated for use in aerospace and nuclear industries (285). The stability of a 0.51 mm diameter wire thermocouple in an induction-heated vacuum furnace has been shown to be ± 2 percent for 15 hours at 2600 °C (285).

When a nonflame atomizer is employed, even if an inert gas is used as a sheath gas, oxidation of the thermocouple can occur, and the thermocouple lifetime is expected to be shorter. Furthermore, attachment of any thermocouple to the atomizer presents a practical problem. Therefore, direct temperature measurement and regulation, despite its fundamental advantages, suffers from major practical

limitations.

The instrumentation required for direct temperature control is similar to that employed in the current technique except that the thermocouple output voltage is amplified and applied to the control operational amplifier instead of the voltage drop across the sensing resistor R_{cs} . However, in temperature measurements, the parameter of importance is the thermal time constant, τ_{th} , of the measuring device. For a very fine thermocouple, which is immersed in an environment of high thermal conductivity, τ_{th} is about 1 sec or less. For nonflame atomizers, the temperature continuously changes with time and it is necessary to measure the temperature instantaneously. However, when a thermocouple is subjected to a temperature step, its temperature approaches the steady state value after several time constants. The temperature growth, to a *first* approximation, is exponential for the thermocouple. The output voltage of the thermocouple V(t) as a function of time t is given by Equation 62

$$V(t) = V_0(1 - e^{-t/\tau th})$$
 (62)

where V_0 is the thermocouple output voltage corresponding to the steady state temperature. Differentiating Equation 62 with respect to time, gives Equation 63

$$\tau_{\text{th}} \frac{dV(t)}{dt} = V_0 e^{-t/\tau} th \qquad (63)$$

which when substituted in Equation 62 provides the following equation

$$V_{o} = V(t) + \tau_{th} \frac{dV(t)}{dt}$$
(64)
Theoretically, by combining the temperature at any instant V(t) with the rate of change of temperature, $\frac{dV(t)}{dt}$, the ultimate temperature, V_0 , can be measured instantaneously. When a nonflame atomizer is heated, it can be assumed that the atomizer is subjected to an infinite number of temperature steps before the final steady state temperature is achieved. The ultimate output of the thermocouple for *each step* V_{01} is given by an Equation similar to Equation 64. If the resulting ultimate thermocouple output for *each step* can be evaluated instantaneously, a stair case waveform pattern which is proportional to the heat input to the atomizer can be generated. This stair case function $\sum_{i=1}^{n} V_{0i}$ can be

utilized as the controlling variable for the input to the control operational amplifier. This also prevents temperature overshot which might occur because of the slow response of the thermocouple.

Evaluation of V_{oi} can be either performed by software or by analog circuitry. When a minicomputer is available, the thermocouple output voltage V(t) is amplified and applied to the ADC of the computer, where A-to-D conversions are made at a specified rate. A real-time calculation routine can be employed for evaluation of V_{oi} , and \sum V_{oi} is subsequently fed to the control operational amplifier. Since the computer should function as a digital integrator for the AA or AF signals, it may be advantageous that evaluation of V_{oi} be executed by an analog circuit. An analog circuit for the determination of V_{o} has recently been described (286). The limiting factor in the evaluation of V_{o} is the electronic time constant of the circuit. Calculation of ultimate thermocouple output for each temperature step can be executed in 0.1 msec when the thermocouple time constant τ_{th} is about 100 msec.

6. Influences of Flow Rates and Heating Methods on Atomizer Temperatures.

The influence of the flow rate on the platinum loop under currentprogrammed heating was discussed in Chapter V. It was noted that the atomizer temperature decreases with the flow rate. The decrease in temperature is due to convective and conductive losses by the atomizer. Since only ohmic heating was assumed in deriving Equation 61, the effect of these losses on atomizer temperature cannot be predicted from the equation.

Figure 56 demonstrates the influence of three heating methods and sheath gas flow rates on the atomization temperatures of a graphite braid and a Pt loop atomizer. The vertical markings around each experimental point indicate the standard deviation of 4 successive measurements. A ten second cooling period between measurements was used in all cases. The atomizer emission intensity was monitored instead of atomizer temperature in all cases. The GBA and Pt loop temperatures for an inner and outer sheath gas flow rate of 1 1/min were about 1650 and 1200 °C, respectively. When the radiation method is utilized, the atomizer temperature for both the GBA and the Pt loop does not change with the flow rate. Furthermore, the temperature measurements are reproducible. With both the power and the current techniques, the Pt loop temperature decreases with gas flow at nearly the same rate. Although the power technique compensates for resistance changes caused by the flow rate variation, it cannot correct for convective and conductive heat losses in the system.

When the current and power techniques are applied to the GBA,



Figure 56. Influence of flow rate and heating methods on the atomizer temperature.

the d crea in t tive tecr tig in at ta Ciji ra t va th t C t the atomizer temperature appears to pass through a minimum, but increases when the flow rate becomes greater than 6 1/min. The decline in temperature at lower flow rates can be explained in terms of convective and conductive losses by the GBA. The gas flow also causes a decrease in the electrical resistance of the atomizer holder. At higher flow rates, the holder resistance is further decreased and this allows more current through the *atomizer* with a subsequent increase in temperature. This should also explain the higher standard deviation at higher flow rates. Note that the precision of the atomizer temperature, provided by the power control technique, is superior to the current control method. In both cases, the precision at higher flow rates should be improved when the holder is kept at constant temperature either by water cooling or by allowing cooling periods of greater than 10 seconds.

For the Pt loop atomizer, the current control technique seems to provide higher reproducibility, in terms of atomization temperature, compared to the power control technique. No explanation of this variation in precision can be provided at this point.

D. AA and AF Analytical Applications of GBA

In order to evaluate the graphite braid atomizer for AA and AF spectrometry, analyses of a variety of elements were performed and analytical curves and detection limits were obtained. A brief matrix effect study was also conducted and the atomizer was used for the analysis of iron and copper in serum to illustrate its potential application for biological samples.

1. Analytical Curves and Detection Limits

Analytical data were obtained for 15 elements in aqueous solutions. The experimental conditions employed in the AF and AA analysis are summarized in Tables 13 and 14, respectively. The current programming method for heating the GBA was used in the early part of this work, but later the power control technique was used. Except for the atomization stage, where a rough optimization was performed, no other parameters in the system were optimized in obtaining these data. Analysis of Hg, Cd, Zn, and Pb were performed by atomic fluorescence using pulsed hollow cathode lamps or metal vapor discharge lamps as radiation sources. The description of the pulsed hollow cathode lamps and the computercontrolled system is given in the next chapter.

The detection limits for these elements are given in Table 15. All of the analytical curves showed good linearity over 1.5 - 3 orders of magnitude in concentration. A typical calibration curve for Cd is shown in Figure 57. The line parallel to the analytical line is an arbitrary unity slope line.

Atomic absorption data were obtained for Cd, Zn, Tl, Pb, Cu, Mn, Mg, Sn, Au, Ag, Fe, Ni, Co, and Pt using dc hollow cathode lamps as the radiation sources. The detection limits for these elements are summarized in Table 16. Analytical curves were obtained for all the above elements except Tl and Pt, and all working curves exhibited good linearity over 1.5 - 3 orders of magnitude. The working curves for Au, Fe, Ni, Ag, Zn, Co, and Mn are shown in Figures 58 to 64.

The relative standard deviation of measurements both in AA and AF was usually between 4-7% at concentration of one order of magnitude greater than the detection limits. Since all of the above data were

El ements	Vertical Distance Between Siit and Atomizer, cm	Sheath Gas Flow Rate &/min	Radiation Source (1),(2)	Radiation Source Current mA	Source on Time, msec	Heating Method	Sample Matrix	Drying Power, W (3)	Atomization Power, W	Atomization Temp. °C	Atomization Time, sec	Monochromator Slit Midth, mm	Analysis Navelength Ma	PM Tube (4),(5)
3	0.5	2	¶C ₩C	200	2	Power	cdCl,	ص	130	1650	-	2	228.8	SB
۲,	-	2	PHCL	426	4	Power	Zn(NO,),	01	130	1650	1.3	2	213.86	1P28
ĘH	-	2	PHCL	00 4	4	Power	Hg(NO ₂),	2	130	1650	1.3	2	253.65	1P28
£	0.2	-	PHCL	220	2	Current	Pb(NO ₁),	9	350	2500	0.42	-	283.31	SB
3	0.1	-	MVL	1200	•	Current	cdCl, '	m	95	1485	m	1.5	228.8	1P28
Zn	0.1	-	W	1200	ı	Current	Zn(N0 ₃)2	e	95	1485	3	1.5	213.86	1P28
	ICI - mulcard hol	Ter cathode 1												

Table 13. Experimental Parameters in the Study of Graphite Braid Atomizer in Atomic Fluorescence Spectrometry

PHCL: pulsed hollow cathode lamp
 PMU: metal vapor discharge lamp
 The drying time was 11 sec. in all experiments
 Sec solar blind photomultiplier
 PMT supply voltage was 800 V in all cases except for Pb analysis where it was 1000 V

Element	Hollow Cathode : Type	Radiation Source Current, mA	Heating Method	Sample Matrix	Drying Power, W	Drying Time, sec.	Atomization Power, W	Atomization Temp. °C	Atomization Time, sec.	Monochromator Slit Width, mm	Analysis Wavelength, mm	PM Tube
F	JA45570	10	Power	TINO	10	1	130	1650	-	0.4	276.79	SB
Αu	JA45433	10	Power	HAUCI	9	21	250	2250	1.6	0.2	242.8	SB
Ł	JA45472	15	Power	MnC1,	9	12	250	2250	1.6	0.05	279.48	SB
Fe	JA45455	15	Power	FeCl	9	21	250	2250	2	0.2	248.33	SB
Ņ	JA45433	10	Power	NICIS	9	21	250	2250	1.6	0.2	232.0	SB
Ag	JA45448	10	Power	AgNO3	9	11	152	1737	1.6	0.2	328.06	1P28
Zn	JA45459	01	Power	Zn(NO ₃),	15	1	130	1650	1.6	0.2	213.8	SB
3	JA45462	10	Power	cdC1,	9	16	130	1650	1.6	0.2	228.8	SB
S	JA45456	15	Power	cocl,	9	21	250	2250	1.6	0.2	240.73	SB
5	JA45451	15	Power	MgCl	9	=	350	2500	0.5	0.2	285.21	SB
Pt	JA22851	50	Power	H ₂ PtCl ₆	7	1	350	2500	m	0.03	265.95	SB
CL	JA45448	15	Current	cu(NO3),	e	Ξ	165	1900	m	0.2	324.75	1P28
PP	ML22927	80	Current	Pb(NO ₃)	e	11	165	1900	m	0.2	283.31	1P28
Sn	JA45463	10	Power	snc14	3	11	250	2250	1.6	.2	224.61	SB
The f	ollowing pa	rameters were	the same	for all ele	ments:							
>	ertical Dis	tance Between	i Atomizer	and Monochr	omator S]	it, cm.0.	-					
ω σ	Heath Gas F MT Supply V	'low Rate, 2/m 'oltage, V	ılı			80	٥ō					

Table 14. Experimental Parameters in the Study of Graphite Braid Atomizer in Atomic Absorption Spectrometry

•

Element	Radiation Source	Detection Limit, $\mu g/ml$
Cd	PHCL	0.002
Zn	PHCL	0.2
Hg	PHCL	0.01
РЬ	PHCL	0.005
Cd	MVL	0.005
Zn	MVL	0.005

.

 Table 15.
 GBA Detection Limits in Atomic Fluorescence

PHCL = pulsed hollow cathode lamp.

MVL = metal vapor discharge lamp.

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Elements	Detection Limit, µg/ml
Cd	0.0005
Zn	0.0005
TI	0.04
РЪ	0.01
Cu	0.01
Mn	0.006
Mg	0.002
Sn	0.1
Au	0.02
Ag	0.007
Fe	0.004
Ni	0.02
Со	0.004
Pt	0.9

Table 16. GBA Detection Limits in Atomic Absorption



Figure 57. Cadmium working curve (AF signal has arbitrary unit).



Figure 58. Gold working curve (AA signal has arbitrary unit).



Figure 59. Iron working curve (AA signal has arbitrary unit).



Figure 60. Nickel working curve (AA signal has arbitrary unit).















Figure 64. Manganese working curve (AA signal has arbitrary unit).

obtained without optimization of instrumental parameters, it can be expected that detection limits and the linear dynamic range can probably be improved substantially if the system is optimized as shown in Chapter V.

2. Matrix effect studies with the GBA

One of the major advantages of GBA over the filament-type atomizers is that when the sample is placed on the atomizer, it soaks down between the graphite fibers. Heating the fibers produces a furnacetype environment with a high surface area. Since the sample is trapped by the fibers, the diffusion rate of atomized particles should be influenced and this should decrease the amount of interference. Because of the high atomization efficiency of the GBA, most matrix effect interferences should not occur on the atomizer, but should be attributed to the cold environment above the filament atomizer. In other words, the lifetime of the free atoms decreases because of condensation of the analyte atoms on the interfering species.

The interferences caused by the samples matrix were studied for Fe, Ni, Mn and Cd for a variety of salts, and the results of these studies are shown in Table 17. The concentration of the analyte in all cases was 200 ppb and the interfering species were present at concentrations ten times that of the analyte. The interference studies were conducted for Fe, Ni, and Mn by AA and for Cd by AA and AF. Although no enhancement of the signal was observed, some suppression of the AA signal was encountered for Fe and Ni. Even for these elements, signal depressions smaller than 5 percent can be assumed to be insignificant. It is interesting that Al, which produces a considerable matrix interference in flames, has a negligible effect on the GBA results.

			Ana 1	yte	
Interferent	Salt	Fe	Ni	Mn	Cd
Al	A1C1 ₃	0	-2	0	0
Со	CoCl2	-10	0	0	0
Со	Co(N0 ₃) ₂	-10	0	0	0
Cu	Cu(N0 ₃) ₂	0	-2	0	0
Fe	FeC1 ₃	-	-3	-	-
Mg	MgC1 ₂	0	-5	0	0
Mn	MnC1 ₂	0	-2	-	0
Ni	NiCl2	0	-	0	0
Pb	Pb(N0 ₃) ₂	0	0	0	0
Zn	Zn(NO ₃) ₂	0	0	0	0
C1	HC1	0	0	0	0
N03-1	hno ₃	0	. 0	0	0

Table 17.	Percentage Depression Caused by	10-Fold	Amount of	f Matrix
	Ion on Analytical Signal			

3. Application of the GBA to Real Chemical Systems

Of the 37 analytically detectable elements present in the human body, 26 are metallic in nature, and many are present in trace concentrations. The significance of several of these metals in mediating biological processes has prompted investigation of their physiological values and variation of these values in pathological states. The ability of a nonflame atomizer to utilize samples in complex matrices is one of its greatest assets. In order to test the GBA in a practical analyses, copper and iron in serum samples were analyzed because of their clinical significance. Elevated copper levels, for example, have been reported for patients with rheumatoid arthritis (287).

When copper and iron are analyzed by flame spectroscopy, the serum matrix influences the results, probably because of changes in transport parameters. The transport is nearly 100% efficient in the nonflame atomizer and matrix effects are minimized when appropriate temperatures are used to desolvate, ash and atomize the sample.

Analysis of copper was conducted in two different serum matrices, while iron was analyzed in one serum matrix. Both elements were analyzed by atomic absorption. The first serum matrix (Moni-trol I, Scientific Products, Inc., Detroit, MI) was diluted ten-fold and then spiked with aqueous standard solutions of copper. A 2 μ l sample was placed on the GBA and a three step current programming method was employed to heat the GBA. The sample was dried for 10 seconds at 100 °C, ashed for 30 seconds at 500 °C and atomized at 1900 °C for 3 seconds. The standard addition analytical curve shown in Figure 65 demonstrates the excellent linearity in a complex matrix without any difficult sample preparation steps. It should be noticed that a rough



optimization for the ashing step was performed to obtain these data. The relative standard deviation ranged between 4% to 16% with a sample population of 3. Because of the relatively high volume requirements of the sample cups in the automated sampler, a syringe was used to transport the sample, and the high relative standard deviation of the individual points can be attributed to the difficulty of placing samples on the atomizer in a reproducible manner. A change in the sample cup design should allow analysis of μ l volumes with the automated sampler.

The second serum sample (lot No. CALC 102 A-2, DADE Division, American Hospital Supply Corp., Miami, FL) contained 220 and 204 $\mu q/100$ ml copper and iron respectively as reported by the supplier. These concentrations, however, are above the linear region of the copper and iron calibration curves. Several methods can be employed to obtain analytical curves that are linear to higher concentrations. The methods available included dilution of the sample with either deionized water or an organic solvent such as isooctane or methyisobutyl ketone; use of a smaller sample volume; increasing the vertical distance between the GBA and light beam from the hollow cathode lamp; and use of a less sensitive spectral line. Each method exhibits certain limitations or drawbacks. Dilution is time consuming and use of sample volumes smaller than about 0.2 ul increases the relative error of dispensation and the danger of non-representative sampling. Increasing the distance between the GBA and the light beam to about 10 mm is satisfactory for simple matrices, but there is the possibility of enhancing the chemical interferences with the complex serum matrix.

The method actually chosen was a combination of the above methods. In both cases, a sample volume of $l \mu l$ was used, and the vertical

distance between the GBA and the light beam was increased to 5 mm. The serum sample was also diluted 10-fold with deionized water. Although the 372 nm iron line has a sensitivity about one-fifth that of 248.3 nm line, the use of this line was discarded because of possible emission interference from the GBA.

Using the power technique for heating the GBA and the above conditions, analytical curves were linear to about 3 μ g/ml for aqueous standards of copper and iron. The concentrations of copper and iron were then obtained from the standard addition analytical curves under the conditions shown in Table 18. The analytical results are summarized in Table 19 and again indicate the excellent capability of the GBA to handle complex samples.

E. Conclusions

The graphite braid nonflame atomizer has been shown to be a medium power alternative to the more commonly used graphite rods and furnaces. In addition to the high operating temperature and other advantages of nonflame atomizers which are preserved, the graphite braid provides a furnace-type environment with uniform temperature throughout the GBA. The atomizer requires relatively low power and no cooling system is necessary. The good detection limits and precision suggest that the GBA should have widespread application in AA and AF spectrometry.

Five different methods of programmed heating of nonflame atomizers were also presented along with the required instrumentation for each technique. The method of programmed heating was shown to influence the atomizer lifetime, the time required for the atomizer to reach a

Table 18.	Experimental	Parameters	for Analysis	of Iron and	Copper with th	le GBA	
Element	Drying Temp. °C	Drying Time, sec	Ashing Temp. °C	Ashing Time, sec	Atomization Temp. °C	Atomization Time, sec	Cooling Period, sec
Fe	100	15	600	30	2250	3.0	25
Cu	100	10	500	25	1900	2.5	25

with	
Copper	
and	
Iron	
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lysis	
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19.	
Table	

Element	Supplier values, µg/100 ml.	GBA Results, µg/100 ml
je L	204	207±15.6
Сu	220	221±19.8

steady state temperature and the separation and optimization of atomization parameters. Power programmed heating provides the biggest improvement in terms of atomizer lifetime. The radiation method results in the best separation of atomization parameters.

VII. TIME-DIVISION MULTIPLEXED ATOMIC FLUORESCENCE SPECTROMETRY

A. Introduction

The possibility of eliminating the monochromator from an atomic fluorescence spectrometer would allow the construction of a multielement nondispersive instrument with only one detector. Unlike AE, or to a lesser extent AA, the system can be arranged so that only one fluorescent species is stimulated at any desired moment. Thus, only one set of suitably modulated atomic lines emerges from the vapor cell at any particular instant. In AE, the atomizer stimulates all elements in the atomic reservoir simultaneously and spacial isolation of the atomic lines is necessary. In AA spectrometry, a nondispersive system is not advantageous because the full radiation of all the emission lines from the source would strike the detector. Thus, the sensitivity would be greatly reduced if the nonresonance lines and the unwanted filler gas lines were not separated from the resonance lines by a monochromator.

Therefore, full utilization of all of the available signal is not possible in AE and AA. Furthermore, nondispersive atomic fluorescence spectrometry has many features which makes it extremely valuable for nearly simultaneous analysis. First, at low atomic concentrations, the intensity of the fluorescence radiation is proportional to the intensity of the excitation source. Second, since the fluorescence radiation is viewed at an angle with respect to the exciting radiation, the non-resonance lines from the source do not interfere. This

arrangement also allows simultaneous focusing of a number of radiation sources on the vapor cell. Third, provided that a low background atomizer is available, simultaneous collection of multiple lines for elements with a complex fluorescence spectrum and the greater energy throughout can provide higher signal-to-noise ratios than can be achieved when a monochromator is employed in the system. Fourth, the instrumentation can be simpler, less expensive and more rugged compared to other multielement techniques.

In this chapter a new automated multielement atomic fluorescence spectrometry which can determine the concentration of 4 to 8elements in a total analysis time of less than 3 seconds, is described. The system operates in the time-division multiplexed (TDM) mode with both flame and nonflame atomizers and employes a single channel detection system. The basic components of the automated AF spectrometer include a bank of pulsed hollow cathode lamps, a sheathed burner or nonflame atomizer, a solar blind PMT, a synchronous integrator and a minicomputer. The first part of this chapter describes the principle of TDM operation along with the integral components of the system. The influences of the burner parameters and radiation source characteristics are presented in the second part along with the analytical data obtained with flame and nonflame atomizers and with both dispersive and nondispersive systems. The spectrometer is employed for multielement analysis of Fe, Ni, Co, Mg, Hg, Cd, Zn, and Pb with flame and nonflame atomizers. The use of fiber optics for AA and AF multielement analysis is also discussed in this section.

B. Time-Division Multiplexed Atomic Fluorescence Spectrometer

1. Principles of Time-Division Multiplexing

Time-division multiplexing is a fairly common technique for the transmission of multiple channels of electrical information (288,289). A general 4-channel TDM system is illustrated in Figure 66a. The multiple channels of information are switched into a common transmission path by a multiplexer (selector switch) with each channel alloted a separate time slot. For analog electrical information sources, the multiplexing operation produces a transmitted signal that consists of interlaced pulse trains of identical repetition rate. Each pulse train is amplitude modulated by the sampled value of the information signal in one channel. Other pulse modulation schemes, such as pulse duration modulation and pulse code modulation can also be used, but pulse amplitude modulation is most common and easiest to implement. Figure 66b shows a typical waveform observed in the transmission path for a pulse amplitude modulation (PAM) scheme.

At the receiving end of the TDM system a demultiplexer switch, synchronized to the multiplexer switch, separates the signals and sends them to separate information receivers. When PAM is used, a low pass filter is generally employed at the information reception site to extract the information signal from the modulated pulse train.

TDM systems have several advantages when compared to the other common multiplex technique, the frequency-division multiplex (FDM) method. First, the instrumentation for a TDM system is normally much simpler than that for an FDM system (288). Second, crosstalk among





channels is usually rather easy to minimize with the TDM technique. The only requirement for negligible interchannel crosstalk is that the transmission system must have sufficient bandwidth and linearity in order to prevent the pulse waveforms from overlapping into adjacent time slots.

The major disadvantage of the TDM technique is that the information is transmitted sequentially rather than simultaneously as in FDM systems. However, the simplicity of recovering the individual information channels in a TDM system can often make it nearly as fast a transmission method as an FDM system.

2. Multichannel Atomic Fluorescence Spectrometry

For atomic fluorescence spectrometry, time-division multiplexing can be achieved in the optical domain by sequentially pulsing several hollow cathode lamps in a low duty cycle mode. Figure 67 shows a general block diagram of a computer-controlled, 4-channel, TDM atomic fluorescence spectrometer. Each hollow cathode lamp is focused on a flame or nonflame atomic vapor cell. The minicomputer controls the circuitry for pulsing each hollow cathode lamp so that the ON and OFF times of all lamps can be controlled by software for optimization purposes. If a nonflame atomizer is utilized, the computer also controls the programmed heating of the atomizer.

The fluorescent radiation from each element is transmitted through the same optical path, but separated in time. The optical signals thus appear as amplitude modulated, time-division multiplexed pulses of radiant energy. A solar blind photomultiplier tube (PMT) is used to transduce the radiant energy pulses into electrical current pulses.





An analog integrator, synchronized to the time slot of each channel under computer control, integrates and holds the PMT output from each fluorescence pulse. During the hold time of the integrator, an analogto-digital converter (ADC) produces a digital representation of the output of the integrator.

Demultiplexing of the information signals is accomplished by the minicomputer, which directs the ADC outputs for each information channel into separate locations in core memory. The cycle of multiplexing, transmission, transduction, and demultiplexing is then repeated for a preselected number of times (usually 20) to improve the signal-tonoise ratio in each information channel. With the present system 4 elements can readily be determined in less than 1 sec and 8 elements in less than 3 seconds with flame atomization.

3. Instrumentation

a. <u>Atomization Systems</u>. Because the system operates without wavelength dispersion, a low background atomizer is necessary. Flame and nonflame atomizers were employed throughout this work. A separated air-hydrogen flame was used with a burner system similar to that described originally by Larkins (48). The burner was modified (47) by Eugene Palermo in these laboratories, and consisted of two parallel stainless steel plates which could be mounted on a Jarrell Ash premixed burner. The top plate has two circular arrays of holes, and fuel, oxidizer and sample droplets pass through a hole in the bottom plate and up to the inner circular array. Argon sheath gas enters the bottom plate through tygon tubing and a channel, and passes through the outer circular arrays of holes in the top plate. With this design,

the sheath gas surrounds the flame without coming in direct contact with the fuel, oxidizer, or sample droplets.

The nonflame atomizers consisted of a 90% - 10% Pt - Rh wire loop and the graphite braid atomizer (GBA) described in Chapter VI. The atomizer was mounted slightly below the optical system as described in Chapter IV. For all the multielement studies, the atomizer was held in place by a holder from the bottom rather than from above to decrease scattered radiation. Gas sheath design II was also utilized throughout this work, and the Ar flow rate was kept constant at 2 1/min. A 4 µl sample was placed on the atomizer by a syringe or the automatic sampler. Since only aqueous samples were analyzed, a two-step heating program, using either current regulation or power regulation, was employed for heating the wire loop or the GBA.

b. <u>Radiation Source and Computer Interface</u>. For the atomic fluorescence measurements reported in this chapter, hollow cathode lamps operated in the pulsed mode were utilized. The radiation from each lamp was focused on the vapor cell by a one inch diameter planoconvex and biconvex quartz lens (Esco Optics Products, Oak Ridge, NJ). Four lenses were employed to focus the radiation of four HCL's on a common point. In order to perform a simultaneous or nearly simultaneous multielement analysis, all of the radiation sources must be operated at the same time. If a single channel detection system is to be employed, a mechanism of distinguishing the fluorescence signals of the various elements is required. This may be accomplished in one of two ways. The first method involves simultaneous modulation of radiation sources at different frequencies. The fluorescence intensities could be determined by transforming the amplitude-vs-time
spectrum to an amplitude-vs-frequency spectrum by the Fourier transformation technique. Another possibility is the TDM mode where all the radiation sources are operated at the same frequency, but out of phase. With a minicomputer, the latter method is more attractive for rapid multielement analysis.

The circuitry for pulsing the hollow cathode lamps was similar to that described earlier (47,241) except that the ON and OFF times of the lamps were controlled by the minicomputer. The circuit for operating four lamps in a pulsed mode is shown in Figure 68. An operational amplifier controls the voltage applied to the base of a driver transistor. A current booster amplifier (EU-900-CA, Heath Co.) was used in conjunction with the control OA when the operational amplifier was incapable of providing the required current. The feedback control for current regulation was obtained by connecting the feedback resistor, R_{f} , to the emitter of each transistor. The current through each lamp, i_1 , is given by the expression in Figure 68, and could be individually adjusted for each lamp by varying the corresponding input resistor, ${\sf R}_{\sf in}.$ The lamp current was experimentally monitored by measuring the voltage drop across the resistor R_s . The FET switches (8-bit analog switch, Model EU-900-JA, Heath, Co.) enable the power supply to be operated in an intermittent mode by switching the reference voltage, e_r , ON and OFF. The FET switch with the $\overline{A+B+C+D}$ control signal was used to ensure complete turn off of the radiation sources when they were not in operation.

The pulse width or ON time of each lamp was usually 2-10 msec, and it was controlled by the computer. This information was transferred through four channels by the computer interface shown in Figure



Figure 68. Circuit for pulsing four hollow cathode lamps in TDM mode.





69. The computer was programmed to provide input-output instructions 6311 to 6341 with a software selected time pattern. The Device Select signals 31 to 34 were connected to the Data Latch card inputs, and the corresponding Data Latch card outputs provided ON signals for the radiation source FET switches A, B, C, And D and the integrator, to be described later. The input-output instruction 6151 was also utilized to turn the ON lamp OFF.

In order to transfer this information, the Latch card required two gating signals. The Device Select signals (31-34) were also connected to OR gate 1 and its output along with Device Select 15 was sent to the OR gate 2. The output of OR gate 2, the IOP1 were utilized as the gating signals for the Data Latch card. This arrangement provided great versatility in optimizing the ON and OFF times, which was particularly important when measuring transient signals from nonflame atomizers. For both flame and nonflame atomization a duty cycle of 1/16 was utilized. The ON times of the lamps were 2-10 msec for both systems. These times were often varied to account for different atomization rates for different elements with nonflame atomizers. The lamps were operated only during the atomization period. The delay time between pulses for successive lamps was usually three times the ON time. A typical sequencing diagram for a 4-channel system is shown in Figure 70.

c. <u>Detection System and Computer Interface</u>. In order to detect the fluorescence radiance, a R166 solar blind photomultiplier (Hamamatsu Corp., Lake Success, NY) was utilized as the radiation transducer. The phototube assembly was mounted directly in front of the vapor cell at an angle of 90° with respect to the radiation sources. The PMT



Figure 70. Cycle time of four pulsed HCL's in the TDM mode.

was also connected to a photomultiplier power supply (Model EU-24A, Heath Co.). The phototube output current was converted to a voltage by a Keithley Model 427 current amplifier.

In order to average the AF information present during each time slot, an integrator operated in synchronism with the firing of the hollow cathode lamp was employed. The integrator and its computer interface are shown in Figure 71. The output of the current-to-voltage converter was connected through a FET switch to the OA voltage integrator. A FET switch was also employed to discharge the capacitor in the integrator feedback loop.

The timing pulses from the computer, which cause each lamp to turn ON, also control the FET switch at the input of the integrator. The sequence of operation for one cycle is shown in Figure 72. When the first lamp is turned ON, the integrator is also turned ON for a preset time. The lamp is then turned OFF by a command from the computer, and the integrator input is opened, which causes the integrated signal to be held for a period twice the lamp ON time. During the integrator hold time, the ADC is enabled, and the resulting digital signal is stored in one location in the core memory. The integration capacitor is then discharged, and a program-controlled delay time equal to the lamp ON time is begun. Then lamp 2 and the integrator are turned ON, and the digitized signal for the second element is stored in a second location in core memory. The above process is repeated for the remaining lamps, which ends the first data cycle. Thus, for a 4-channel system, the result of one cycle is the storage of 4 digital representations of the AF information in separate core memory locations. The process is then repeated for a preset number of cycles (usually 20),





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which represents one experiment. The computer then enters an integration routine and the integrated AF signal for each lamp is printed on the teletype. Under program control the entire process can be repeated for a preset number of experiments, after which average values and standard deviations are calculated. In the case of nonflame atomization, each experiment corresponds to a repetition of the processes of sample deposition on the atomizer, desolvation, atomization and acquisition of the AF information.

d. <u>Sequential, Dispersive AF system</u>. For comparison of the nondispersive, TDM AF system to a sequentially-operated dispersive AF system, a monochromator (Model EU-700, Heath Co.) was inserted into the system, and the software was modified to allow sequential pulsing of the hollow cathode lamps. No change in the pulsing circuitry hardware or the integrator was required. One hollow cathode was pulsed for a preset number of cycles, the monochromator was scanned to a new wavelength, the next lamp pulsed for a preset number of cycles, etc. It should be noted that with the TDM system, the total analysis time for N elements is reduced by a factor of \approx 1/N compared to the sequential system because of the interlacing of pulses from other lamps during the OFF time of any one lamp. The sequential method, however, allows the optimization of parameters between the determination of each element.

e. <u>General Software Description</u>. The software was written in assembly language (Macro-8), and it is assumed that the fixed volume sampler is utilized in conjunction with a nonflame atomizer. When a flame atomizer is employed, the sample delivery, the desolvation

and ashing stages are deleted in the initialization step. The lamps were operated only during the atomization step.

The length of the atomization period is determined by the lamp ON time, t_{ON} , the duty cycle, d_c and the number of data points (cycles) d_p requested as shown by Equation 65.

Atomization period =
$$t_{ON} \frac{1}{d_c} \cdot d_p$$
 (65)

For example, for a lamp ON time of 5 msec and a duty cycle of 1/16, the atomization period would be 1.44 sec if 18 data points are obtained for each lamp.

When a nonflame atomizer is utilized, because of the transient nature of the signal, the digital data should contain as much of the relevent information in the original signal as practicable. Whatever definition of information is used, if the digital data can be converted back into an analog signal that can be exactly superimposed on the original signal, then the digitized signal is an accurate representation of the original signal. Any difference between the two signals may be called digitization error. For instance, in order to have an error of 0.01% in the peak height measurement, 630 and 11 data points are required for representation of a Lorentzian and a Gaussian signal, respectively (290). For single element analysis, the nonflame transient signal is approximately Gaussian in shape. If multielement analyses of mixtures containing low boiling points and high boiling point elements are to be performed, it should be expected that the signal from the low boiling point elements would exhibit more of a Lorentzian than a Gaussian shape. In order to keep the atomization period constant and at the same time minimize

the digitization error, t_{ON} can be decreased. For example, for a t_{ON} of 2 msec, 45 points could be obtained to allow a 1.44 sec atomization period. Optimization of the lamp ON time is not required for a flame atomizer, because of the continuous nature of the signal.

After the data acquisition is complete, the atomizer is shut off and the integrated signal for each element is printed on the teletype. The program then enters a display routine, and the AF signal corresponding to the first hollow cathode lamp is displayed on an oscilloscope for visual observation. Under keyboard control the data for the other three elements can also be displayed.

The actual time, relative to the start of atomization, that the atomic vapor for each element is in the observation window varies according to the boiling point of the element. In the analysis of a mixture containing Hg, Cd, Zn, and Pb, the AF signals appeared in time as the elements are arranged. However, there was overlap of the peaks which would rule out the possibility of sequential operation.

The display routine can be ended by typing the character "R" and the program starts a new experiment. After the preselected number of experiments is completed, the average, the standard deviation and the percent relative standard deviation are printed on the teletype. The program then enters the Optimization or the Normal submode as described in Chapter IV.

C. Analytical Results

1. Burner Parameters

Among the parameters optimized in flame studies were the position



Figure 68. Circuit for pulsing four hollow cathode lamps in TDM mode.





69. The computer was programmed to provide input-output instructions 6311 to 6341 with a software selected time pattern. The Device Select signals 31 to 34 were connected to the Data Latch card inputs, and the corresponding Data Latch card outputs provided ON signals for the radiation source FET switches A, B, C, And D and the integrator, to be described later. The input-output instruction 6151 was also utilized to turn the ON lamp OFF.

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C. Analytical Results

1. Burner Parameters

Among the parameters optimized in flame studies were the position

of the burner with respect to the observation window, and the flow rate of the sheath gas in both dispersive and nondispersive systems. Burner position profiles obtained in the dispersive mode dictated that the burner should be placed as close to the observation window as possible for the maximum AF signal. However, in the nondispersive mode, the burner should be positioned as far away from the observation window as possible to reduce flame background. Thus for nondispersive operation, a compromise has to be reached to obtain high signal-tonoise ratios. The burner was positioned at 2 and 5.25 inches below the observation window in the dispersive and nondispersive modes, respectively.

In order to determine the influence of sheath gas flow rate on the fluorescence intensity and background signals, flow rate profiles were obtained with the optimum burner position. The argon flow rate profiles for Ni, Mg, Co, and Fe are shown in Figure 73 and 74. The signal-to-noise ratio and the fluorescence intensity initially increase as the flow rate increases. This is due to the fact that the sheath gas renders the concentration of atoms more uniform, reduces the quenching effects of atmospheric nitrogen, and reduces the flame background by separating the flame into its primary and secondary zones. Furthermore, the atomization efficiency should also improve because the sheath gas reduces the diffusion of atmospheric oxygen into the flame and subsequent oxide formation. As the flow rate increases further, the flame temperature decreases and the fluorescence intensity declines. The optimum flow rate was taken at 15 1/min for Mg and 20 1/min for Ni, Co and Fe.

Flow rate profiles were also obtained in the nondispersive mode.





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Figure 74. Cobalt and Iron fluorescence intensity (arbitrary unit) as a function of argon flow rate.

However, measurements could not be made at low flow rates, because the flame was not effectively separated, and hence the flame background was too great. An argon flow rate of 35 l/min was utilized for multi-element analysis.

2. Pulsed Source Characteristic

One of the advantages of using pulsed hollow cathode sources is that the increase in current during the ON time is accompanied by a corresponding increase in the emission intensity, while the average current over a full cycle is still maintained at a safe operating level. The exact relationship between the intensity, I, and the current, i, has been given by L'vov (9)

$$I = a i^{n}$$
(66)

where a and n are specific constants for each combination of cathode material and filler gas, respectively. If self-absorption occurs in a lamp, there will be a deviation in the relationship between I and i, which will appear as a deflection of the slope toward the horizontal axis in a plot of Log I vs Log i. Once n (i.e., the slope of the line) for a lamp has been calculated, the gain in intensity, for the same average lamp current, may be determined from the following equation

$$\frac{I_{pulsed}}{I_{dc}} = \left(\frac{i_{pulsed}}{i_{dc}}\right)^n$$
(67)

For the experimental data presented, peak currents of normally 200 to 300 mA were employed. Since the duty cycle was 1/16, the corresponding mean currents were 12 to 18 mA. Since the atomic fluorescence sensitivity and the detection limit are proportional to the intensity of the source, maximum source current should be used without arriving at the point of self-reversal. The maximum current at which lamps can be operated was determined by monitoring the current through the resistor R_s on an oscilloscope. As long as the lamp is not overloaded, the lamp current follows the shape of the square pulse which has been applied from the computer. An overloading of the lamp appears as a distortion of the square shape of the pulse during its last part.

The gain in intensity shows a definite dependence on the type of lamp and filler gas. The gain ranged between 12 to more than 200 as reported by Cordos and Malmstadt (240). This is, however, achieved at the expense of the dispersion of radiation as we have noticed in our laboratories. Since the radiation is dispersed, it is not possible to focus the radiation on the vapor cell to take the full advantage of all the available radiation. Dispersion of radiation results in AF detection limits which are not as low as predicted by the gain in intensity. When the lamp ON time is decreased, the problem is minimized, however. With the present source power supply, it was not possible to achieve lamp ON times shorter than 2 msec.

The effect of pulse width on lamp intensity was also investigated for Hg, Cd, Zn, Mg, Ni, Co, Pb, and Fe lamps. Pulse widths of 1 to 5 msec were employed, and results for a Zn lamp are listed in Table 20. Except for a pulse width of 1 msec, the intensity appears to be independent of the lamp ON time. Similar results were obtained for other lamps. The stability of the lamp radiances was determined by introducing a metal cylinder between the sources and the detection system to produce a scattered light signal. For a pulse width of 5

ON Time	Relative Intensity, Arbitrary Units ^a	
l msec	200	
2 msec	245	
3 msec	265	
4 msec	265	
5 msec	274	

Table 20. Relative Lamp Intensity as a Function of ON Time

^aZn hollow cathode lamp.

msec, a duty cycle of 1/16, and 20 total pulses, the relative standard deviations of the scattering signals ranged from 0.67 to 0.85%.

3. Flame Analytical Results

In order to test the computer-controlled system, the analysis of mercury and cadmium was performed, and the detection limits obtained with this system were found identical to those obtained with a hardware-controlled system designed in these laboratories (47). Detection limits and working curve were then obtained for Mg, Ni, Co and Fe. The calibration curves were linear over 1.5 orders of magnitude and all showed a slope of unity. Table 21 summarizes the detection limits obtained with the flame atomizer in the sequential, dispersive mode. Similar results were obtained for TDM operation. Extreme care should be exercised in focusing the sources on the atomizer in multielement analysis. Inferior results are obtained if the radiance reaching the vapor cell is smaller than the radiance in sequential analysis.

The detection limits obtained for Co, Ni and Fe are not unreasonable considering that these are high boiling point elements, 2900 °C, 2732 °C, and 3000 °C respectively. However, the detection limit for Mg appears quite high considering the fact that its boiling point is only 1107 °C. The discrepancy may be explained by the fact that the gain in intensity of the Mg hollow cathode lamp is only 12 when operated at a peak current of 220 mA compared to dc operation as reported by Cordos and Malmstadt (240). This lack of intensity increase is probably due to the ease of self-reversal in the case of Mg.

The solutions that were used for the working curves were composed of mixtures of the four elements. To determine if any interelement

Elements	Peak Current	Optimum Ar Flow Rate (l/min)	Detection Limit (ppm)
Hg	265	0	2
Cd	200	20	.02
Mg	200	15	1
Ni	275	20	10
Co	290	20	2
Fe	330	20	20

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Table 21.	Detection Limits Obtained with Computer-Controlled Multi-
	element Flame A.F.S. System.

effects were present, the fluorescent signals obtained for the mixture solutions were compared to fluorescence signals obtained for solutions containing only the single element. All solutions were made from the chloride salts. The data obtained are presented in Table 22. As can be seen only slight interelement effects were obtained for these elements.

4. Nonflame Analytical Results

With a 90% Pt - 10% Rh wire loop atomizer wirking curves were determined for four elements, Cd, Hg, Zn, and Pb in the dispersive mode. For these working curves, the atomizer was positioned directly below the entrance slit of the monochromator, and the radiation from the source was focused directly above the atomizer. The detection limits obtained with the loop atomizer are shown in Table 23. For Cd and Hg, the detection limits were lower than those obtained with the flame system. This decrease in detection limit is due to the fact that background noise from the nonflame atomizer is less than the background noise from the flame atomizer. Because the Pt loop temperature cannot exceed 1500 °C, the detection limit for Pb is high.

Detection limits were then obtained for Cd, Hg and Zn with the nonflame, TDM, AF system. These detection limits are also shown in Table 23. The detection limits for Cd and Hg are comparable to those obtained in the dispersive mode. However, the Zn detection limit is higher. This increase is due to the fact that the atomizer position had to be lowered relative to the observation window because of the radiation from the atomizer and because of scattering of the primary sources caused by the dispersion of radiation. As the loop is lowered,

Element	Concentration (ppm)	Average A.F. Signal, Arbitrary Units	
		Mixture	Single
Ni	50	123	130
	200	326	287
	1000	662	657
Со	50	311	419
	200	600	718
	1000	1402	1317
Fe	50	400	386
	200	719	600
	1000	1728	1540
Mg	50	550	403
	200	1271	1232
	1000	2230	2557

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Table 22. Fluorescence Signals Obtained with Multielement and Single Element Solutions

Element	Atomizer	Sequential Dispersive µg/ml.	TDM Nondispersive µg/ml.
Cd	Pt loop	0.008	0.005
Hg	Pt loop	0.5	0.5
Zn	Pt loop	0.1	2.0
РЬ	Pt loop	50	
Cd	GBA	0.002	
Hg	GBA	0.01	
Zn	GBA	0.2	
РЬ	GBA	0.005	

1 × 2

Table 23. Detection Limits Obtained with Platinum Loop and Graphite Braid Atomizer

the temperature decreases drastically. Hence the atomic population decreases. The nonflame TDM system may be used for multielement analysis. However, the detection limits obtained for certain elements will be inferior to those obtained for the single element dispersive case.

Analytical results were also obtained with the GBA in the dispersive mode under the experimental conditions described in Chapter VI. It can be seen from Table 23 that the GBA detection limits are at least equivalent or superior to those obtained with the Pt loop atomizer.

5. <u>Application of Fiber Optics in Atomic Absorption and Atomic Fluores</u>cence Spectrometer

In order to perform simultaneous or near simultaneous analysis, it is necessary that the radiation from various radiation sources be focused to a common point on the vapor cell. As the number of lamps is increased, the spatial problem becomes more and more critical. Even for four HCL's, we encountered extreme difficulty in focusing the radiation. This was particularly true when filament-type nonflame atomizers were utilized as atomization devices. In contrast to the flame where the atomic population is distributed over a larger cross sectional area, the atom population in nonflame filament atomizers is concentrated in a small area. Focusing of radiation sources is therefore more critical with nonflame devices.

Fiber optics may be utilized in reducing the spatial problem. It has been used in atomic emission (291) for simultaneous measurement of two adjacent wavelengths, but no application of fiber optics have been reported for simultaneous analyses, by either AA or AF. We have

designed a four branch light guide for multielement analyses by AA and AF. The four branches are combined at one end. The radiation from four different radiation sources is focused on four separate branches, 6.3 mm in diameter each, of the light guide and is directed to a single beam spectrometer. The total length of the light guide is about 40 cm, with the common end having a diameter of 1.27 cm. This type of arrangement in conjunction with pulsed hollow cathodes allows sequential multielement analysis by AA if a rapid scanning monochromator is available.

For AF analysis, where the dispersing element can be eliminated, multielement analysis can be performed in the TDM mode. The only disadvantage of fiber optics is its low radiation transmission. Our initial results (292) indicate that the transmission is about 10 percent of the incident radiation. This system is currently under more extensive investigation in our laboratories.

VIII. PROSPECTIVES

A. Improvements in Instrumentation

Various improvements can be made in the sample handling, atomization, and excitation systems. The second automatic sampler should be made faster and more versatile in terms of the number of samples which it can handle and the capacity of the sample cups. Without major modifications, the sample turntable can be replaced with one that has 20 sample cups instead of 6. The sample cups would, therefore, have a smaller sample capacity which is valuable for clinical analysis. The sample turntable motor, however, should be replaced with a stepping motor to allow more accurate positioning of the sample cups.

For complete automation, the variation of the sheath gas flow rates and the three dimensional positioning of the atomizer should also be automated. One possible method for electronic flow measurement and control is to heat the gas stream uniformly, before it reaches the atomization chamber, by a heater coil and to monitor the gas flow at upstream and downstream positions by two sensors. When there is no gas flow, a balanced bridge circuit is established to provide a zero flow output signal. As the gas flows, a temperature difference is created between the upstream and downstream sensors, which is related to the mass flow rate. The resulting signal can be applied to the input of an instrumentation amplifier, and the amplifier can generate a dc voltage output which is related to the mass flow rate. The output

signal may be utilized to drive a motor for flow adjustments.

For accurate atom profile studies, automation of the three dimensional positioning of the atomizer is desirable. This can be accomplished by a combination of stepping motors which are operated under computer control.

Various improvements can also be made in the radiation sources. For pulsed operation of HCL's, a new power supply should be designed which allows pulsing of the lamps on the μ sec time scale and which can provide larger output currents. The shorter the lamp ON time, the easier the focusing of the radiation sources. Furthermore, we predict that operation in μ sec time intervals should diminish the possible self-absorption problem and should improve the spectral line intensity.

As far as the dimensions of the HCL's are concerned, attention should be directed in miniaturizing these sources for multielement analysis. Fiber optics can also be utilized where spatial problems exist in focusing the radiation sources on the vapor cell.

B. Future Application of the GBA

It is obvious from the work presented here that the GBA should prove to be an excellent nonflame atomizer for the analysis of solutions. The low power requirements of the GBA and its high atomization efficiency suggest that the GBA should have widespread application in AA and AF spectrometry. It is interesting to note that the cost of each GBA is less than 1 cent. The GBA cost is so small that it is incomparable to other commercially available atomizers. The atomizer should be tested for more elements, and its capabilities in real
sample analysis should be further demonstrated. A complete matrix
effect study should also be undertaken. The matrix effects, if present,
can be minimized by surrounding the atomizer with a H₂ diffusion
flame.

For GBA's of about 0.5 mm in diameter, it was shown in Chapter VI that only 120 Ware required to reach atomization temperatures of 2500 °C. The capability of this small diameter graphite filament atomizer (GFA) should also be studied. For direct analysis of solids, the GBA can be replaced with a graphite tape atomizer (GTA) of a width of about 1 cm. Solid samples can be directly placed on the center of the GTA. This atomizer should also be valuable for the analysis of solutions.

The GBA, GFA, and GTA can also be utilized as sample vaporization sources for a miniature spark and an induction - coupled plasma. Because of the porous nature of these atomizers, they have applications in gas and liquid chromatography as well as in electrochemistry.

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