#### ABSTRACT

## AN EXPERIMENTAL AND THEORETICAL INVESTIGATION INTO NONFLAME ATOMIZATION

By

Scott Roy Goode

The widespread application of nonflame atomization to routine atomic absorption (AA) or atomic fluorescence (AF) analyses is a relatively recent phenomenon. Even though nonflame AA or AF analysis is not as precise or as easy to perform as is flame AA or AF analysis, the high sensitivity achieved by nonflame atomization methods makes it a valuable tool. An experimental and theoretical investigation was performed to see if the major sources of imprecision could first be isolated and then minimized.

The design of a completely automated nonflame atomic fluorescence spectrometer is described. The system was used to investigate the phenomena occurring at a very simple nonflame atomizer, an electrically heated platinum loop atomizer. The extent of automation made it feasible to perform tens of thousands of analyses in order to characterize fully the effects of the instrumental parameters on the final readout.

A study of the events occurring at the atomizer is described. The fundamental study of atomization and the experimental study of the effects of the instrumental parameters on the readout were used to fully optimize the nonflame spectrometer. Data taken by the fully optimized system are presented and critically analyzed.

The results of the study of atomization were used to design a new spectrometer which uses a braid of graphite fibers as an atomizer. This new atomizer is characterized and analytical data are presented to demonstrate the overall utility of the graphite braid atomizer.

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### A DISSERTATION

Submitted to Michigan State University in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

To my Mother and Father

They understand

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iii

### TABLE OF CONTENTS

P	age
LIST OF TABLES.	viii
LIST OF FIGURES	ix
I. INTRODUCTION	1
A. Flame Atomization	3
B. Nonflame Atomization	5
C. Filament Atomizers	7
II. HISTORICAL	8
A. Furnace Atomizers.	9
1. The L'voy Furnace	9
2. The Massman Furnace	12
3. The Woodriff Furnace	13
4. Other Furnaces	14
B. Filament Atomizers	20
1. The West Atomizer	20
2. Commercial Graphite Filament Atomizers	27
3. Other Graphite Filament Atomizers	29
4. Metal Filament Atomizers	31
C. Conclusions	34
III. THEORETICAL DESCRIPTION OF ATOMIC FLUORESCENCE FROM A NONFLAME ATOMIZER	35
A. The Experimental Observation of Atomic Fluorescence	36
B. Expressions Describing the Line Radiance of Atomic Fluorescence	37
1. Atomic Absorption with a Continuum Source	37
2. Atomic Absorption with a Line Source	40
3. Radiance Expressions for Atomic Fluorescence	41

	С.	Characterization of the Atom Population of a Nonflame Atomizer
		1. Time Dependence of Atom Population 45
		2. Time Integrated Atom Population Expressions
	D.	Time Dependence of Temperature
		1. Heat Sources and Heat Sinks in a Filament
		2. Zero Order Perturbation Terms
		3. First Order Perturbation Terms
	-	Nodified Fatimates of Atom Desulation 50
	E.	Modified Estimates of Atom Population 59
IV.	INSTR	UMENTATION
	Α.	Design Criteria
		1. The Atomizer 65
		2. The Spectrometer 67
	Β.	Sequence of Events
	С.	Sampling to the Atomizer
	D.	Electrical Control of Atomizer Temperature 74
	E.	Optical Design
		I. Primary Excitation Sources for Atomic Fluorescence
		2. The Atomizer
	F.	Photocurrent Integration
		1. Analog Integration
		2. Digital Integration
		3. Photon Counting
	ODTIM	
۷.	UPTIM	IZATION OF INSTRUMENTAL PARAMETERS
	А.	optimization of Signal-to-Noise Ratio 98
	Β.	Experimental 100
		1. Instrumentation 100
		2. Procedure
	С.	Experimental Variables 104
		1 Sample Size 106

		2. Sheath Gas Flow Rate 10	7
		3. Power Applied to Atomizer	0
		4. Integration Parameters 11	2
	D.	Interaction of Variables 11	4
	Ε.	Analytical Results	9
		<b>1. Stability</b> 11	9
		2. Calibration Plot 11	9
VI.	CHARA	CTERIZATION OF THE ATOMIZATION PROCESS 12	8
	Α.	Characterization of the Platinum Filament	8
		1. Evaporation of the Filament Material 12	8
		2. Changes in the Physicochemical Properties of the Platinum Filament Atomizer	n
	<b>D</b>		, ,
	В.	Events at the Atomizer Surface	2
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 2
		3. Time Resolution of Events Prior to	5
		Atomization	4
		4. Post Atomization Events 13	7
VII.	APPLI	CATION OF EXPERIMENTAL RESULTS 14	4
	Α.	Optical Considerations 14	5
		1. The Monochromator 14	5
		2. Nondispersive Optical Systems 154	4
	Β.	Photocurrent Integration 15	5
	С.	The Sampling System	6
	D.	Temperature Programming 15	6
	Ε.	Analytical Applications	0
		1. Optimization for Selectivity 16	0
		2. Calibration Plot 16	1
	F.	The Graphite Braid Atomizer 16	4
		1. Advantages 16	4
		2. Optimization of the Graphite Braid Atomizer	6

		3.	Ana	lyt	ica	1	App	oli	ca	ti	on	S		•	•	•	•	•	•	•	•	168
VIIL	SUMMAR	Υ.	••	•	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	173
LIST	OF REF	EREN	CES	•	• •	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	175
VITA		• •		•		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	180

### LIST OF TABLES

Table			Page
1.	Comparison of Methods of Peak Integration	•	93
2.	Optimum Spectrometer Parameters	•	106
3.	Interaction of Instrumental Parameters	•	117
4.	Optimum Platinum Loop Atomizer Parameters	•	118
5.	Spatial and Temporal Atom Distribution as a Function of Time	•	139
6.	Experimental Conditions for the Determination of Stray Radiant Energy	•	153
7.	Matrix Effects of Platinum Loop Atomization	•	162
8.	The Signal at the Limit of Detection	•	170
9.	Effects of Atomization Temperature on Cadmium in Severa Matrices	ı	172

### LIST OF FIGURES

Figur	e					Page
1.	The Atomic Vapor Cell	•	•	•	•	38
2.	Growth Curves for Atomic Fluorescence	•	•	•	•	44
3.	Dependence of Atom Concentration on Residence Tim Observation Cell	ei •	n •	•	•	47
4.	Dependence of Atom Concentration on Atomization T	ime	2	•	•	49
5.	Comparison of Theoretical Prediction of Atom Conc with Experiment	ent •	rat	ior	ו י	61
6.	Comparison of Theoretical Predictions of L'vov (8 this Work	6)	anc •	1	•	62
7.	Sample Delivery System	•	•	•	•	73
8.	Block Diagram of Triac Power Control Circuit .	•	•	•	•	77
9.	Circuit Diagram of Triac Power Control Circuit	•	•	•	•	78
10.	Atomizer Assembly	•	•	•	•	82
11.	Optical Diagram of the Atomizer Assembly	•	•	•	•	84
12.	Fixed Time Integration	•	•	•	•	87
13.	Digitization Circuit	•	•	•	•	89
14.	Photon Counting Circuit	•	•	•	•	94
15.	Photon Count Rate as a Function of Direct Current		•	•	•	97
16.	Block Diagram of Automated Nonflame Spectrometer	•	•	•	•	101
17.	Circuit Diagram of Spectrometer Control System	•	•	•	•	103
18.	Dependence of Precision on Sheath Gas Flow Rate	•	•	•	•	109
19.	Dependence of Integrated Signal on Power Applied Atomizer	to	the	2	•	111

# Figure

20.	Dependence of Precision on Power Applied to the Atomizer	113
21.	Dependence of Precision on Integrator Parameters	115
22.	Long Term Stability of Nonflame Spectrometer	120
23.	Integrated Fluorescence as a Function of Cadmium Concentration Under Fully Optimized Conditions	122
24.	Peak Atomic Fluorescence as a Function of Cadmium Concentration Under Fully Optimized Conditions	124
25.	The Signal at the Limit of Detection	125
26.	Photon Count Rate as a Function of Cadmium Concentration.	126
27.	Time Resolution of Events at the Platinum Loop Atomizer .	127
28.	Peak Atom Population Profiles	143
29.	The Slit Transfer Function	147
30.	Comparison of the Varying Slit Width and Limiting Absorbance Method of Determining SRE	152
31.	Dependence of Integrated Fluorescence on Ashing Temperature	159
32.	Calibration Plot for Cadmium in Several Matrices Obtained with Temperature Programmed Atomization	163
33.	Dependence of Integrated Fluorescence on Atomization Temperature of GBA	167
34.	Calibration Plot; GBA Fully Optimized	169

#### I. INTRODUCTION

One of the largest problems facing the analytical chemist is in the nature of sample treatment prior to analysis. The ideal elemental analysis is independent of the history of the sample. The results of a cadmium analysis, for example, should not be altered if the cadmium is in an aqueous solution, organic solvent, or protein matrix. One method of eliminating matrix effects is to break the compound into its constituent atoms, and then to perform the analytical measurement on the atomic vapor. The atoms, once produced, exhibit no memory effect. It is precisely this advantage which makes atomic spectrometry such a powerful analytical technique.

The three atomic spectrometric techniques of atomic emission, atomic absorption, and atomic fluorescence all require the production of an atomic vapor from the analytical sample. The average analytical sample must undergo a series of steps before it is atomized, and these steps are the same in all three atomic spectrometric techniques. First, the solvent must be stripped from the analyte (assuming it is in a solution) to form crystals of a salt of the analyte. Second, the crystals must be vaporized, and third, the molecular vapor must be broken into its constituent atoms.

If the atomic vapor is sent into a heated cell, such as a flame, some of the atoms will be excited, in accordance with the Boltzmann distribution. When the radiational deactivation of a thermally excited atom is observed, the phenomenon is called atomic emission. The "intensity" of the emission signal is proportional to the excited state population, which in turn is proportional to the ground state population. The emission signal, or the integrated line radiance, to be more exact, is a linear function of concentration at low concentrations and is proportional to the square root of concentration at high concentrations. In practice, the calibration plots for atomic emission are linear over three to four orders of magnitude.

Atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) both require an external radiation source to excite the ground state atoms. In AAS the attenuation of the external source radiation is measured, while in AFS the intensity of radiation emitted after radiational activation is observed. The fluorescence radiance is proportional to the radiance of the source, and in theory, AFS is never less sensitive than AAS. Only the lack of intense sources has prevented AFS from becoming widely used in analytical spectrometry.

Obviously, for any of the three atomic spectrometric methods to work, the number of analyte atoms produced must be proportional to the number of analyte atoms in the sample. For the best sensitivity, the atomization efficiency should be 100%, and should not be dependent on matrix. The sample matrix usually does not affect the measurement performed on the atomic vapor. When the sample is broken into its constituent atoms, only a fraction of the total analyte will appear as neutral, ground state atoms within the

area of observation. The fraction atomized is generally dependent on matrix.

A. Flame Atomization

The most common method of atomization is to spray a liquid sample into a flame. The flame first evaporates the solvent, leaving particles of the analyte salt. The particles are vaporized into a molecular gas, and the molecules are finally atomized. The atomization process is thus dependent on the type and chemical properties of the molecules formed. Aluminum chloride particles for example, are more easily atomized than aluminum oxide particles.

Flames have been successfully used as atomizers for many years (1). The use of flames as atomizers was inherited from the technique of flame emission spectroscopy where the flame was used both to atomize the sample and to excite the atoms. Even when used only as an atom reservoir for AAS and AFS, the chemical combustion flame has many advantages.

- 1. Flames are convenient, reliable, and reasonably safe.
- The atom population is due to the vaporization and atomization of large numbers of particles. This leads to high precision due to the effective averaging of many individual particles.
- A variety of flames are available with chemical environments ranging from strongly oxidizing to strongly reducing. Flames have temperatures from 520 K to 5900 K (1).

The wide choice of flames allows the spectroscopist to choose appropriate conditions to atomize different samples.

Flames, however, also have several disadvantages which limit their applicability.

- The flame is a dynamic, poorly understood system consisting of a mixture of violent chemical reactions. The reactants, products, and their intermediates may all be excited and produce intense background emission. The analytical signal may be lost in this large background.
- Flames generally cannot atomize solid samples. In fact, most flames require about 1 ml of liquid for an analysis, so that micro-samples cannot be analyzed.
- The expansion of the flame gases dilutes the atomic vapor.
  This limits the maximum attainable atom concentration.
- 4. Precise control cannot be exercized over the chemical environment. Oxygen supported flames will always contain some oxygen, no matter how rich the mixture. The oxygen may react with the analyte to form refractory oxides which are very difficult to atomize.

The flame products, in addition to reacting with the analyte, may also undergo collision with the excited state atoms and provide a path for radiationless deactivation. In general, the flames which are the best atomizers are also the best quenchers, so atomic

fluorescence is seldom attempted in these flames.

The first two disadvantages are both practical in nature. It is possible to choose a flame which does not exhibit intense emission at the wavelength of interest, and is conceivably possible to design a flame system for small samples and for solids. The latter two disadvantages are fundamental in nature. Expansion of flame gases will always dilute the analyte atoms, and full control over the chemical environment around the analyte cannot be achieved.

The disadvantages of flame atomization are manifested in detection limits which are far worse than predicted by theory (2), and in the need for relatively large sample volumes. The entire information contained in an analytical sample cannot be obtained unless the analysis technique is sufficiently sensitive. In order to improve the quality of the analyses, many researchers have investigated nonflame atomization as an alternative to flame atomization.

#### B. Nonflame Atomization

The simplest nonflame atomizers consist of a heating element, such as a graphite filament, which atomizes the analytical sample. The nonflame atomizers have several advantages over flame atomizers.

 The sample transport is nearly 100% efficient. This is in contrast to flame atomizers where, at best, only 15% of the sample is even presented to the flame (3).

- 2. The atomization process is also more efficient in a nonflame atomizer than in a flame. For certain elements, the efficiency has been estimated at 100% (4). This produces a higher concentration of atomic vapor than normally found in a flame (5).
- 3. Control over the chemical environment can be maintained by surrounding the atomizer with the appropriate atmosphere. Argon might be selected if atomic fluorescence is desired, because argon has a low quenching cross-section. The atomization temperature is also controlled electrically and can be optimized for individual elements.

The only background emission is the black-body type continuum emitted by the atomizer. The background emission is separated from the analytical signal by either modulation techniques as are used in flame spectrometry, or by viewing the atomic vapor at a spatial location away from the atomizer.

Although nonflame atomizers have several fundamental advantages when compared to flame atomizers, the advantages are not fully realized in practice. The relative imprecision in placing a small sample on the atomizer may limit the overall precision of the analysis. The complexity and lengthy analysis procedure impose practical limits on the apparent widespread applicability of nonflame atomization (6).

#### C. Filament Atomizers

In order to design an atomizer which incorporates most of the advantages of both flame and nonflame atomization, with few of the disadvantages, a fundamental study was undertaken to describe the processes occurring during atomization from a platinum loop atomizer and the dependence of the atomization process on the various experimental variables. The variables were found to be dependent on each other, and the fundamental phenomena underlying the dependence of the atomization and each of the variables are described. From a knowledge of how the variables effect the atomization and how they affect each other, optimum conditions could be rationally chosen. Analytical data are presented for a nonflame atomizer in which parameters have been fully optimized.

The fundamental study of atomization from a heated wire filament, described in this thesis, and studies conducted by Mr. Akbar Montaser (7) in these laboratories led Mr. Montaser to propose a new filament atomizer with superior characteristics. The new atomizer, the graphite braid atomizer, was used in conjunction with a new atomic fluorescence spectrometer, designed specifically for use with nonflame atomizers. The analytical results are quite promising, and the graphite braid atomizer (8) exhibits the potential to be of widespread use in nonflame atomic fluorescence spectrometry.

#### II. HISTORICAL

The applications of nonflame atomizers in atomic absorption and atomic fluorescence spectrometry have been reviewed by Kirkbright (9) and more recently by Winefordner and Vickers (10). The technique of nonflame atomization actually pre-dates flame atomization for both AA (11) and AF spectrometry (12). The first analytical application of nonflame atomization was reported by L'vov (13) in 1959, and only a few papers on nonflame atomization were published prior to 1969. Since the introduction of commercially available nonflame atomizers in 1971, the number of publications has grown so rapidly that only the most important advances will be reviewed in this section.

The nonflame atomizers most widely applicable to AA and AF spectrometry are "thermal" atomizers in which the sample is atomized by the application of heat. Several other mechanisms have been investigated including a long-path stabilized DC arc (14), a pulsed arc atomizer (15), RF plasmas (16, 17) and hollow cathode excitation (18). A promising technique is that of laser sampling (19). A not so promising technique is the "explosion" atomizer (20) where the sample is mixed with a solid prepellant powder and exploded in the light beam of an atomic absorption spectrometer. Only one publication exists concerning this technique.

Thermal atomizers fall into two main classes, based on design. Furnace-type atomizers confine the atomic vapor within the atomizer,

whereas filament-type atomizers allow the vapor to diffuse. Each type has inherent advantages and disadvantages which are discussed in the sections to follow.

#### A. Furnace Atomizers

#### 1. The L'vov Furnace

The first furnace used as a source of neutral atoms was the King furnace (21). The sample was placed in a graphite tube furnace, the furnace was evacuated, and then heated. L'vov modified the King furnace for use as a nonflame atomizer for AA spectrometry (13). The L'vov furnace itself consists of a tube of graphite, 30 to 50 mm long and 2 to 4 mm i.d. The analytical sample is placed on a graphite electrode, and the electrode is inserted into the furnace to form a "T"-shaped assembly. The entire furnace is enclosed in a metal chamber with silica windows along the light path.

The furnace is heated electrically; approximately 4 kW of power (400 A, 10 V) are needed to raise the temperature of the furnace to 2900 K. To aid in vaporizing the sample, an auxiliary arc (70 A, 15 V) was struck to the sample electrode. A collimated beam from one of several primary light sources is passed through the furnace, and the atomic absorption is recorded. The original furnace was lined with tantalum foil to prevent the sample from diffusing through the furnace walls. The later versions were lined with pyrolytic graphite, and the furnace was also filled with argon, usually at atmospheric pressure, to prevent diffusion.

The primary light sources consist of hollow cathode discharge

tubes, microwave excited electrodeless discharge lamps (EDL's), and a deuterium continuum source. The radiation from any two atomic line sources is combined by a static beamsplitter, and the combined radiation is alternated in time with the radiation from the continuum source. Another beamsplitter is used in conjunction with two monochromators so the output of each monochromator alternates between the atomic line and the continuum.

Two photomultipliers are used to convert the radiant power of both beams to a proportional electrical current. The photocurrents are sent to a series of sample-and-hold amplifiers which are synchronized to the signal. The difference in absorption of the atomic line and the continuum is considered to be directly related to the atom concentration in the furnace, since any non-specific molecular absorption will be subtracted. This process is repeated for the second wavelength, and an absorbance ratio is obtained by a log-ratio type circuit. The second channel and ratio circuit permit the use of an internal standard. The inclusion of an internal standard allows the precision to be improved from 10-25% relative standard deviation to 5-8% relative standard deviation. These data are representative of the precision when a solid is placed in the furnace. If a solution is used, the precision improves by a factor of approximately three.

L'vov has prepared calibration plots for 37 different metals. The limits of detection, defined as the amount of sample needed to produce 0.05 absorbance units, ranged from 5 x  $10^{-9}$  g for boron to 6 x  $10^{-14}$  g for cadmium (6). L'vov feels that these detection limits

would be improved by a modern spectrophotometer which could resolve changes of 0.001 absorbance units. The effects of the matrix on the absorbance were determined by preparing manganese standards in various bases. Even a  $10^4$  fold excess of NaCl, Pb(NO<sub>3</sub>)<sub>2</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> produced no significant change in the absorbance of the manganese standard.

The calibration plots for most of the elements are markedly non-linear, even over a narrow concentration range. The shape of the working curve is unaffected by concomitants, so one calibration plot can be used for the same element in different matrices.

The L'vov furnace is not limited to the determination of heavy metals. L'vov and Khartzyzov (22) used the graphite furnace to determine phosphorous, sulfur, and iodine. They used a vacuum UV monochromator and purged the monochromator and furnace with argon. The excitation sources were microwave excited EDL's made in fused silica tubes. All the other optics were lithium fluoride. L'vov reported sensitivities in terms of absorbance units per gram, so the detection limits have been calculated assuming that 1% absorption (0.0044 absorbance units) is the minimum detectable signal. The detection limits ranged from 4 x  $10^{-10}$  g for sulfur at 180.71 nm to 9 x  $10^{-12}$  g for phosphorous at 178.3 nm. Furnace temperatures were 1800 K for iodine and 1900 K for phosphorus and sulfur.

The L'vov furnace has many advantages necessary for a nonflame atomizer, but it is very difficult to use. Only a few samples may be analyzed each hour, the power consumption is large (approximately 7.5 kW) and the atomizer is bulky. The importance of the L'vov

furnace cannot be overestimated. It is indeed fortunate that the first nonflame atomizer investigated performed so well, because it illustrated many of the fundamental advantages of nonflame atomization with such remarkable results. L'vov has summarized the analytical results and investigations into physical phenomena with the graphite furnace (23). The applications in fundamental research include the measurement of the Lorentz widths of resonance lines, determination of the absolute values of oscillator strengths, and the determination of atomic diffusion coefficients.

#### 2. The Massman Furnace

The King furnace was modified in a slightly different manner by Massman (24) for use in AA and AF spectrometry. Massman's graphite cuvette is similar to L'vov's furnace, but the analytical sample is placed directly into the tube, rather than into a separate electrode. The cuvette intended for use with AA spectrometry is simply a graphite tube 55 mm long, 6.5 mm i.d., and with walls 1.5 mm thick. The fluorescence cuvette has a slit cut in the side for observation of AF.

The graphite cuvette is heated to 2900 K within a few seconds by a 400 A power supply. The cuvette is either purged with argon between samples or enclosed in an argon filled chamber, if atomic fluorescence is to be measured.

Massman used modulated hollow cathode discharge tubes for AAS in order to discriminate against the background. To obtain an AF signal, the hollow cathodes were pulsed with high current, low duty-cycle pulses. The Massman furnace accepts 5 to 200  $\mu$ l of liquid

(5 to 50  $\mu$ l in the AF cuvette) and up to a 1 mg solid sample. Larger samples gave unacceptable background absorption effects. Even the background correction system (25), which determined the atomic absorption signal by computing the difference in absorption of the resonance line and a nearby fill gas or nonresonance line, could not correct for very large background signals.

The limits of detection ranged from  $4 \times 10^{-14}$  g for zinc (by AFS) to  $2 \times 10^{-9}$  g for selenium (by AAS). Relative standard deviations were from 4 to 12% and matrix dependent. The precision was improved by using a two-channel spectrometer and an internal standard.

#### 3. The Woodriff Furnace

The L'vov furnace was modified by Woodriff (26) who made it larger (150 mm long) and used a constant flow of argon through the furnace. The Woodriff furnace requires sample introduction through a sidearm, but can be modified to accept a nebulized sample carried by the purge gas. The tube furnace is electrically heated to a maximum temperature of 3300 K. The sample in the sidearm is atomized and then swept into the heated furnace by the argon purge gas. The analytical data show detection limits from  $10^{-11}$  g to  $10^{-10}$  g for 15 elements. The calibration plots are linear over at least one order of magnitude; for example, absorbance is directly proportional to the absolute mass of lead from 0.1 to 20. The precision was not reported, but Woodriff recommends at least triplicate analyses.

The optics and electronics have been modified to allow background correction by a unique method (27). Collimated radiation

from a line source and from a continuum source are combined in a Glan-Turner prism, which also polarizes each beam. The combined beams are then passed through the furnace. At the exit of the monochromator are two polarizers which move in and out of the beam. The continuum absorption is sent to a reference channel and subtracted from the atomic absorption. The precision for the analyses obtained with background correction was not reported but the calibration plots in the later papers are curved. When Woodriff used the sample electrode to collect airborn particulates, by forcing air through the electrode, the calibration plot for lead was totally curved, from 0.5 to 8 ng, but was still usable in that region (28).

#### 4. Other Furnaces

Numerous furnace methods have been proposed for atomization, but have not been as completely characterized as the three furnaces discussed previously. These other furnaces will be divided into two groups on the basis of construction. One large group of furnaces is heated directly. The other group of furnaces are constructed from a dielectric material, such as silica or alumina, and wrapped in a heating element.

a. <u>Furnaces Heated Directly</u>. This category includes the only widely available commercial furnace designed as a nonflame atomizer (29). The furnace, distributed by the Perkin-Elmer company, is called the Heated Graphite Atomizer (HGA) by its manufacturer. It is very similar in design to the Massman furnace, but only atomic absorption can be measured in the HGA. The commercial version has

a channel cut into the furnace so that a sample of 5 to 100  $\mu$ l may be reproducibly placed in the furnace. The furnace can also atomize finely divided powders.

The HGA is heated by a two-step temperature program. First, current through the furnace is adjusted to desolvate and to ash the sample. Finally, the current is readjusted to atomize the sample. The furnace is heated to 2900 K by dissipating about 5 kW (400 A, 12 V) in the furnace. Not only is the HGA similar in design to the Massman furnace, but the detection limits and precision are also similar.

A matrix study on atomic absorption measurements with the HGA has been completed (30) and several severe interelement effects have been found. Zinc was used as a test element and "all the ions tested caused interference" (30). Zinc is a very volatile element and prone to interferences, however. The reproducibility for 5 ng of zinc was 6%. The authors concluded that a temperature gradient was responsible in part for the poor precision. The HGA was applied to the determination of trace transition metals in seawater (31), and an extraction procedure was found to be necessary for some samples. The reproducibility for samples in a seawater matrix was also 6%.

The Massman furnace is the basis for another commercial furnace, but in a miniaturized form. This furnace, the Varion Carbon Rod Atomizer, is also restricted only to AA measurement. A graphite tube about 10 mm long and 3 mm i.d. is held between two graphite support rods. The sample, 1 to 5  $\mu$ l is inserted into the CRA with

a teflon-tipped microsyringe. This teflon prevents the syringe from scarring the atomizer, so precision is increased. The reported relative standard deviation is 1.6% for AA measurements on a 50 pg sample of cadmium in water (32). Other matrices, including leaves, bovine liver, caviar, and pears were examined. The samples were merely diluted in nitric acid, and the results agreed with independent analyses. The precision was good; the relative standard deviation was on the order of 5% for the various matrices.

A very simple graphite tube atomizer has been used for the determination of lead in blood (33). The design is similar to that of Massman (24), but the system is simplified by eliminating any sheathing or enclosure. A sample is placed in a tube, and dried on a hot-plate. The tube is then clamped in the atomizer and heated electrically, in two steps. The first step ashes the sample and the second step atomizes it. The relative standard deviation of AA results was 10.5%. The graphite tube was discarded and another one snapped into the holder for the next analysis.

Both the sample and the atomizer required some pretreatment. The graphite tubes were degassed in an argon atmosphere prior to analysis. After a 20  $\mu$ l sample of whole blood was added and dried, 80  $\mu$ l of 30% hydrogen peroxide was added. The oxidized sample was then dried on a hot plate two minutes, and the tube was ready for the atomizer.

The results of the AA technique agreed quite well with the results from a complicated solvent extraction procedure. The 10% relative standard deviation and the cost of replacing the graphite

tubes prior to every sample were considered minor disadvantages when compared to the sensitivity and ease of determining lead samples in a complex matrix.

The graphite furnaces described are in general large and bulky, with the Varian CRA and its small graphite tube being the exception. The atomizers all require water cooling of the electrical contacts, and require about 6 kW of power to be heated to 2900 K.

A different approach was chosen by Robinson (34) who coupled a 6 kW radio-frequency generator to a bed of carbon particles by an induction winding. The analytical results were affected by the matrix and exhibited poor precision, probably because the maximum temperature was only 1700 K. The RF furnace does, however, allow the analysis of gases for cadmium, zinc, and mercury (35). Since Robinson's furnace simultaneously desolvates, ashes, and atomizes, a background signal due to nonspecific absorption may exist. Robinson corrects for this effect by looking up the background signals in a table (36) and subtracting the value from his results.

A similar furnace has been used by others (37), but modified to give a temperature of 2700 K. Even at this temperature, matrix effects were prevalent, but the analyses could be easily performed on solid samples. The standards were made in the same matrix as the unknown, and even though calibration plots were curved, they were still usable. The relative standard deviation of 10 AA analyses was 7%.

b. <u>Furnaces Heated Indirectly</u>. Although electrically heated graphite furnaces probably have the widest utility, furnaces made

from other materials have been used in specific instances. Fuwa and Vallee (38) used a Vycor tube wrapped in heating tape as an atomic vapor reservoir. The actual atomization was accomplished by aspirating the sample into a chemical combustion flame. The atomic vapor and flame gases were directed into the furnace, and atomic absorption measurements were made in the furnace.

Absorption in Fuwa tubes was shown to follow Beer's law as the furnace length was varied from 1 cm to 70 cm. The detection limits for the six test elements, including both volatile and nonvolatile elements, were all better than found in flame AAS. Matrix effects are present in Fuwa tubes (39), but are different than in flames. The formation of refractory oxides, for example, does not occur in Fuwa tubes, but the presence of volatile inorganic salts produces a background absorption due to absorption by molecular vapor. The presence of molecular absorption prompted Koirtyohann and Pickett to propose a method of background correction which has been widely adapted (40). Their method has been previously mentioned, but not in detail. They essentially performed two absorption measurements. In the first measurement, a narrow atomic line source is used; the total absorption measured is due to the sum of the atomic absorption and molecular absorption over the width of the line source. The second measurement is made with a continuum source. The source line width is now much wider than the absorption line, and even if the atom concentration is high enough to completely absorb the radiation over the absorption line width, it is only absorbing radiation over a width of about 0.001 nm. Thus, the atomic absorption

can be considered negligible, and any absorption measured with the continuum source may be considered to be molecular absorption.

The original work of Koirtyohann and Pickett involved two separate measurements, but the method is easily modified for use in conjunction with an AC system. A chopper can alternate between the line source and a continuum source. The AC signal is sent to a difference amplifier and demodulator so that the net atomic absorption may be recorded in "real" time.

Fuwa tubes are still being used. They were recently applied to the determination of trace metals in silicate rocks (41). Since the sample matrix had to be chemically treated prior to analysis, a solvent extraction step was added to eliminate the bulk of the matrix. The added sensitivity of the Fuwa tube avoided extensive extraction procedures, which would have been necessary even if a long path length flame were used. The experimental relative standard deviation of AA measurements was 1 to 5%. Analysis of known standards showed that the errors were random so that the accuracy and precision could be considered identical.

Another approach to nonflame atomization is to use a flame to heat a tube furnace. This approach was taken by Delves (42) who used this technique to determine lead in whole blood.

A 10  $\mu$ l sample of blood was placed in a small nickel crucible, oxidized with hydrogen peroxide, and dried on a hotplate. A nickel tube was placed on an air-acetylene flame and the crucible was placed in an opening at the bottom of the furnace. The sample was atomized by the thermal energy of the flame which has been transferred

to the nickel tube and crucible. The AAS results were comparable to those obtained by a spectrophotometric analysis, which required 0.5 ml of blood. No background correction was found to be necessary for the AA spectrometric method. The calibration plots were linear from  $10^{-9}$  g to 2 x  $10^{-8}$  g of lead which corresponds to concentrations of 10 µg/100 ml to 200 µg/100 ml of whole blood. The upper end of the "normal" range is 36 µg/100 ml (43) and the "dangerous" level is 80 µg/100 ml (44), so the sensitivity of the Delve's cup technique is sufficient for clinically significant levels of lead.

#### B. Filament Atomizers

Atomizers which have no provision to confine the atomic vapor within the atomizers have several advantages when compared to furnaces. They are usually less bulky and require less power to achieve the same temperatures as furnaces. The major disadvantage of filament atomizers is that the atomic vapor has a chance to cool, and condensation effects may be seen if other elements are present. A large fraction of the research performed with filament atomizers has been concerned with methods to reduce the interelement effects.

#### 1. The West Atomizer

T. S. West and co-workers have authored a series of papers on a carbon filament atom reservoir (CFAR) (45-57). The atomizer started out as a carbon rod 40 mm long and 1-2 mm in diameter. The CFAR was enclosed in a Pyrex housing with silica windows. The filament-type construction allows observation of AF as well as AA, so enclosures were also made with silica windows placed to allow the observation of fluorescence at right angles to the excitation beam. The chamber was filled with argon flowing at 3.8  $\ell$ /min. The sample, approximately 5  $\mu$ l, was placed on the atomizer and 500 W (100 A, 5 V) was dissipated across the CFAR. The sample was atomized in about 5 sec, and the atomic vapor produced an absorption or fluorescence peak. Even though the electrical contacts to the carbon rod were water cooled, the atomizer took two minutes to cool sufficiently to place the next sample on the atomizer.

The peak absorbance or fluorescence was plotted as a function of concentration for two elements, silver and magnesium. The calibration plots were linear over about one order of magnitude, and the detection limits of both elements were  $10^{-10}$  g when AA measurements were used. Detection limits improved to 3 x  $10^{-11}$  g for silver and  $10^{-16}$  g for magnesium by AFS. Hollow cathodes were used as excitation sources for AAS and high intensity hollow cathodes for AFS. The relative standard deviations were usually about 9% increasing to about 30% near the limit of detection.

The AA and AF peaks were recorded on a slow (1 second full scale response) recorder, and the electronic distortion was thought to cause curvature in the calibration plots. The recorder was replaced by an oscillograph and a laminar sheath of argon was used to shield the CFAR (46). A small notch was cut into the filament to ensure reproducibility in sample placements. To perform an analysis, the sample was placed on the filament with a glass micro-pipette and the atomizer was "programmed" to first desolvate the sample,

then atomize it. The current to the atomizer was switched on and off for precisely 90 seconds at the fastest rate achievable by the operator. The atomizer temperature rose to approximately 150° C during this step. The full power was then applied for 2-3 sec. This heats the atomizer to 2900 K with 700 W (10 V, 70 A) of power.

The calibration plots were linear over 2-3 orders of magnitude and detection limits ranged from  $10^{-11}$  to  $10^{-14}$  g for magnesium, silver, lead, zinc, bismuth, thallium, and gallium. These elements were all determined by AFS with high intensity hollow cathode lamps as sources. The detection limit for magnesium was  $10^{-12}$  g rather than the previously reported  $10^{-16}$  g. The relative standard deviations were less than 2%, which is surprising since the precision of the sample delivery was estimated to be 2%.

The apparatus was further modified (47) by removing the enclosure. A detection limit of  $1.5 \times 10^{-13}$  g (or 0.15 ng/ml) was observed for cadmium by AFS after a light guide was installed to prevent the background emission from the CFAR from reaching the detector. Unfortunately, almost every conceivable interference was present as an interelement effect. The determination of gold (48) was the first time that West's CFAR was used to determine an element not considered to be volatile. Gold has a melting point of 1336 K and a boiling point of 2873 K. The samples were atomized sufficiently well that a detection limits of  $5 \times 10^{-12}$  g by AFS and  $2 \times 10^{-10}$  g by AAS were observed. The relative standard deviations were only 1% for a 5 µl sample. The study of interelement effects was more detailed, probably in light of the problems encountered with cadmium (47). The interferences were clearly shown to be due to reactions in the vapor state, because the interferences were found to be the same magnitude even when the sample and interferent were placed on separate atomizers. This was true for AAS as well as AFS, so ground state atomic vapor was somehow depleted. The interferences, all depressions, were not dependent on the sample-to-interferent ratio as much as on the absolute value of the mass of the interferent. The elements which gave the largest interferences were elements with volatilities similar to that of the analyte. The interferences were not too severe: a  $100 \ \mu$ g/ml Pd concentration depressed the AF signal from 1  $\mu$ l of a 0.1  $\mu$ g/ml gold solution by 25%, and this was the worst depression of 26 elements. In fact, only Mo, Fe, and Cr depressed the signal more than 8%.

A study of the depression as a function of height was performed, and for all elements the interference became worse further away from the atomizer. It became easier to collimate the light beam and optimize the detector optics to observe AA within 1 mm of the CFAR than to observe AF there, so AA was used as the technique of choice in the remainder of the papers in the series.

When solvent extraction was evaluated as a means of eliminating the matrix effect (49), the AA and AF signals were found to be matrix dependent unless a desolvation step was inserted prior to analysis. No interelement effects were observed, primarily because no interferring elements were present. A detailed study of the effects of 62 ions on 8 elements (50) added more evidence that the interferences were due to some reaction, probably a condensation, in the vapor phase. The interferences were negligible when the observation was

made 0.5 mm above the CFAR. The largest matrix effects were observed when the concomitant elements were relatively volatile. The AA signals for several elements were found to be very dependent on height above the atomizer, even when concomitant elements were not introduced (51). The signals for copper, lead, and nickel almost disappeared 5 mm above the atomizer, and the signal for aluminum was already indistinguishable from the background at 1 mm above the atomizer.

When matrices other than water were analyzed, a three step temperature program was found advantageous. For the analysis of silver and copper in lubricating oils (53) a desolvation (280° C, 15 sec) and ashing (750° C, 30 sec) step were needed prior to atomization. A linear calibration plot was obtained for copper from 0.5 to 3 ng of copper in the oil sample. The silver plot was linear between 0.3 and 0.6 ng of silver. The limited linear range and observed precision (1-10% relative standard deviation) are certainly acceptable considering the ease with which the difficult sample was handled. The only observed interferences were due to the presence of barium (a 1000-fold excess enhanced by silver signal by 20%) and calcium (a 600-fold excess depressed the copper signal by 17%). The depressing effects of calcium were less for AAS with the CFAR than for a high voltage spark source emission spectrographic determination.

With the optical arrangement modified to view an area of only 5 mm x 10 mm, a detailed study of the interelement effects on nickel was performed (54). These observations showed that the worst
interferences resulted from elements with similar volatility to the analyte element. The interference was unrelated to the melting point, boiling point, or heat of formation of the metal chloride. The conclusion was that the mechanism of interference is very complex.

A study of iron (55) showed the first serious anion effects observed for the CFAR. Iron is an interesting element because its boiling point is 3300 K, above the maximum temperature of the atomizer, and it forms a stable carbide ( $Fe_3C$ , melting point 2110 K). West reported the best sensitivity was obtained when the atomizer was new and the best accuracy when the atomizer was old. The possibilities of sample carry over and porosity effects were ignored. It was found, however, that NH<sub>3</sub> and NaH<sub>2</sub>PO<sub>4</sub> enhanced the iron absorption signal. Since the strongly reducing environment at the atomizer reduces the iron compounds to the same base, as shown by the identity of signals from chloride and sulfate salts of iron, the logical explanation is that the atomizer is less porous to the iron salts formed in the presence of NH<sub>3</sub> and NaH<sub>2</sub>PO<sub>4</sub>. This is feasible since NH<sub>3</sub> will precipitate iron as the hydroxide and NaH<sub>2</sub>PO<sub>4</sub> will precipitate the phosphate.

The general tenor of the work of West and co-workers is that the CFAR is better for involatile elements than for volatile elements. Thus, the technique is complementary to flame atomization, where the atomic vapor is held at a temperature lower than the atomization temperature of the CFAR, but at a temperature higher than in the observation window above the filament.

The large number of interelement effects observed for low and medium volatility elements is seemingly a black mark against filament atomizers and a strong point in the favor of furnace atomizers, but as of this date, no detailed studies of interelement effects have been made for the commercially available heated graphite atomizer. When West tested the HGA (30) he found that the zinc absorption was affected by every element tried, but sometimes 10,000 fold excesses were needed to affect the signal. When zinc was studied using the CFAR (58) and the interferent data are compared to the data obtained with the HGA (30) the following observations may be made: the filament atomization shows little dependence on the anion present whereas furnace atomization does; volatile cations, particularly the alkali metals, depress the absorption signal observed in the furnace to a greater extent, but the transition metals depress the signal above the filament more than the signal in the furnace; also, at high concentrations of interferences, (5000-fold excess) the signal above the filament is depressed less than the signal in the furnace but at low concentration of interferring elements (100-fold excess) the furnace seems superior.

The results of the comparison are obviously valid only for the test element, zinc, but they seem to indicate that the matrix effects are similar in the filament and the furnace. This is expected since the manufacturers of commercial furnace and filament atomizers do not publish interference data in their advertisements. The data taken on the more sophisticated L'vov furnace (23) show significantly smaller matrix effects.

#### 2. Commercial Graphite Filament Atomizers

The West-type atomizer was modified and made available commercially as the Carbon Rod Atomizer by Varian Associates (59). The atomizer has been modified at least three times since its introduction and is now considered a furnace-type atomizer by its manufacturer (29). It has been described briefly in the furnace section of this review. Research performed on the original version is, however, indicative of results achieved with filament-type atomizers.

The commercial version was provided with a temperature programming unit which allowed the operator to use up to three temperature steps with electrical control over the temperature and the time for each step. If the nitrogen or argon sheath gas were replaced with hydrogen, a diffusion flame surrounded the atomizer. The flame increased the temperature around the rod and prevented vapor phase condensation (60). Two different atomizer designs were compared; one was the West-type filament and the other was similar to the Massman furnace. The furnace was shown to exhibit smaller matrix effects than the filament initially, but if a hydrogen diffusion flame were used, it eliminated interelement effects (all less than 10%) for the filament. The test element in this study was lead, and the observed precision was good; 5% relative standard deviation for lead concentrations of 5 ng/ml in urine.

The determination of lead in petroleum (61) was actually simpler than lead in aqueous samples. No interferences (less than 10% depression) were observed with 1000-fold excesses of Ba, Ca, Ce, Co, Cr, Cu, Fe, Mg, Na, Ni, Zn,  $NO_3^-$ ,  $PO_4^{3-}$ , and  $C1^-$ . No differences

were observed with the hydrogen diffusion flame, other than an increase in the lifetime of the atomizer. This is probably due to the reaction of hydrogen with the available oxygen to prevent oxidation of the atomizer.

The temperature of the atomic vapor is obviously an important parameter. Bratzel and Chakrabarti measured the temperature of the atomic vapor in the Massman-type and West-type atomizer (62). The two line method (63) was used to measure the temperature of the atomic vapor. Measurements were made using indium and gallium as test elements and the following results were obtained: the maximum temperature of the indium vapor in the furnace was 2080 K, decreasing to 1750 K with the hydrogen diffusion flame present. Above the filament, the temperature was 1620 K decreasing to 1250 K with the hydrogen flame. For gallium, the furnace temperatures were 2770 K, but only 1850 K with the hydrogen flame present. The corresponding filament temperatures were 2350 K and 2150 K.

The temperature measurements tend to indicate that the furnacetype environment produces higher temperature in the atomic vapor. The temperature above filament-type atomizers decreases with height, at a rate of 200-250 K mm<sup>-1</sup>. A hydrogen diffusion flame surrounding the atomizer actually lowers the maximum temperature, but since the matrix effects are found to be decreased when the flame is present, the effects of the flame cannot be judged solely by the temperature achieved. The temperature of the flame is high enough to preclude interferences due to analyte condensation above the atomizer, and the flame effectively removes oxygen from the atomizer region, which

prevents the formation of refractory oxides.

#### 3. Other Graphite Filament Atomizers

Several workers have used filament atomizers modelled after the West atomizer (46). The research, for the most part, has been oriented toward the analytical application of the atomizer. Winefordner and co-workers have used a graphite rod atomizer to determine trace heavy metal concentrations in matrices that would involve lengthy sample preparation prior to analysis if a flame atomizer were used. The atomizer was used in conjunction with a hydrogen diffusion flame (64), which was found to either increase the precision of the analysis, or enhance the absorption signal.

The atomizer was used for the determination of copper in serum (65), and for silver, copper (66) and magnesium (67) in jet engine oils. The filament construction allowed for the observation of AF from the vapor above the atomizer.

The hydrogen diffusion flame, even when diluted with argon, was found to improve AA to a greater extent than AF, probably due to quenching effects from the hydrogen. The hydrogen flame, however, was found to be superior to a sheath of pure argon (68). Thermostatted electrodeless discharge lamps were used as primary excitation sources, and linear working curves were obtained for cadmium, copper, mercury, thallium, and zinc, in aqueous solution, and for silver, lead, and tin, in oil. The curves were linear from  $10^{-11}$  g to  $10^{-8}$  g, except for cadmium which was linear from  $10^{-12}$  to  $10^{-9}$  g. These are a factor of ten better than the best AA or AF results found using flame atomization.

The use of the very high intensity EDL's allowed the excitation beam to be collimated to a few  $mm^2$  without losing sensitivity in AA. A detailed study of atom concentration as a function of flame height (69) showed that the atom population decreased with respect to height above the atomizer, even with a hydrogen diffusion flame. The rate of decrease, however, was less with the hydrogen flame than with an argon sheath. There was still a measurable atom population 15 mm above the atomizer when the hydrogen flame was used. The temperature of the flame was only 200 - 300 °C at this point, so temperature effects could almost be ignored. Winefordner postulated that either  $\rm H_2$  or  $\cdot \rm H$  was reducing the metal oxide by a chemical reaction. This mechanism, however, was not the dominant atomization mechanism within a few mm of the atomizer, because when the viewing field was restricted to the area directly above the atomizer, the atom population was found to be higher when argon was used as the sheath gas rather than hydrogen.

Winefordner has looked at the possibility of sequential multielement determinations by programming the atomizer temperature (70). A hollow cathode containing both silver and copper was used as the primary excitation source for AA measurements. The monochromator was set midway between the silver 328.1 nm line and the copper 327.4 nm line, and the slit was opened until the spectral bandpass of the monochromator increased to include both lines. The atomizer temperature was programmed to first desolvate and ash the sample at 800 K, then to atomize silver (approximately 1300 K) and finally to atomize copper (approximately 2100 K). An atomic absorption signal was observed for both silver and copper with 4-7% relative standard

deviation. The sequential method gave poorer precision than singleelement determinations (3-5% relative standard deviation) but is still acceptable for many analyses.

#### 4. Metal Filament Atomizers

Atomization techniques in which a sample is carried into a flame by a wire loop or filament date back to Bunsen in the original work describing flame emission spectroscopy (71). Sampling boats, however, have recently been reinvented by Kahn <u>et al</u>. (72). They used a tantalum boat to hold a 1 ml sample and a hinge-type system to swing the sample into an air-acetylene flame. Detection limits for lead were 0.01  $\mu$ g/ml which allowed the fast direct determination of clinically significant amounts of lead in urine. The reproducibility of the analyses was not very good.

a. <u>Electrodeposition Onto Filaments</u>. Ulvarson (73), Brandenburger and Bader (74) and Brandenburger (75) collected nanogram quantities of mercury as an amalgum on a wire. The wire was then heated to vaporize the mercury vapor in the optical path of an AA spectrometer. The filament technique has been used to determine cadmium, zinc, lead, thallium, copper, silver, and gold after electrolytic deposition on a filament (74). Electrolytic techniques have also been used in conjunction with carbon filament atomizers. Fairless and Bard (76) used constant potential electrolysis to deposit copper onto a graphite filament atomizer. They found that electrolyzing from a large solution volume gave almost quantitative electrodeposition so the effective detection limit was improved, in terms of concentration, by a factor of  $10^5$ . They also tried

electrodeposition within the sample well on the filament. The *in situ* electrolysis increased the precision, from 5.8% to 4.0% relative standard deviation, decreased the matrix effects, but reduced the signal about 20-fold.

b. <u>Electrically Heated Loop Atomizers</u>. Bratzel, Dagnall, and Winefordner have used a platinum loop atomizer for AFS (77). A 1  $\mu$ l sample was placed on a platinum loop, 0.75 mm in diameter formed from 30 guage wire. The loop was heated electrically and AF was observed for cadmium, mercury, and thallium, with detection limits of 10<sup>-14</sup> g, 10<sup>-8</sup> g, and 10<sup>-7</sup> g respectively. The loop was sheathed by flowing argon in order to prevent atmospheric nitrogen from quenching the atomic fluorescence.

The time duration of the AF peak was found to be dependent on sample size. The detection system was too slow to follow the true AF signal, so the measured peak heights were not truly proportional to analyte concentration. The authors recognized this fact and proposed integration of the AF peaks as a more valid measure of concentration. The sluggishness of the detection system was probably responsible for the experimental observations in an interference study. The presence of 1000-fold excesses of carbonate and silicate had no effect on the AF signal, but sulfate and phosphate produced an enhancement in the peak height. The enhancement was probably achieved as sulfate and phosphate reduced the rate of vaporization, which produced a signal more easily followed by the electronics.

Further studies with the loop atomizer (78) showed that if

the AF signals were integrated, the integrated signals were nearly independent of loop material (platinum or tungsten), loop temperature, anion type, solvent, and sheath gas flow rate. These near utopian conditions allowed rapid and accurate (7% relative standard deviation) analysis of silver, beryllium, bismuth, cadmium, copper, gallium, mercury, magnesium, lead, thallium, zinc, arsenic, indium, antimony, selenium, tin, and tellurium. The detection limits ranged from  $10^{-14}$  for cadmium to  $10^{-8}$  g for gallium, and the calibration plots were linear over 2 to 3 orders of magnitude. A tungstenrhenium loop (97% - 3%) has recently been used as an atomizer (79). The high melting point, 3500 K, enlarges the advantages of the hotwire atomization technique.

c. <u>Electrically Heated Filament Atomizers</u>. Donega and Burgess (80) used a filament type atomizer similar to the original West atomizer (44) except the filament was formed from tantalum foil rather than carbon. Only 30 to 50 A (at 12 V) were required to heat the atomizer to 2500 K within 0.1 sec. The atomizer was enclosed by a chamber with silica windows to allow the atomizer to be surrounded with an inert gas at pressures between 1 and 760 mm of mercury. Detection limits were in the range  $10^{-9}$  g to  $10^{-12}$  g for most elements. One advantage of the tantalum filament atomizer is that it can utilize "large" volumes, 50 to  $100 \ \mu$ l, to improve sensitivity.

The tantalum filament atomizer is commercially available (81) with a temperature programmer and plastic housing. The interferences of various acids have been investigated for copper, iron, and chromium (82). The effects could be minimized to less than 10% for 0.1

*M* nitric, hydrochloric, perchloric, and phosphoric acid by optimizing the atomization temperature. Several cations, however, produced severe interferences on the atomic absorption of chromium (83). Even 10-fold excesses of the alkaline earths depressed the signal by 20%. When the chromium content of 9 difficult steel samples was determined, however, the agreement with known values was within statistical error. The precision for samples simply dissolved in aqua regia varied from 3.0 to 4.2% relative standard deviation.

### C. Conclusions

The rapid development and utility of nonflame atomizers during the past few years is the best evidence that the nonflame atomizers are truly an advantageous addition to the analytical laboratory. The atomizers show high absolute sensitivity which permits small samples to be analyzed effectively by AAS and AFS. The only drawback to nonflame atomizers is that their precision is not as good as the precision of flame atomizers, which can achieve 0.5 to 1% relative standard deviation. Even though interferences have been stressed throughout this brief review, the selectivity of well optimized nonflame systems is better than for flame systems. There is, however, room for improvement in the area of nonflame atomization. The first step is to improve our understanding of the atomization processes.

# III. THEORETICAL DESCRIPTION OF ATOMIC FLUORESCENCE FROM A NONFLAME ATOMIZER

In order to understand the atomization process, one must know of the fundamental principles which provide the basis for theoretical descriptions of atomization. In this section, the theoretical expressions are examined with respect to their assumptions, the final expressions are simplified, and limiting cases are described.

The expressions describing the line radiance of atomic fluorescence were taken from Reference 84. The relationship of radiance and atomic concentration are simplified to limiting cases for high and low concentrations.

The transient nature of the AF signal from a nonflame atomizer is examined. The equations describing the time dependence of the atom population (85) are analyzed, and the assumptions inherent in the derivation are pointed out. One of the assumptions, that the atomization temperature is linearly related to time, is subjected to detailed analysis.

The well known thermodynamic relationships of electrical heating, conduction losses, and radiative losses are applied to the platinum loop atomizer. The resulting equation cannot be solved exactly, but an approximate solution is derived. The temperature is shown to be proportional to time raised to the 5/3 power. The physical phenomena responsible for this seemingly unnatural relationship are discussed.

Finally, the derived temperature function is used to predict the shape of the transient AF signal from a platinum loop atomizer. The predicted shapes are compared with the experimental observations, and the improvement derived from the  $t^{5/3}$  relationship is noted.

# A. The Experimental Observation of Atomic Fluorescence

Atomic fluorescence spectrometry, as the name implies, deals with atoms. Before a sample may be analyzed by AFS, the analyte must be atomized. The steps leading to atomization have been mentioned and will be discussed in detail in the following sections of this work. If a sample can be atomized, then the observation of atomic fluorescence becomes possible.

When radiation of the appropriate energy is directed into an atomic vapor cloud, there is a probability that a fraction of the radiation will be absorbed, and the atom will undergo an electronic transition to an excited state. If the excited atoms relax to the ground state by a radiative mechanism, the emitted photons may be observed. The following treatment assumes that the fluorescence is of the same wavelength as the excitation source and that the fluorescence terminates in the ground state (resonance fluorescence).

# B. Expressions Describing the Line Radiance of Atomic Fluorescence

The optical diagram for observation of atomic fluorescence from a vapor cell is shown in Figure 1. The source, either a line source or a continuum, source illuminates an area of width L and height  $\ell$ '. The path length, or depth, of the cell is  $\ell$ . In order to calculate the fluorescence, first the amount of radiation which is absorbed must be determined. This will be done for the case in which a line source is used and for when a continuum source is used (84).

#### 1. Atomic Absorption with a Continuum Source

Let  $B_{AAC}$  be the total radiance absorbed in W cm<sup>-2</sup> sr<sup>-1</sup>, the subscript denotes atomic absorption with a continuum source.

$${}^{B}AAC = {}^{B}C\lambda_{0}{}^{A}t$$
(1)

where  $B_{C\lambda_0}$  is the spectral radiance of the continuum source over the absorption line half-width,  $\Delta\lambda_A$ , and  $A_t$  is the integral absorption given by

$$A_{t} = \int_{0}^{\infty} [1 - \exp(-k_{\lambda} \ell)] d\lambda$$
 (2)

where  $\ell$  is the path length for absorption and  $k_{\lambda}$  is the atomic absorption coefficient. The atomic absorption coefficient can be described in terms of fundamental parameters if the line width can be assumed to be governed by the Voigt profile expression. This is generally the case for a single isolated spectral line



where broadening is primarily Gaussian (Doppler broadening) and Lorentzian (collisional and natural broadening), and  $k_{\lambda}$  can be written

$$k_{\lambda} = \frac{a\kappa_0 n f_{0u}}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-y^2) dy}{a^2 + (v-y)^2}$$
(3)

where

$$v = \frac{2\sqrt{\ln 2} (\lambda - \lambda_0)}{\Delta \lambda_D}$$
(4)

$$\alpha = \frac{\Delta \lambda_{\rm D}}{\Delta \lambda_{\rm D}}$$
(5)

$$\Delta \lambda_{\rm D} = \frac{2\lambda_{\rm O}}{c} \sqrt{\frac{2(\ln 2)kT}{M}}$$
(6)

$$\kappa_{0} = \frac{2\sqrt{\ln 2}x\lambda_{0}^{2}}{\sqrt{\pi} c\Delta\lambda_{D}}$$
(7)

$$\chi = \frac{\pi e^2}{mc} \tag{8}$$

where  $\lambda$  is any wavelength in cm;  $\lambda_0$  is the wavelength at the line center, cm; *M* is the atomic weight of the atom, g;  $f_{Ou}$  is the absorption oscillation strength of the ground state (0) to upper state (*u*) transition, dimensionless; *m* is the mass in grams and *e* is the charge, in esu, of the electron; *c* is the speed of light, cm sec<sup>-1</sup>;  $\Delta\lambda_D$  is the Doppler half-width;  $\Delta\lambda_L$  is the Lorentzian half-width; *a* is the classical damping constant, dimensionless; *v* is a variable dimensionless wavelength interval taken with respect to  $\Delta\lambda_{\rm D}$ ; *y* is a dimensionless integration variable; *n* is the atomic concentration in atoms cm<sup>-3</sup>; and k is Boltzmann's conscant. Note that the atomic absorption coefficient  $k_{\lambda}$  includes *n*, the atomic concentration.

Equations (1) and (2) show the dependence of the absorbed radiance on the integrated absorption,  $A_t$ . The dependence is best seen in two limiting cases:

$$A_{t} = [1 - \exp(-k_{\lambda} \ell)] d\lambda \cong \ell \int_{0}^{\infty} k_{\lambda} d\lambda$$
 (9)

when the optical density, i.e. n, is small. When the integration is carried out,

$$A_{t} = \frac{\sqrt{\pi} \kappa_{0} f \ell \Delta \lambda_{D}}{2\sqrt{\ell n 2}} \cdot n \qquad (10)$$

at high concentrations, however,

$$A_{t} = \sqrt{\frac{\sqrt{\pi}\kappa f \ell a \Delta \lambda_{D}^{2}}{\ell n 2}} \cdot \sqrt{n}$$
(11)

So at low concentrations,  $A_t$  is proportional to n, the atomic concentration. At high concentrations, however,  $A_t$  is proportional to the square root of n. At intermediate concentrations,  $A_t$  is dependent on a, the damping parameter.

#### 2. Atomic Absorption with a Line Source

If a line source is used for AAS, the radiance absorbed,  ${\it B}_{\rm AAL}$  is given by

$$B_{AAL} = B_{L}[1 - \exp(-k_{m} \ell)]$$
(12)

where  $k_{\rm m}$  is the average atomic absorption coefficient at the absorption line center. This implies that the line width of the source is less than the absorption half-width. The opposite assumption is implicit in the derivation of the equations governing the continuum case.  $B_{\rm L}$  is the radiance of the line source in W cm<sup>-2</sup> sr<sup>-1</sup>.

For low concentrations of the analyte (i.e. small  $k_{\rm m}$  )

$${}^{B}_{AAL} \cong {}^{k}_{m} {}^{k} {}^{B}_{L}$$
(13)

since  $k_{\rm m}$  is related to the atom concentration, n, the absorbed radiance is directly proportional to atom concentration at low concentrations. At high concentrations, however

$$B_{AAL} \cong B_{L}$$
 (14)

The physical significance of this equation is that at sufficiently high concentrations, all the excitation source radiation is absorbed, and the absorbed radiance is independent of concentration.

#### 3. Radiance Expressions for Atomic Fluorescence

Fluorescence is considered to be isotropic, thus occurring in all directions with equal magnitude. The radiance of atomic fluorescence is obviously proportional to the fraction of primary source radiation collected by the atomic vapor cell, which is  $\Omega/4\pi$ where  $\Omega$  is the solid angle collected and  $4\pi$  is the number of sr in a sphere.  $B_{\rm AF}$  is proportional to the radiance absorbed,  $B_{\rm AA}$ , and also proportional to the number of atoms in the plane L x  $\ell'$  of Figure 1. This plane is directly in line with the monochromator. The observed fluorescence is inversely proportional to the cell depth and height because so many of the planes will be out of the field of observation of the monochromator. The observed fluorescence is finally proportional to the quantum yield, Y, as shown in Equation 15.

$$B_{AF} = \frac{\Omega}{4\pi} B_{AA} \frac{L \times \ell'}{\ell \times \ell'} Y$$
 (15)

There is, however, a chance that some of the fluorescent radiation will be reabsorbed by the atoms between point of fluorescence and the monochromator. This term, the self absorption factor, F, is given by the ratio of the radiance absorbed in the emission path to the radiance in the emission path as shown in Equation 16.

$$F = \frac{A_t(nL)}{\int_0^{\infty} k_{\lambda} L d\lambda}$$
(16)

At low optical densities (low nL), F can be reduced to

$$F = \frac{\int_{0}^{\infty} [1 - \exp(-k_{\lambda}L)] d\lambda}{\int_{0}^{\infty} k_{\lambda}L d\lambda} \cong \frac{\int_{0}^{\infty} k_{\lambda}L d\lambda}{\int_{0}^{\infty} k_{\lambda}L d\lambda}$$
(17)

For high optical densities, F is given by

$$F = \frac{\int_{0}^{\infty} [1 - \exp(-k_{\lambda}L)] d\lambda}{\int_{0}^{\infty} k_{\lambda}L d\lambda} \approx \frac{\sqrt{\pi \kappa_{0} n f L a \lambda_{D}^{2}}}{\sqrt{\pi \kappa_{0} n f L \Delta \lambda D}} = \frac{2\sqrt{a}}{\sqrt{\pi \kappa_{0} f L}} \cdot \frac{1}{\sqrt{n}}$$
(18)

Thus the self absorption factor will increase with the square root of concentration under high concentration conditions. The final expression for the fluorescence radiance is

$$B_{\rm AF} = \frac{\Omega}{4\pi} B_{\rm AA} \frac{L}{2} Y F$$
(19)

When log  $B_{AF}$  is plotted as a function of log *n*, as in Figure 2, several points become obvious. At low concentrations, the relationship is linear, with unity slope. At high concentrations, the slope levels off to zero, and fluorescence becomes independent of concentration for a continuum source. This happens because the absorbed radiance becomes proportional to  $n^{1/2}$  at high concentrations, while the self-absorption factor, F, becomes proportional to  $n^{-1/2}$ . When a line source is employed, the fluorescence actually decreases with increasing concentration at high concentrations. The physical significance of this is that all the source radiation is absorbed, and the excited state atom population has reached a maximum. As concentrations increase beyond this point, the self absorption becomes dominant and the slope of the log-log plot approaches -1/2, which clearly shows the significance of the  $n^{-1/2}$  term in the self absorption expression.

Figure 2 has been redrawn from Winefordner, Svoboda, and Cline (84); this excellent review is also the source of the radiance expressions presented here.



Figure 2. Growth Curves For Atomic Fluorescence (84).

C. Characterization of the Atom Population of a Nonflame Atomizer

The preceding expressions examine the dependence of  $B_{AF}$  on n, the atom concentration. When using nonflame atomizers, the atom population in any volume is a function of time. The following derivation is from L'vov's work (86).

#### 1. Time Dependence of Atom Population

. . .

If a(t) is the rate of atomization and c(t) is the rate at which atoms leave the cell, then the atom population may be described by

$$\frac{dN}{dt} = a(t) - c(t)$$
 (20)

where N is the atom concentration at any time. L'vov chose to assume that the atomization rate is directly proportional to time,

$$a(t) = At \tag{21}$$

The coefficient A may be evaluated by integrating the rate of atomization over the time of atomization,  $\tau_A$ 

$$\int_{o}^{T} A_{a}(t) = N_{o}$$
 (22)

or

$$a(t) = \frac{2N_0}{\tau_A^2} t$$
 (23)

where  $N_0$  is the total number of analyte atoms in the sample. The rate at which the atoms leave the cell is

$$c(t) = \frac{N}{\tau_c}$$
(24)

where  $\tau_{c}$  is the mean residence time of an atom in the cell. If Equations (22) and (23) are substituted into equation (21) the result is

$$\frac{dN}{dt} = \frac{2N_{o}t}{\tau_{A}^{2}} - \frac{N}{\tau_{c}}$$
(25)

A pair of equations results if the variables are separated and the Equation (25) is integrated as done in Reference (85).

$$N = \frac{2N_0\tau_c^2}{\tau_A^2} \left[\frac{t}{\tau_c} - 1 + \exp(-t/\tau_c)\right] \text{ for } t \le \tau_A$$

$$N = \frac{2N_{o}\tau_{c}^{2}}{\tau_{A}^{2}} \left[\frac{A}{\tau_{c}} - 1 + \exp(-\tau_{A}/\tau_{c})\right] \exp[-(t-\tau_{A})/\tau_{c}] \text{ for } t \ge \tau_{A}$$
 (26)

The dependence of N/N<sub>0</sub>, the relative atom concentration, on time is shown in Figure 3. The time axis is in units of  $\tau_A$ , the atomization time, so the plot demonstrates the effects of restraining the atoms in the observation cell. The results are clear: if the mean residence time spent in the observation can be increased, the signal will increase.

The residence time in the observation cell, however, is generally related to the design of the atomizer and invariant from sample to sample. The atomization time can be varied, usually by varying the temperature of the atomizer. When the residence time is assumed to be constant, and the atomization time is varied, the resulting dependence of atom population on time is plotted in



Figure 3. Dependence of Atom Concentration on Residence Time in Observation Cell.

Figure 4. For very short atomization times, the peak population approaches the sample population, but the peak signal is very dependent on the atomization time. For example, if  $\tau_A/\tau_c = 0.1$  then  $N_{peak} = 0.95$ , but if  $\tau_A/\tau_c = 0.2$ , then  $N_{peak}$  decreases to 0.90.

2. Time Integrated Atom Population Expressions

If the integrated population, Q, is measured, then

$$Q = \int_{0}^{\tau_{A}} \frac{N_{0}\tau_{c}}{\tau_{A}} [1 - \exp(-t/\tau_{c})] dt + \int_{\tau_{A}}^{\infty} \frac{N_{0}\tau_{c}}{\tau_{A}} [1 - \exp(\tau_{A}/\tau_{c})] - \exp[-(t - \tau_{A}/\tau_{c}]] dt$$

$$(27)$$

or

$$Q = N_0 \tau_c$$
(28)

This shows that the integral method provides an exact measurement which is independent of atomization time. The sensitivity of the integral method may be increased by increasing the residence time of the atoms in the observation cell. If the residence time is constant, as in the large majority of nonflame atomizers, then the integral method becomes independent of the atomization parameters.

The peak method depends on the atomization time being constant. This may not be a good assumption for samples containing a large concentration of the analyte, or even a small concentration of the analyte and a large concentration of other elements.



Figure 4. Dependence of Atom Concentration on Atomization Time.

#### D. Time Dependence of Temperature

The atomization of a sample occurs as the atomizer temperature is changing from a low initial temperature to a higher, steady state temperature. L'vov assumes that the temperature (atomization rate) is linearly related to time over the atomization region. This assumption will be examined in detail in later sections.

#### 1. Heat Sources and Heat Sinks in a Filament

The fundamental hypothesis describing conduction of heat in isothermal solid is

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2}$$
(29)

where T is temperature; t is time, K is the thermal conductivity of the solid, and x is the distance along any arbitrary axis. This equation will not describe the temperature of an electrically heated filament as normally used for nonflame atomization. Effects from the edges will be ignored. The atomizer is heated by electrical current at a rate R given by

$$R = \frac{jI^2}{\rho c A^2 G}$$
(30)

where I is the current; j is a conversion from joules to calories;  $\rho$  is the density of the filament, A is the cross-sectional area of the filament; c is the heat capacity; and G is the electrical conductance.

Another source of heat arises from the Thomson effect which can be expressed as

$$R = \frac{Is}{\rho cA} \frac{\partial T}{\partial x}$$
(31)

where s is the Thomson coefficient for the filament.

Heat losses are due to conductive losses or radiative losses, if convective losses may be ignored. The rate of heat loss due to conduction can be expressed as

$$-R = \frac{Hp}{\rho cA} (T - T_0)$$
(32)

where H is the surface conductance; p is the perimeter; and  $T_0$  is the temperature of the medium surrounding the filament.

Radiative heat losses are given by

$$-R = \frac{H'p}{KA} (T^{4} - T_{o}^{4})$$
(33)

where H' is the product of the Stefan-Boltzman constant and a function related to the emissivity of the atomizer and the surroundings, and K is the thermal conductivity of the atomizer.

When all the terms are summed, Equation (34) results

$$\frac{\partial T}{\partial t} = \frac{K}{\rho c} \frac{\partial^2 T}{\partial x^2} - \frac{sI}{\rho cA} \frac{\partial T}{\partial x} - \frac{Hp}{\rho cA} (T - T_0) + \frac{JI^2}{\rho cA^2 G} - \frac{H'p}{KA} (T^4 - T_0^4)$$
(34)

where  $K/\rho c = \kappa$ . The electrical conductance and thermal conductivity are both functions of temperature, as shown in Equation (35) and (36) and must be included in Equation (34).

$$\frac{1}{G} = \frac{1}{G_0} (1 + \alpha T)$$
(35)

$$K = K_0(1+\beta T)$$
(36)

where  $G_0$  and  $K_0$  are the initial electrical conductivity and thermal conductivity, and  $\alpha$  and  $\beta$  are arbitrary parameters which provide the best fit to the experimental data. When Equations (35) and (36) are substituted into Equation (34), the result is

$$\frac{\partial T}{\partial t} = \frac{K_{o}}{\rho c} \frac{\partial}{\partial x} \left[ (1+\beta T) \frac{\partial T}{\partial x} \right] - \frac{sI}{A\rho c} \frac{\partial T}{\partial x} - \frac{Hp}{\rho cA} T + \frac{HpT_{o}}{\rho cA}$$

$$\frac{+jI^{2}}{\rho cA^{2}G_{o}} (1+\alpha T) - \frac{H'p}{K_{o}(1+\beta T)A} (T^{4}-T_{o}^{4})$$
(37)

If the only information desired is the variation of temperature with time at points well away from the edge, then  $\frac{\partial T}{\partial x}$  may be set to zero because the filament will be of uniform temperature. This leads to

$$\frac{dT}{dt} = \left[\frac{jI^{2}_{\alpha}}{\rho cA^{2}G_{0}} - \frac{Hp}{\rho cA}\right] T + \frac{H'p}{K_{0}A} \left[\frac{T^{4}-T_{0}}{1+\beta T}\right]$$

$$+ \frac{HpT_{0}}{\rho cA} + \frac{jI^{2}}{\rho cA^{2}G_{0}}$$
(38)

If the terms with similar dependencies on T are gathered together, Equation (39) results.

$$\frac{dT}{dt} = A'T + B'(\frac{T^4 - T_0^4}{1 + \beta T}) + C'$$
(39)

#### 2. Zero Order Perturbation Terms

Equation (39) describes the variation of temperature with time at the nonflame atomizer, without convection terms. It cannot be solved exactly, but an approximation might be sufficient to describe the relationship of time and temperature. The perturbation method of Horne and Anderson (87) was chosen as being the most promising method of simplifying the equation. In this method, estimates are made for the coefficients of the various terms, but small terms are not ignored; rather they are included as perturbation terms so that the effect of possible errors in the initial estimates are minimized.

Equation (38) can be rewritten as

$$\frac{dT}{dt} = \left[ \alpha A_1 - A_2 \right] T + B \frac{T^4 - T_0^4}{1 + \beta T} + A_1 + A_2 T_0$$
(40)

where

$$A_{1} = \frac{J_{2}}{\rho c A^{2} G_{0}}$$
$$A_{2} = \frac{Hp}{\rho c A}$$
$$B = \frac{H'p}{K_{0}A}$$

÷ 7

If T  $\approx 1000$  K at the time of atomization then  $A_1 \approx 10^8$ B and  $A_2 \approx 10^5$ B. To aid in scaling the coefficients and making rational judgment concerning their magnitudes, let  $\tau = T/1000$  and  $\beta = \beta'/1000$ . Then Equation (40) can be written as

$$\frac{d\tau/1000}{dt} = (\alpha A_1 - A_2)(1000\tau) + B\left(\frac{10^{12}\tau^4 - 10^{12}\tau_0^4}{1+\beta'\tau}\right) + A_1 + 1000A_2\tau_0$$
(41)

or

$$\frac{d\tau}{dt} = (\alpha A_1 - A_2)\tau + A_2\tau_0 + A_1 + 10^{12}B(\frac{\tau^4 - \tau_0^4}{1 + \beta'\tau})$$
(42)

If 10<sup>12</sup>B is factored out of Equation (42), Equation (43) results

$$\frac{d\tau}{dt} = 10^{12} B \left\{ \frac{\tau^4 - \tau_0^4}{(1+\beta'\tau)} + \frac{\alpha A_1 - A_2}{10^{12} B} \tau + \frac{A_2}{10^{12} B} \tau_0 + \frac{A_1}{10^{12} B} \right\}$$
(43)

Approximate ratios of the four terms in brackets are

$$1 : 10^{-7} : 10^{-4} : 10^{-7}$$

Now a perturbation expansion (87) may be introduced since the ratios are known. The four terms in Equation (43) will be multiplied by  $\varepsilon$  to the appropriate power in order to keep track of their relative magnitudes

$$\frac{d\tau}{dt} = 10^{12} B \left\{ \varepsilon^{\circ} \frac{\tau^4 - \tau_0^4}{1 + \beta' \tau} + \varepsilon^2 \frac{(\alpha A_1 - A_2)}{10^{12} B} + \varepsilon^{A_2} \frac{A_2}{10^{12} B} \tau_0 + \varepsilon^{A_1} \frac{2^{A_1}}{10^{12} B} \right\}$$
(44)

The temperature term is expanded in a Taylor series.

$$\hat{\tau} = \varepsilon^{\circ} \tau_{\phi} + \varepsilon \tau_{1} + \varepsilon^{2} \tau_{2}^{2} + \varepsilon^{3} \tau_{3}^{3} + \dots$$
(45)

The parameter  $\varepsilon$  is simply a bookkeeping device which aids subsequent manipulation of Equation (45). When  $\varepsilon$  is 1, then  $\hat{\tau} = \tau$ in Equation (45). After the appropriate mathematical operations are completed,  $\varepsilon$  will be set to unity; in the interim, however, the power of  $\varepsilon$  is used to aid in making rational decisions about the relative sizes of the various coefficients. As in any perturbation scheme, one cannot be certain a priori whether the solution of Equation (45) converges when  $\varepsilon = 1$ . Hopefully Equation (45) does converge rapidly and may be truncated with minimal error. The  $\tau_{g}$  term represents the zero order perturbation and is not to be confused with  $\tau_0$ , the initial value of  $\tau$ .

The first step is to collect the zero order perturbation terms

$$\frac{d\tau_{\phi}}{dt} = 10^{12} B \frac{\tau_{\phi}^4 - \tau_0^4}{1 + \beta' \tau_{\phi}}$$
(46)

where  $\tau^4$  has been evaluated from Equation (45) and all terms of order  $\epsilon, \ \epsilon^2,$  etc, have been ignored.

Equation (46) may be solved exactly:

$$t = \frac{4\sqrt{2}\tau_{0}^{3}}{10^{12}B} \log \frac{\tau_{\phi}^{2} + \tau_{0}\tau_{\phi}\sqrt{2} + \tau_{0}^{2}}{\tau_{\phi}^{2} - \tau_{0}\tau_{\phi}\sqrt{2} + \tau_{0}^{2}} + 2 \arctan \frac{\tau_{0}\tau_{\phi}\sqrt{2}}{\tau_{0}^{2} - \tau_{\phi}^{2}} + (\beta' 2\sqrt{2}\tau_{0}) \arctan \frac{\tau_{\phi}^{2}}{\tau_{0}^{2}}$$

$$(47)$$

To extract  $\tau_{p}$  from this equation, to collect the first order perturbation terms, and then solve exactly the first order perturbation equation is impossible. Equation (46) may be rewritten with the denominator expanded in a Taylor series, and truncated after one term

$$\frac{1+\beta'\tau_{\phi}}{\tau_{\phi}^{4}+\tau_{o}^{4}} d\tau_{\phi} = 10^{12} Bdt$$
 (48)

or

$$10^{12} Bdt = \frac{1+\beta'\tau \phi}{\tau_{\phi}^{4}(1-\frac{\tau_{0}^{4}}{\tau_{\phi}^{4}})} d\tau_{\phi}$$
(49)

Now, let

$$x = \frac{\tau_0}{\tau_{\phi}}$$
  $0 \le x \le 1$  (x ≈1/3 to 1/4) (50)

and substitute into Equation (49).

$$10^{12} Bdt = \frac{1+\beta' \frac{\tau_0}{x}}{\frac{\tau_0}{x^4}(1-x^4)} \frac{(-\tau_0)dx}{x^2}$$
(51)

$$10^{12} Bdt = \frac{(x+\beta'\tau_0)x}{\tau_0^3(1-x^4)} dx$$
 (52)

$$10^{12} \text{Bdt} = - \frac{x(x+\beta'\tau_0)}{\tau_0^3} (1+x^4+x^8+...)$$
 (53)

The series arises from the expansion of  $(1-x^4)^{-1}$ . Since  $x<\frac{1}{3}$ , then  $x^4$  and higher order terms may be truncated and still be accurate within a few percent. Equation (53) is easily integrated to produce

$$-10^{12}B\tau_0^{3}t = \frac{1}{3}x^3 + \frac{1}{2}\beta'\tau_0\frac{\tau_0^2}{\tau_p^2} + \text{ constant}$$
 (54)

If Equation (50) is substituted into Equation (54),

$$-10^{12}Bt = \frac{1}{3\tau_{p}^{3}} + \frac{\beta'}{2\tau_{p}^{2}} + \text{ constant}$$
 (55)

The boundary conditions demand  $\tau_{\not p} = \tau_0$  at time t = 0, so the constant may be evaluated as

$$\frac{1}{3\tau_{\phi}^{3}} + \frac{\beta'}{2\tau_{\phi}^{2}} = -10^{12}Bt + \frac{1}{3\tau_{o}^{3}} + \frac{\beta'}{2\tau_{o}^{2}}$$
(56)

This equation can be "simplified" to

$$\tau_{\not p}^{3} - \frac{\beta'}{2(\frac{1}{3\tau_{0}^{3}} + \frac{\beta'}{2\tau_{0}^{2}} - 10^{12} \text{Bt})} \tau_{\not p} + \frac{1}{3(10^{12} \text{B} - \frac{1}{3\tau_{0}^{3}} - \frac{\beta'}{2\tau_{0}^{2}})} = 0 \quad (57)$$

Equation (57) has one real and two imaginary roots. The real root

$$\tau_{\phi} = \left\{ \frac{1}{-6M} + \sqrt{\frac{1}{36M^2} + \frac{(\beta')^3}{216M^3}} \right\}^{1/3} + \left\{ -\frac{1}{6M} - \sqrt{\frac{1}{36M} + \frac{(\beta')^3}{216M^3}} \right\}^{1/3}$$
(58)

where

$$M = \frac{6 \times 10^{12} B \tau_0^{3} t - 2 + 3 \beta' \tau_0}{6 \tau_0^{3}}$$
(59)

If temperature is related to time, then

$$6 \times 10^{12} B \tau_0 t >> 1$$
 (60)

or else M becomes almost independent of t. Note that this implies that  $B>6x10^{12}$  is true. This cannot, at the moment, be documented.

Under these conditions, [*i.e.* for (60) true],  $\tau_{\phi}$  can be written

$$\tau_{\phi} = -2\left(\frac{1}{3.6 \times 10^{13} \text{Bt}}\right)^{1/3}$$
(61)

The zero order effect is the radiative loss of heat. It is obvious that this cannot be used as an approximation since conductive losses and Ohmic heating do not appear until the first order terms are included.

### 3. First Order Perturbation Terms

Since  $\tau_{\phi}$  is known, first order perturbation terms may be collected.

$$\frac{d\tau_{1}}{dt} = \tau_{1} \left\{ 10^{12} \frac{(\tau_{\not o}^{4} - \tau_{o}^{4})}{(1 + \beta' \tau_{\not o})^{2}} \beta' - \frac{4\tau_{\not o}^{3}}{(1 + \beta' \tau_{\not o})} \right\}$$
(62)

The solution to this differential equation is

$$\tau_1 = \exp(K_1 t^{5/3} + K_2 t^{1/3})$$
 (63)

where

$$\kappa_{1} = \frac{9 \times 10^{6} B^{2/3} + 6.6}{\beta'}$$

$$\kappa_{2} = -\frac{1.44 \times 10^{-2} \tau_{0}^{4} B^{-1/3}}{\beta'}$$

The assumption  $1+\beta' \approx 1$  was made to solve Equation (62). This contributes no more than 5% error over 300 to 1100 K.

Now if the zero and first order perturbation terms, are summed

$$\tau = \tau_{\phi} + \tau_{1}$$

$$\tau = \frac{-2}{3.3 \times 10^{4} B^{1/3}} t^{-1/3} + \exp\left[\frac{9 \times 10^{6} B^{2/3} + 6.6}{\beta'} t^{5/3} + \frac{1.44 \times 10^{-2} \tau_{0}^{4} + B^{-1/3}}{\beta'} t^{1/3}\right] \quad (64)$$

 $\tau = c_1 t^{-1/3} + \exp(c_2 t^{5/3} + c_3 t^{1/3})$  (65)

It is known that during the first part of the atomization step, the temperature is increasing, so that the  $t^{5/3}$  term must be dominant; the coefficients of the other terms are negative and represent temperature losses. If Equation (65) is expanded and truncated after one term.

$$\tau \alpha t^{5/3}$$
(66)

The nature of the dependence of temperature on time seems strange; few natural phenomena are related by  $t^{5/3}$ . This term is actually a combination of two terms. If only heating effects are considered

$$\frac{dT}{dt} = \frac{const}{1+\alpha T}$$

for Ohmic heating. This is easily solved.

$$T = At + Bt^2$$

Note that Equation (66) also shows that the dependence of T on time is between a linear and a squared dependence. The  $t^{5/3}$  relationship results because the perturbation approach gave relative weights to the t and  $t^2$  terms, and provided a weighted average as  $t^{5/3}$ .

## E. Modified Estimates of Atom Population

The differential equation describing the atomic concentration in the vapor cell Equation (20) is still correct

$$\frac{dN}{dt} = a(t) - c(t) \tag{20}$$

where a(t) is the atomization rate and c(t) is the rate at which atoms leave the cell. But a(t) was shown in Equation (66) to be proportional to  $t^{5/3}$ 

$$a(t) = At^{5/3}$$
 (67)

The coefficient comes from the normalization equation

$$\int_{o}^{\tau} A a(t) = N_{o}$$
 (22)

and can be shown to be

$$A = \frac{3}{8} \frac{N_o}{\tau_A}$$
(68)

Equation (20) can now be rewritten as

$$\frac{dN}{dt} = \frac{3}{8} \frac{N_o}{\tau_A} t^{5/3} - \frac{N}{\tau_c}$$

..

A solution to this equation is

$$N = \frac{N_{o}}{\tau_{A}^{8/3}} t^{8/3} \exp(-t/\tau_{c}) \quad 0 \le t \le \tau_{A}$$
(69)

and

$$N = N_0[exp(-\tau_A/\tau_c)]exp[-(t-\tau_A)/\tau_c]$$

This solution is not exact, but the error is always less than 1/e.

The theoretical atom fraction is plotted as a function of time, and compared to the experimental result in Figure 5. The experimental signal is the observed atomic fluorescence from a  $4 \times 10^{-7}$  g cadmium sample. The data are normalized so the maximum population and the peak signal coincide.

The time axis of Figure 5 is expanded in Figure 6. It can be seen that Equation (69) fits the experiment at least as well as does Equation (26). Equation (69) is based on the relationship of time and temperature implied by Equation (66) and has its basis in fundamental thermodynamic relationships; L'vov's equation (Equation 26), however, assumes that atomization is a linear function of time, and no basis is given for this assumption. Neither equation is a perfect fit to the data.

A glance at Figure 6 shows that the  $t^{5/3}$  relationship fits the


Figure 5. Comparison of Theoretical Prediction of Atom Concentration with Experiment.

Theoretical (Assuming T  $\alpha$  t<sup>5/3</sup>). Experimental.





shape of the predicted relationship quite well. The addition of the factors contributing to heat loss would tend to flatten the curve at the top, and the fit would be better yet.

#### **IV. INSTRUMENTATION**

Many of the problems uncovered by researchers using nonflame atomizers are caused by improper choice of atomizers and measurement instrumentation. If the process of atomization is to be studied, some effort must be made to choose the atomizer most conducive to the study, and to utilize the appropriate measurement technique. Atomizers designed specifically for analytical applications, for example, may not be suitable for use in a fundamental study of the atomization process. When this study was started, the lack of *any* commercial system necessitated the construction of a nonflame spectrometer.

The platinum loop atomizer of Bratzell, Dagnall, and Winefordner (77,78) was the first choice for an atomizer. The practical factors, such as ease of use, dominated the temperature limitations in the choice. The platinum loop atomizer is not as good for analytical purposes as some other atomizers, but the disadvantages are relatively minor. The criteria used to design the nonflame spectrometer are divided into two parts, with the atomizer and the spectrometer considered spearately. The fundamental and practical limitations are presented and an attempt has been made to outline the necessary compromises made in the construction of the nonflame spectrometer.

## A. Design Criteria

### 1. The Atomizer

Only two rigid requirements were imposed on the atomizer. The first was that it be capable of atomizing an analytical sample. The second requirement was that the atomizer must be adaptable enough to be useful throughout a complete characterization. Since the initial results would direct future research, a flexible atomizer was necessary. This eliminated furnaces; their geometry precludes the observation of atomic fluorescence.

a. <u>Practical considerations</u>. One important detail often overlooked in the design of the atomizer is the ease of placing the analytical sample on the atomizer. The effects due to sample introduction must be isolated from atomization. For maximum sampling precision not only must identical volumes of sample be placed on the atomizer, but the sample must be placed in the same spot every time. Again, this tends to rule out furnaces.

Another very important detail in the construction of an atomizer is the ease of temperature control. The best control would obviously be achieved if electrical heating were used. Unfortunately, no resistive element can convert electrical power to heat with 100% efficiency. There are also radiative losses, both in the visible and radio frequency regions of the electromagnetic spectrum. Visible radiation can be tolerated, but electromagnetic interferences (EMI) can cause severe problems. Even a small amount  $(10^{-3} \text{ W})$  of EMI may cause any nearby electronic instrument to produce erroneous results. This is an intolerable condition in a research laboratory

which contains complex electronic instruments such as digital voltmeters, strip chart recorders, and digital computers located in the vicinity of and sometimes used in conjunction with the atomizer.

The radiated portion of the EMI occurs chiefly when an alternating current crosses zero. If a 6 kW transformer were used to heat a carbon filament atomizer, like West's (44), the EMI would be quite large. This problem can be minimized by using direct current, but a 1000 A power supply is prohibitively expensive.

An alternative solution is to avoid using a large power supply. If the power could be kept below a hundred watts, then EMI would probably be negligible. The carbon filament atomizer was reluctantly eliminated due to its high power consumption. A platinum loop atomizer, however, could easily be used under low power conditions.

b. <u>Fundamental considerations</u>. Platinum metal is considered to be inert to all mineral acids, except aqua regia. Under oxidizing conditions, fused alkali metals will attack platinum but only to a small extent. Molten halides, carbonates, and sulfates have little effect on platinum. The dissolution and separation of platinum is, in fact, a difficult analytical problem. The best methods for dissolving platinum are fusions (88). Platinum is soluble in a zinc metal fusion at 800° C, but the zinc is volatilized at 1000° C. A lead fusion is also used, but takes two hours at 1200° C to dissolve platinum. These chemical reactions are insignificant to the application of platinum as a nonflame atomizer. Platinum will form a black oxide, Pt0, if heated in the presence of oxygen. The oxide,

however, decomposes at 550° C. Platinum is also attacked by chlorine gas at elevated temperatures, but all the platinum chlorides decompose at temperatures less than 585° C.

The major disadvantage of using platinum is that it has a relatively low melting point, 1769° C. This is approximately 600° C less than can be achieved with graphite filament atomizers. This was not considered a severe disadvantage because an atomization study could be made simply by using a volatile element for the study.

The platinum loop atomizer has one fundamental advantage over graphite; there are no problems arising from the sample soaking into the atomizer when platinum is used. This can be important if the temporal and spatial characteristics of the atomization process are to be studied.

# 2. The Spectrometer

If all the advantages of nonflame atomization are to be preserved, then the measurement system must not degrade the improvement gained by atomization. Both the optics and electronics may have to be different than those used for flame atomizers.

a. <u>Optical considerations</u>. One of the most obvious advantages of nonflame atomization is the minimal background signal. If the atomic vapor is viewed a few millimeters above the atomizer, the background due to the atomizer is essentially zero. This advantage is much more important in atomic fluorescence spectrometry than in atomic absorption spectrometry. In AAS, the signal of interest is the small attenuation (by absorption) of a relatively high source radiance. In AFS, the signal is a small increase above the

background. At the limit of detection, the dominant noise source is source flicker noise in AAS, while in AFS the largest noise sources are shot noise in the signal and flicker noise in the background. If a low background nonflame atomizer is used in conjunction with atomic fluorescence measurements, the system will be limited by fundamental noise. This is a very desirable circumstance as the shot noise limit can never be improved.

Since the atomic fluorescence signal is directly proportional to the radiance of the primary excitation source (if a line source is used) it is obviously desirable to use the most intense source possible. The spectrometer should also incorporate wide-angle optics in the monochromator. The observed AF signal is directly proportional to the acceptance angle of the monochromator. The monochromator does not have to be a high resolution instrument because the resonance fluorescence produced from atoms is itself highly monochromatic. Hence the light reaching the monochromator due to atomic fluorescence is already monochromatic if a monochromatic source is employed. In practice, however, light reaching the monochromator consists of stray light and non-resonance fluorescence as well as resonance fluorescence. The monochromator should be able to separate the desired fluorescence radiance from the stray light for optimum instrument performance. The major sources of stray light, include room light, and light from the primary excitation source which has been reflected into the monochromator by the atomizer or other nearby reflective surfaces.

b. <u>Electronic considerations</u>. The radiation must be transduced

into an electrical signal to permit flexible signal processing. It is easier to filter, shape, or digitize an electrical signal than an optical signal. The ideal transducer will be the one which is most sensitive and least noisy. A multiplier phototube, more commonly called a photomultiplier tube (PMT) has been found to be the transducer of choice for the measurement of low radiant sources. The background (dark current) is approximately equivalent to  $10^{-8}$  W of radiant power at the input (photocathode surface) which is equivalent to about 100 photons sec<sup>-1</sup> at a wavelength of about 220 nm.

The photomultiplier transduces the fluorescent radiation into a proportional current. The transfer function is linear over approximately 8 orders of magnitude (89), so the amplitude distortion introduced by the detector is minimal. The frequency response of the PMT is considered to be about 20 MHz (89), high enough to respond to transient AF signal (duration in tens of milliseconds) without distortion.

The photocurrent should be converted to a voltage and amplified to prevent electrical noise sources from becoming a major source of error. Voltages of approximately 1 V are also more easily treated than currents of  $10^{-7}$  A. The signal, now a voltage, is ultimately transformed into a number, but further electronic modifications may be necessary before the digitization step. Many analog-todigital converters (ADC's) will not digitize a signal properly if the signal is "noisy", *i.e.* contains noise spikes on top of a smooth signal. An ADC which is designed to reject noise spikes may also reject part of the signal.

The electronic signal conditioning must be easily varied if the nonflame spectrometer is to be used for a variety of measurements. The electronics will be needed to reproduce faithfully the timedependent fluorescence, but should also be able to produce a signal proportional to time-integrated fluorescence. The amplitude of the electrical signal must be large enough so that the signal can be digitized with minimal error.

The instrumentation used in the study of nonflame atomization was varied throughout the study. Obviously, if modification of the instrumentation improved the results, then the modification was preserved. Since the components of the measurement system affect the electrical analog of the AF signal to a large extent, they were varied in the course of the experiment.

# B. Sequence of Events

The "normal" nonflame AF analysis consists of a series of separate events. First, the sample is placed on the atomizer. The atomizer is heated, and the sample is atomized. The resultant atomic vapor absorbs radiation from a primary excitation source and the radiational deactivation (fluorescence) is observed. The timevariant fluorescence is transduced into an electrical signal which is suitably modified so that it can be accurately digitized. The ultimate result of every measurement is a number.

The instrumentation involved in each of these steps will be described in the following sections. Many of the events are controlled electrically, so some sort of master controller must exist to determine the sequence of events. The controller consists of a clock to produce a series of pulses and some other circuitry to guide the pulses to the proper destination. This is necessary to insure that the appropriate sequence of events is followed in every analysis.

The design of the master controller is actually trivial. The procedure followed in the actual research was to evaluate the instrumentation separately for each step, and then to develop the master control unit. The design of the instrumentation assumed that timing pulses could be provided in the correct sequence.

### C. Sampling to the Atomizer

To characterize adequately nonflame atomization required approximately 20,000 separate samples. Even before the study was started, it was apparent that a large number of samples would be necessary. In every study cited in Chapter II, the analytical sample was placed on the atomizer either with a syringe or pipet. The time-consuming nature of the sampling process probably accounts for the lack of research into the nature of atomization. If such research is to be performed in a reasonable length of time, then the sampling process must be automated.

The sampler must deliver precise volumes and place them on the atomizer in a reproducible manner. A glass microsyringe is capable of reproducibility with relative standard deviations of less than 2%, in the hands of a skilled operator. This precision may be lost if the operator accidentally jars the platinum loop atomizer while placing the sample on the atomizer.

The first automated sampling system delivered the sample to the atomizer from a quartz capillary positioned beneath the atomizer. The analytical sample was placed in a reservoir and pumped into the capillary in discrete steps by a peristalic pump. The peristalic pump is shown in Figure 7. A movable "wiper" attached to a motor compresses the tubing leading from the sample to the atomizer against a machined radius and forces a sample through the tubing. The precise sample size is determined by the internal diameter of the tubing, the length over which the wiper compresses the tubing, and the distance between the machined radius and the wiper. The latter is variable and was used to adjust the delivery volume from 2  $\mu$ l to 40  $\mu$ l with 0.8 mm i.d. tygon tubing.

The capillary construction and position relative to the loop are also shown in Figure 7. The sample clings to the loop rather than the capillary, probably due to increased surface tension at the loop. The height of the tip of capillary must be the same as the level of the sample in the reservoir, or siphoning effects will be seen. The level of the sample was kept constant by a reservoir similar to the mercury reservoir used with a dropping mercury electrode.

When the pump was tested, the relative standard deviation for dispensing five 4  $\mu$ l samples was 2-4%. The only disadvantages of this system were adsorption onto the tygon tubing and a large dead volume. After several hours of use, the test element could become adsorbed onto the walls of the tubing. This produced high values when the blank and very dilute solutions of the analyte were run. The adsorption onto the tygon tubing was no particular problem





during the study of atomization when the analyte concentration was kept constant, and at a level significantly above the detection limit. When calibration plots were run, a syringe was used to deliver the sample.

# D. Electrical Control of Atomizer Temperature

Platinum is readily heated to incandescence by dissipating a few watts of electrical power across the platinum filament. To heat a 32 guage platinum wire to 1600 K requires less than 10 W of power. The resistance of platinum increases as temperature increases. This is a common phenomena in metallic conductors and actually simplifies the design of temperature controllers. The term "temperature control" or "temperature program" is a little misleading. In the study being described, as well as all those cited in Chapter II, an electrical parameter, such as current or voltage, is being *controlled*; temperature is measured. Temperature, current, and voltage are inter-related. If the current and voltage are known, then a resistance may be calculated from Ohm's law. The dependence of the resistance of platinum on temperature is very well known.

If a constant voltage is placed across a platinum filament a large initial current will be present, which decreases to a smaller steady-state value because as the filament is heated the resistance increases. If a sample is placed on the atomizer, the atomizer temperature will remain at the boiling point of the solvent until the sample has been desolvated. The temperature then increases to a steady-state value when the Ohmic heating equals the conductive, radiative, and convective losses. If the steady state temperature is chosen properly, the sample will be atomized at some time following the desolvation, but prior to the time when the steady state temperature is reached.

The choice of atomizer voltage is obviously important. If the applied voltage is too high, the Ohmic heating may be much larger than the heat due to desolvation. Under these circumstances the sample will boil furiously, and the possibility of sample loss due to splattering and sample explosion is large. If the applied voltage is too low, the sample may not be completely atomized.

The voltage control to the platinum loop atomizer should be continuously variable so that the applied voltage may be optimized for each element and matrix. The voltage control must also be free from EMI if any digital electronics are to be used in the vicinity. A simple solution is to use an autotransformer (Variac) to set the applied voltage and to use a switch to turn on the voltage whenever it is desired. This type of circuit will not, however, minimize EMI.

The origins of electromagnetic interferences are not well known. The magnitude of the EMI is known to be proportional to the second derivative of current with respect to time (90A). If a switch is turned ON, the current goes from zero to a finite value in a few microseconds. The second derivative is larger yet. If, however, an alternating current is switched ON precisely as it crosses zero, the magnitude of the EMI will be minimized. The switch must be

bounce-free or the advantages gained by switching at the zero crossing will be lost. No mechanical switch is absolutely bounce free, so a solid-state switch must be used. The only solid-state device capable of switching alternating current is called a bi-directional triode thyristor, or triac (90). A block diagram of a bounce free power switching circuit is shown in Figure 8. The zero crossing switch senses when the alternating current crosses zero, and produces a pulse which straddles every zero crossing. The pulse is amplified and then directed to the gate of the triac. The triac turns ON and completes the circuit containing the platinum loop atomizer. A fraction of the 6.3 V platinum loop power source is selected by the autotransformer and applied across the loop. The low voltage is advantageous because it eliminates the shock hazard of the circuit.

The complete circuit diagram is shown in Figure 9. A logic level signal at the input activates the CA3059 integrated circuit which produces a series of zero crossing pulses. The pulses appear at pin 4 of the IC, and are directed to the base of a transistor. The output of the first transistor (2N3393) is sent to a second transistor (2N3053) and then to the gate of the triac (2N5444). The two transistors comprise the amplifier of Figure 8. The 6.3 V source is transformer T2, and the transformer T3 is the autotransformer.

The entire circuit can be considered as an EMI free power supply. When a signal is present at the input, power is gated across the load, in this case, a platinum loop. The loop is heated



φ6.3 v AC





Figure 9. Circuit Diagram of Trial Power Control Circuit.

and the sample is atomized. The input signal is then removed, another sample placed on the loop, and the atomization is repeated.

# E. Optical Design

The fluorescent radiation incident on the detector depends on the optical relationship of the source, atomizer, and detector. The optimum arrangement has the maximum source radiance collected by the atomic vapor cell, and the maximum fluorescence radiance collected by the detector.

# 1. Primary Excitation Sources for Atomic Fluorescence.

The intensity of fluorescence is directly proportional to the source intensity integrated over the absorption line. The "best" sources for AF should exhibit high signal-to-noise ratios, long lifetimes, low cost, and be easy to use. No single source meets these criteria at present, so many different sources have been used in atomic fluorescence spectrometry.

a. <u>Metal vapor discharge lamps</u>. The first source ever to be used in AFS was a metal vapor discharge lamp (91). These sources consist of the metal and an inert gas (at 1-10 mm of Hg) in a quartz tube. The tube also contains an oxide-coated metal filament at each end. To start the lamp, the filaments are heated electrically; when they are red-hot, the current is sent through the tube, creating an arc-like atmosphere.

These lamps are useful only for cadmium, zinc, and thallium; other elements produce very broad lines. The metal vapor lamps are also very sensitive to temperature changes, so should be thermostatted.

b. <u>Hollow cathode discharge lamps</u>. Presently, hollow cathode discharge lamps (HCDL's) are available for almost every element that is possible to cast into a cathode. They emit very narrow atomic lines after excitation by sputtering (92). The lamps consist of a cathode made from the material of interest (or an alloy) inside a tube. The tube is filled with an inert gas at reduced pressure. Large enough anode-to-cathode voltages will ionize the fill gas and accelerate the positive ions to the cathode. The ions strike the cathode and sputter off some of the cathode material. The atomic vapor from the cathode is in an excited state immediately after the sputtering process and emits radiation as it returns to the ground state.

Hollow cathodes are not generally intense enough to use as AF sources. Many researchers have tried to increase the intensity by pulsing the current to the lamp, or adding auxiliary electrodes (and more power supplies), but other sources are superior to HCDL's.

c. <u>Electrodeless discharge lamps (EDL's</u>). An EDL is similar in nature to a metal vapor discharge lamp. The excitation, however, is done by microwaves, rather than by an electrical current. When the microwave-lamp coupling is diffuse, as with an "A" antenna, and the EDL's are thermostatted, then these sources produce very intense radiation (93). The stability is good; the S/N is far better than for metal vapor lamps.

d. The tunable dye laser. The tunable dye laser is a promising

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excitation source for AF (94,95). It is very intense, and can conceivably saturate the atomic transition. Under saturation conditions, source flicker and quenching are eliminated. The only problem with tunable lasers is their high cost.

## 2. The Atomizer

The atomizer must be positioned so that the atomic vapor will be in the optical path. The atomic vapor must also be separated from the atmosphere or any fluorescence will be quenched by nitrogen or oxygen. One arrangement to accomplish these ends is shown in Figure 10.

a. <u>Inert gas sheath</u>. The atomizer is surrounded by an argon atmosphere. The argon originates from two concentric rings of holes. The inner ring is 17.2 mm in diameter and the holes are 0.52 mm in diameter, spaced 1.04 mm apart. The outer ring is 17.0 mm in diameter with 0.76 mm holes on 1.57 mm centers. The argon flow rate was variable from 0 to approximately 0.17  $\pounds$  sec<sup>-1</sup>. Flow rates were obtained with uncalibrated rotameters, so the flow rates can only be considered as relative rates.

The quartz delivery capillary emerges from the center of the gas sheath assembly. Both the height of the capillary and the distance from the sheath assembly to the atomizer can be varied independently. The position of the delivery capillary was chosen to minimize turbulence, hence air entrainment, in the argon flow. Optimization of the sheath gas flow rates is discussed in a later section.



- Figure 10. Atomizer Assembly.
  - A.
  - Platinum Loop. Quartz Capillary. Inner Gas Sheath. Β.
  - С.
  - Outer Gas Sheath. Support and Electrical Contact. D. E.

b. <u>Entrance optics</u>. To produce the largest AF signal, the entrance optics should focus the largest possible solid angle from the source on the atomic vapor cell. The atomic vapor should be evenly illuminated by the source so that the maximum number of atoms will be exposed to radiation. Even illumination throughout the atomic vapor cell is actually superior to focusing more light on fewer atoms. In theory, the two methods are equal, but the flicker noise is less if averaged over a larger number of atoms. One possible arrangement of focusing the primary excitation source of the atom cell is shown in Figure 11.

The primary excitation source is focused slightly beyond the atomic vapor cell by a quartz lens. The largest solid angle from the detector is subtended by the lens with the largest diameter and shortest focal length. The lens material (quartz in this case) should be transparent to source radiation at the AF wavelength. An industrial grade quartz lens, f/1.3 (38.1 mm diameter) was used as a reasonable compromise between light gathering power and cost.

The mirror used is a first surface mirror (25 mm in diameter f/2.3). The blank has been aluminized, but the aluminum has not been protected from oxidation, so the reflectivity will drop at wavelengths shorter than 250 mm. The position of the mirror and lens were optimized to produce maximum fluorescence at the wavelength of interest. Any other optimization methods, such as using an index card to follow the light path, or optimizing scatter from the center of the atom cell, are suspect due to chromatic aberrations in the lens.





c. <u>Detector optics</u>. The solid angle collected by the detector optics should include only radiation originating in the atomic vapor cell. If the detector subtends a larger angle it will include extra "noise". If the detector, on the other hand, subtends an angle too small to include the entire atomic vapor cell, then the signal will be diminished. The optimum signal-to-noise ratio results when the detector optics include only the atomic vapor cell.

The detector used was a monochromator (EU-700, Heath/Schlumberger, Benton Harbor, MI) photomultiplier combination. Several different PMT's were tried. The one that gave the best results was a R166 solar blind PMT. (Hammamatsu TV, Lake Success, NY). The photocathode of this PMT is insensitive to radiation of wavelengths longer than 320 nm. The usable response at the lower endis limited by the oxygen absorption bands at 185 nm. The photomultiplier was mounted in a housing integral with a continuously variable highvoltage power supply (EU-701-30 Heath/Schlumberger).

The photomultiplier is used to transduce radiant power into an electrical current. The electrical signal still must be digitized, so several other electronic operations may be necessary. The integral of the AF peak has been shown to be directly related to the atom concentration in the sample in Equation (28). In order to utilize this relationship an integrating measurement system must be employed.

### F. Photocurrent Integration

Several possible methods exist to integrate an electrical signal. They all have various advantages and disadvantages. All the methods are similar in that a "gate" is opened when the signal is present and closed between signals. The only events occurring when the signal is not present are noise; it is intuitively obvious that more confidence can be placed in a measurement which is performed under low noise conditions than under high noise conditions. The integration may be performed on the analog signal or on a digital representation of the signal.

### 1. Analog Integration

A simple gated photocurrent integrator (96) is shown in Figure 12a. The switches may be toggle switches, relays, or solid state switches. When S2 is closed, the photocurrent is integrated. The transfer function may be given by

$$V = \frac{1}{C} \int_{a}^{t} i_{in} dt + k$$

where  $V_0$  is the output voltage; C is the capacitance,  $i_{in}$  is the input current; t is time; and k is the voltage at the output at time zero. The switch across the capacitor, S1, is used to set k equal to zero before every integration.

a. <u>Fixed time integration</u>. The switches can be controlled directly by the atomizer, so that the same signal which controls the application of power to the atomizer also opens the integrator. The timing diagram and typical results are shown in Figure 12b.



(b). Timing Sequence.

After the atomization step is complete, the integrated photocurrent must be digitized. One method of doing this is shown in Figure 13. After the photocurrent is integrated, the integral is present at the output of OAl. The voltage is converted to a frequency by a voltage-to-frequency (V-F) converter, but the frequency is ignored until a "digitize" command appears. The digitize command is simply a pulse produced when the atomizer is turned off. When the digitize command is present, it opens a gate and allows 1 MHz clock pulses through. A frequency meter is used to measure the ratio of frequency of the V-F converter to the 1 MHz clock frequency. The frequency meter, a EU-805 Universal Digital Instrument (Heath/Schlumberger, Benton Harbor, MI), is adjusted to count the V-F converter pulses over a set number of 1 MHz clock pulses. If  $10^6$  clock pulses are chosen, then the counting time is one second and the readout units are in hertz. If the "digitize" pulse should disappear during the counting period, the instrument will not display a result. The only requirement is that the "digitize" pulse be as long as the desired counting period; no errors result if the pulse is too long because the frequency meter can be adjusted to display only one result. The second operational amplifier, OA2, is inserted to prohibit a conversion if the integrator has gone out of its linear region.

The fixed-time integrator was used in the beginning of the study, but was later replaced. Integration over a fixed time has several disadvantages. Since the exact moment of atomization cannot be predicted, the time which integrator gate is open must straddle the expected







atomization time. A ten second time window was chosen to ensure that the atomization would not be missed. The results produced by the integrator were good when the samples were large and the AF signal duration was several seconds. At the detection limit, however, the signal was less than 0.1 sec in duration. Under these conditions the background was integrated over 100 times as long as the signal.

This situation can be tolerated, but not when the background drifts. The input to the integrator is actually the sum of three components

$$i_{in} = i_{BKGD} + i_{OA} + i_{AF}$$

where  $i_{BKGD}$  is due to stray light and photomultiplier dark current;  $i_{OA}$  is the input bias current of the OA; and  $i_{AF}$  is the photocurrent from the atomic fluorescence. The input bias current was found to be the largest source of imprecision. Even though a high quality operational amplifier was chosen, the temperature coefficient of input bias current was approximately  $10^{-9}$  A/°C. If ambient temperature changed by as little as 0.1° C, then the input bias current would change by  $10^{-10}$  A; when integrated for 10 sec the bias current makes the same contribution to the output as an AF photocurrent of  $10^{-7}$  A for 100 msec. Since the peak photocurrent at the limit of detection was less than  $10^{-9}$  A, this system was discarded.

b. <u>Variable-time integration</u>. One possible method of minimizing the amount of background that is included with the signal would be to open the integrator only when the signal is present. This obviously requires that the instrument recognize the presence of the AF peak.

Peak recognition may be accomplished by a device called a comparator. If the input to the comparator is above a certain level, the output is high. The output of the comparator is used to gate the photocurrent to an integrator so that the integrator is ON only when the current is above a certain level. This situation occurs for two cases; for the AF peak and for noise spikes. Since noise spikes have relatively short time duration when compared to the AF peak, they may be discriminated against by using a comparator and noise filter. The short duration noise spikes are removed from the slowly changing signal. If the time constant is chosen to be a few milliseconds, the noise spikes will be disregarded, but only a few milliseconds of the signal will be lost.

The variable time integrator was assembled and tested. Before the performance could be fully characterized, it became obvious that the variable time integrator was a complicated solution to a simple problem.

#### 2. Digital Integration

If the photocurrent is converted to a voltage and digitized periodically, the sum of the digital representations of the signal is proportional to the integrated signal. This type of integration is inherently more simple because it only involves the digitization step, a procedure necessary even when analog integration is used. The photocurrent was modified by a current-to-voltage converter which had a drift of less than 0.005% per °C and 0.005% per day

(Keithley Model 427, Keithley Instruments Inc., Cleveland OH). The conversion of the current to voltage was the only analog operation performed on the signal, so drifts are minimized.

The digital integrator can be made to integrate over a fixed time or peak recognition criteria can also be used. A laboratory minicomputer (PDP Lab 8/e, Digital Equipment Corporation, Maynard, MA) was used to make these operations easier. A real-time clock within the computer was used to provide timing pulses for the analogto-digital converter (ADC). The converted values were stored and summed. The time-integrated atomic fluorescence was outputted via teletypewriter after each sample. The integrals were stored for statistical treatment, background correction, etc.

The variable time integrator was found to produce more precise data than the fixed time integrator for large signals, but when the signal-to-noise ratio (S/N) became small, the computer had trouble recognizing peaks.

In practice, the variable-time integrator was used for the fundamental studies, and a fixed time integrator was used for analytical purposes.

The integrator was tested against the "classical" methods of integrating peaks. A synthetic signal similar in shape to an AF peak was integrated by the digital integrator and also recorded on a strip-chart recorder (Omnigraphic 3000, Houston Instruments Inc., Houston, TX) where the peaks were integrated by planimetry and "cut and weigh" techniques. The synthetic signal was a sine-squared signal, recorded from zero to  $\pi$ , produced by a Wavetek 110 signal

generator, (Wavetek, San Diego, CA). The results of the integration procedures are summarized in Table 1.

Table 1. Comparison of Methods of Peak Integration.

Method	Mean Area	Relative Standard Deviation
Digital	0.684 V-sec	0.38%
Planimetry	0.66 V-sec	0.99%
Cut and weight	0.113 g	1.64%
Peak height (recorder)	0.602 V	
Peak height (oscilloscope)	0.596 V	

The relative standard deviations are based on five samples. When planimetry was used, integration was performed in triplicate and the relative standard deviation represents only the variance among the five samples.

The results indicate that the digital integration method is more precise than the other methods. To test the accuracy of the digital integrator, a square wave of known amplitude and duration was used. The absolute accuracy was found to be the same as the precision.

#### 3. Photon Counting

The output of the PMT has been assumed to be an analog signal i.e., an electrical current. It is actually a series of discrete pulses.

When a photon strikes the photocathode, a photoelectron may be emitted. The probability of this event is given by the quantum efficiency of the photocathode and is wavelength dependent. The photoelectron is accelerated to the first dynode, where 3-4 secondary electrons are produced for each primary electron collected. Each secondary electron is accelerated down the dynode chain (5-14 dynodes) and finally a pulse containing  $10^5$  to  $10^7$  electrons appears at the anode. For the PMT's used in these studies, a 1P28A or R166, the electron gain is approximately  $10^6$ , so the anodic "current" consists of a series of pulses, each containing  $10^6$  electrons. The height of each pulse varies because of the statistical nature of secondary emission. At sufficiently low light levels, these individual pulses may be resolved. An integrator may be built on the photon counting principle; the integral is no more than the sum of the PMT anode pulses collected from an AF peak.

To perform photon counting experiments, the instrumental system shown in Figure 14 was used.



Figure 14. Photon Counting Circuit.

The current pulses at the anode of the PMT are converted to a voltage by  $R_L$ . The voltage is amplified by a fast amplifier. The output consists of large pulses from photoelectrons which have been amplified by the full gain of the PMT, and smaller pulses due to electrons which have been generated by the PMT and have *not* originated from the photocathode. These electrons, which constitute the bulk of the dark current if an analog measurement is performed, arise from cold-field emission, thermonic emission, decay from  $_{19}K^{40}$  in the glass envelope, cosmic radiation, etc. (89). The discriminator rejects all pulses below a reference level, so it can reject some of the dark pulses. Dark pulses originating at the photocathode undergo full amplification and cannot be discriminated from photoelectron pulses. Pulses of amplitude greater than the reference level are shaped for use in the counting circuit and then summed with a digital counting circuit.

The circuit of Figure 14 was built with a Motorola MC1510G (Pioneer Electronics, Detroit, MI) for the amplifier. The amplifier specifications gave the maximum frequency response as 40 MHz. The amplifier was placed on a small circuit board and mounted inside the photomultiplier housing. The circuit was tested by injecting high frequency current pulses at the anode pin of the PMT socket (PMT removed, of course). Under these conditions, the amplifier was found to be usable to 8 MHz (3db point).

The amplifier was tested for linearity by preparing a plot of direct current vs count rate. This plot is shown in Figure 15. Note that the relationship appears to be absolutely linear to 1 MHz.


More rapid photon arrival rates produced a larger dc signal, but the count rate actually decreased. This is due to pulse overlap effects at the amplifier. When the arrival rate of photons exceeds a certain value, the amplifier will not have time to respond to individual pulses from the anode.

The presentation of Figure 15 is log current vs log count rate in order to compress the data to fit the display format. This also has the effect of compressing errors. Even though the slope is 1.00, at low light levels, as found from a least square fit to the data, the amplifier is nonlinear to the extent of 1% for frequencies greater than 100 kHz. This was determined by using neutral density filters in the light path and calculating absorbances.

The non-linearity at high photon arrival rates is not really detrimental to the use of photon counting. It can be used at low light levels where photon counting actually provides higher S/N than dc measurements. The improvement in S/N comes from noise due to the statistical nature of emissions from dynodes, secondary emission noise. Since a dynode may produce 2 - 4 electrons for every electron striking the dynodes then the output at the photoanode may differ from one pulse to the next. The dc measurement system responds to the magnitude of the current pulses, and secondary emission noise is included. Photon counting, however, depends only on the presence or absence of pulses, so the signal-to-noise ratio will be improved by a factor proportional to the secondary emission noise. If instrumental bandwidths are the same for both dc and photon counting measurements, the S/N for photon counting is 5-22% better than for dc measurements (97).

# V. OPTIMIZATION OF INSTRUMENTAL PARAMETERS

The manner in which the experimental variables affect the atomization process must be known if the mechanism of atomization in nonflame cells is to be elucidated. The experimental parameters affect the final readout in several different ways: some parameters actually affect the atomization process, while others affect only the instrumental response to the atomization process. Other parameters affect both the atomization and the instrumental response. In this section, the influence of experimental variables on nonflame AF is described in detail and results are used to select optimum parameters.

## A. Optimization of Signal-to-Noise Ratio

The instrumental parameters may be varied to achieve several different effects. The most obvious effect is the change in the signal. Most spectroscopists immediately "tune" their instruments for the largest possible signal. Unfortunately the conditions chosen to optimize the instrumental response to a standard may not be optimum conditions for any of the analytical samples. Adjusting the parameters for the largest signal may often result in a situation very prone to noise. If the primary excitation source is indiscriminately adjusted for the largest signal, it may also produce the largest blank, due to scatter. The signal magnitude is not

as important to the analytical chemist as is the signal-to-noise ratio (S/N), at any given level of sensitivity. The signal-tonoise ratio can be shown to be directly related to the precision of the analysis. The relative standard deviation (RSD), equals the reciprocal of the S/N (98).

Optimizing the S/N is a relatively straight-forward task. The experimental parameters are varied until the RSD is minimized; at this point the precision (and the S/N) is the highest. The standard deviations are easily calculated, in fact the computercontrolled digital integrator, described in the previous section, is ideal for a study of this type. The computer can record the data and output a signal-to-noise ratio within a few seconds. This allows the operator to vary the parameters and follow the results as the parameters are varied. If the computer were not "on-line", it could take hours, even days, before the operator would know the optimum conditions for analysis.

Signal-to-noise ratio is not the only parameter of interest to the spectroscopist. An optimization for accuracy, sensitivity, or selectivity are alternative goals. The procedure is the same but the S/N is at least as important and as easy to determine experimentally. The low S/N of nonflame atomizers (poor precision) has been said to be its major drawback, so a comprehensive study of the effects of experimental variables on S/N is certainly important. All the experimental data pertain only to the test element, cadmium. This element was chosen primarily for the ease of atomization with the platinum loop atomizer.

#### B. Experimental

#### 1. Instrumentation

The instrumentation used was described in detail in Chapter IV. A fully automated nonflame spectrometer was constructed by placing the automated sampler and atomizer power control under the direction of a hardware master controller. The integration and readout were under the control of a minicomputer. Since the variable time digital integration method is based only on the presence or absence of an AF peak, no timing signals are needed to synchronize the atomization and integration commands. A generalized block diagram of the spectrometer appears in Figure 16. The logic and sequencing unit is the combination of a hardware control system and a digital minicomputer.

The control system instructs the automatic sampler to deliver a sample to the atomizer. When the sampler completes the delivery step, it responds with a signal to the control system, which then turns the sampler off, and provides a signal which switches electrical current through the atomizer. The sample is desolvated, and then atomized when the atomizer is heated. A stream of inert gas carries the atomic vapor to the level of the monochromator entrance slit, where absorption of the radiation from an intense line source produces atomic fluorescence. The fluorescence signal, monitored at right angles to the excitation source, is converted to a proportional electrical current by a photomultiplier tube. The electrical signal is in the form of a current peak, which is integrated, and ultimately read out as a number. The control system outputs





the data, and then repeats the cycle.

a. <u>Control system</u>. The circuit diagram for the control system is shown in Figure 17. The timing sequence is initiated by a pulse from a microswitch on the sampler, which is shaped by NAND gates 1, 2, and 3. The leading edge of the microswitch signal clears all the flip-flops, causing the drive motor on the sampling system to stop. The trailing edge allows flip-flops A and B and NAND gate 5 to function as a single pulse gate, which produces one full clock pulse at the output of NAND gate 5, regardless of the initial state of the clock.

The clock pulse is directed to the circuit which heats the loop, so that the atomization time will be as constant and reproducible as is the clock. All the logic level outputs go through protective devices to prevent the logic system from transients. Alternatively, the entire hardware control system may be replaced by a small computer (99).

b. <u>Fabrication of the loop atomizer</u>. The loop is made from 32 gauge wire, which is 90% Pt and 10% Rh. The platinum-rhodium alloy was chosen for its stiffness and overall strength, higher operating temperature than pure platinum and low susceptibility to oxidation. The diameter of the loop is 2.0 mm, and it is held in place by a spring clip arrangement, which allows replacement in less than a minute. Although fatigue is commonly exhibited in pure metals under repeated heating and cooling, alloying seems to improve the material's fatigue characteristics (100). The platinum-rhodium alloy became weak after repeated use, but not to the extent of



Figure 17. Circuit Diagram of Spectrometer Control System.

pure platinum. Loops were generally replaced after several hundred samples were run by which time changes in the loop could generally be seen.

c. <u>Solutions</u>. Stock solutions were prepared from pure metals. All solutions were stored in polyethylene, and prepared within hours of use to minimize adsorption on the walls of the container.

With the pump-capillary sampling system, the solution to be analyzed was placed in a vessel similar to the mercury reservoir used in polarographic methods. This ensured that the height of the liquid would remain constant to eliminate any siphoning through the peristaltic pump.

# 2. Procedure

The automated sample delivery system had the drawback of possible adsorption onto the tubing. All optimization studies were made using the automated system. However, when working curves were desired, a 10  $\mu$ l syringe (Unimetrics Universal Corp., Anaheim, CA) was used to place the sample onto the loop. All of the experimental data presented on optimizing parameters were obtained with the sampling system which delivers the sample from below the loop. A similar optimization procedure with a second sampler, similar to an automated microsyringe, revealed only minor differences in optimum conditions.

## C. Experimental Variables

The first parameters to be optimized are those which do not affect the atomization process. These parameters include the current to the primary excitation source, the monochromator slit width, the photomultiplier anode-to-cathode supply voltage, and the relative spatial locations of the source, atomizer, and detector.

Most of these parameters affect the S/N in a known manner. Increasing PMT supply voltage increases the S/N, so the voltage was continually adjusted upward. The absolute limit of PMT voltage is a function of the photomultiplier; in practice, the photocurrent due to stray light was kept below  $10^{-6}$  A. Continual use with anodic currents greater than  $10^{-6}$  can damage the PMT.

Adjusting the monochromator slit width affects both the amount of fluorescence and the amount of background which reach the detector. The relationship is different however. Under low background conditions, a wide slit maximizes S/N, but if the background is high, a narrow slit maximizes S/N. Hence, with most nonflame atomizers the S/N increases with slit width up to a certain value and then decreases with further slit width increases. The optimum slit width must be determined experimentally.

The optical system must also be optimized experimentally. The positioning may be optimized for the largest signal, as noise is affected only to a small extent, when the obviously improper extreme choices are rejected. The current to the primary excitation source (a metal vapor discharge lamp) may be optimized in the same manner. As the current increases, the total source radiance increases, but the radiance over the atomic absorption line may actually decrease. This effect is a result of line broadening in the source at sufficiently large currents.

The optimum spectrometer parameters as determined from an experimental optimization procedure are given in Table 2 for AF analyses of Cd.

Parameters	Optimum	
Excitation source	Cd metal vapor lamp	
Source current	1.2 A	
Atomizer position	2.0 cm below slit	
Wavelength	228.8 nm	
Slit width	1.0 mm	
PMT supply voltage	1000 V	

Table 2. Optimum Spectrometer Parameters

## 1. <u>Sample size</u>

The sample size, loop size, signal, and noise all interact in a complex manner. The S/N is further affected by some of the other parameters (e.g. atomization rate), which also change with sample size. In general, the noise decreased as the loop diameter decreased, and the precision increased. If the diameter were made smaller than 2 mm, the signal began decreasing faster than the noise, so the S/N became smaller.

This relationship can be explained as follows: as the loop diameter decreases, the actual point of atomization becomes more readily defined. As the sample is atomized, the metal vapor is swept into the viewing cell by the sheath gas. Although every attempt has been made to ensure uniformity of the sheath, there is probably some degree of turbulence. If the spatial location of atomization is imprecise, the turbulence will multiply this imprecision so that small imprecisions at the atomizer become large imprecisions at the point of observation.

As the atomizer size is decreased the variance (imprecision and variance are approximately interchangeable) introduced by the atomizer becomes smaller. At the same time, simply because the atomizer cannot hold a large sample, the signal becomes smaller and some of the other noise sources start to dominate over atomizer imprecision. Other sources of noise are shot noise in the background, shot noise in the signal, and Johnson noise in the electronics. The overall result is that the S/N decreases as the atomizer size decreases beyond a certain size.

The optimum atomizer diameter was found to be 2 mm. The optimum sample size was found to be about 4  $\mu$ l. A complete optimization is not necessary for these parameters. The RSD does not vary by more than a few percent (4% to 8%) as the atomizer size is varied from 1.5 to 2.5 mm, and the sample size is varied from 3 - 8  $\mu$ l. The relative independence of S/N on small scale variations of instrumental parameters is advantageous because drifts and small errors will not affect the signal to a large extent.

## 2. Sheath Gas Flow Rate

The sheath gas has two functions. It shields the atomic vapor from the atmosphere and also transports the vapor from the atomizer to the observation zone. Argon was chosen as the sheath gas because

of its low quenching cross-section. Actually two parameters must be varied in order to optimize the performance of the sheath. Obviously sheath gas flow rate affects the transportation function of the sheath, but the shielding function is affected more by the design of the sheath than by the flow rate of gas.

The optimization of the design and construction of a laminar flow head for the gas sheath would be a very time consuming process. It was not attempted in this study. The gas sheath was divided into an outer column to prohibit entrainment of ambient air in the vapor cell and a concentric inner sheath to transport the atomic vapor from the atomizer to the observation area.

The flow rates of the inner and outer sheaths were varied and the resultant S/N was recorded. Since the inner and outer sheaths interact with each other, they are plotted on the same graph. Figure 18 shows the results of this study. Contours of constant RSD are drawn for different inner and outer sheath gas flow rates. Note that if the inner flow rate is 2 l/min, then the optimum outer flow rate is about 3 l/min. If the inner flow rate is increased to 3 l/min, now the optimum outer flow rate is a little less than 2 l/min.

An explanation for the exact nature of the relationship between S/N and sheath gas flow rate cannot be provided at this time. The reasons for the behavior at some of the extremes are, however, known. When both the inner and outer flow rates are low, the signal is depressed due to the quenching of atomic fluorescence by atmospheric nitrogen and oxygen. As the outer flow rate increases,





the S/N improves (inner flow rate constant) up to a point, then degrades. This is probably due to turbulence and the entrainment of ambient air in the sheath.

If the outer sheath gas flow rate is held constant, the S/N rises to a maximum as the inner sheath gas flow rate increases. If the flow rate increases beyond a certain point, the S/N starts to degrade. The following explanations are plausible: at low inner flow rates the atomic vapor has time to diffuse out of the observation area. This will decrease the S/N by decreasing the signal. At high flow rates the S/N decreases because the residence time of the atomic vapor in the observation zone decreases. Since the integrated signal is directly proportional to the residence time (Equation 28), the signal decreases with decreased residence time.

# 3. Power Applied to Atomizer

Varying the power applied to the atomizer varies both the steady state temperature and the rate at which the temperature approaches the steady state.

The power affects the signal to a different extent than the noise. Figure 19 shows a plot of the integrated AF signal as a function of atomizer power. The AF signal clearly decreases as the power to the atomizer increases. This behavior is obviously a residence time effect. Since the integrated AF signal is proportional to the product of concentration and residence time, (Equation (28)), then the applied power must be changing one of these parameters.

The most probable mechanism by which the atomizer power affects



the signal is by convection. At high applied powers, the atomizer heats the sheath gas just above the loop and increases the translational energy of the gas. This will either cause turbulence and dilute the atomic vapor or simply speed up the gas flow and reduce the effective residence time. The exact means by which atomizer power affects the signal cannot be identified at this time.

The noise is also affected by the applied power. Although the signal is probably affected more by the change in steady-state temperature (convection currents) than is the noise, the noise is probably affected more by the changing temperature - time behavior than is the signal. At low powers the noise is increased as the sample is atomized slowly and "flicker" effects set in. At high applied power, the atomization process becomes imprecise due to sample explosion from the atomizer.

The signal-to-noise ratio will be low (high RSD) at both very high and very low levels of applied power. This is, in fact, the observed relationship as shown in Figure 20. Hence, there is an optimum applied power for maximum S/N.

## 4. Integration Parameters

The computer-controlled integrator used certain criteria to determine if the input is an AF signal or a noise spike. A signal is defined as any input voltage which remains above a reference level for a specified length of time. The latter criterion is similar to the time constant of an analog circuit and will be designated as the "time constant" in future discussion.

Both the reference voltage and time constant are set by the



Figure 20. Dependence of Precision on Power Applied to the Atomizer.

computer after an initial dialogue with the operator. Increasing the reference voltage and the time constant tends to discriminate against the small, short noise spikes. The amplitude distribution of noise spikes is probably Gaussian. If the reference voltage is adjusted to discriminate against 99.7% of the noise spikes  $(3\sigma)$ , for example, then increasing the reference voltage beyond this would only affect the signal. The time constant probably affects the noise in a similar manner.

At very large time constants and reference voltages a portion of the signal is truncated. In fact, the computer may completely miss some signals. This problem does not occur except when the signal approaches the limit of detection. The signal begins to resemble noise, and the computer may not be able to tell the difference.

A plot of the effects of time constant and reference voltage on precision appears in Figure 21. Again contours of constant RSD are plotted for various reference voltages and time constants. If the time constant (or reference voltage) is held constant at any reasonable value, then the S/N is seen to go through a maximum as the reference voltage (or time constant) is varied. The experimental relationship tends to reinforce the strength of the predictions.

## D. Interaction of Variables

If the variables were independent, the entire optimization procedure would be easy. Unfortunately this is seldom the case in any experiment, and is certainly not the case in this experiment.



The experimental variables clearly interact with each other. If the sheath gas flow rate is increased, the atomizer temperature decreases due to the cooling effect. This in turn changes the atomization rate which in turn changes the temporal characteristics of the peak. The integrator parameters (reference voltage and time constant) may no longer be optimized. The primary effects of changing the sheath gas flow rate are changing in shielding efficiency and transport rate of the gas sheath. Under certain conditions, the primary effects may not be much larger than the secondary effects, so optimization becomes quite complex.

Some of the interactions of the experimental variables are presented in Table 3. This is by no means complete; many other effects are present. The table does, however, illustrate the major interactions and possible mechanisms for the interactions.

The data presented in Figures 18-21 have been produced by varying one parameter at a time and recording the S/N while holding all other parameters constant. The exact optimum value is dependent on the other parameters, although the general shape of the plot of S/N vs variable is not seriously affected. After initial optima were chosen, each parameter was reoptimized while holding the other parameters at their optimum value. The results of the final optimization are presented in Table 4.

The agreement between the values of the final optimization and the optimum values of Figures 18-21 indicate that the conditions under which the data were obtained were close to optimum. If good initial estimates cannot be made, then the optimization procedure

Parameters
Instrumental
of
Interaction
Table 3.

		Parameter Varied	
Parameter Affected	Sheath Gas Flow Rate	Applied Power	Sample Size
Sheath Gas Flow Rate		Higher temperature causes turbulence change in flow velocity	Changes in flow rate needed for adequate shielding
Applied Power	High flow rates cool atomizer		Requires higher power to vaporize sample
Integration Parameters	The magnitude and time duration of AF peak changes so new reference voltage and time constant may be needed	Changes shape of AF peak	Changes shape of AF peak

Optimum
Argon
2.0 1/min.
2.0 1/min.
3.6 A
1.47 V
4 µ1
0.08 V
8

Table 4. Optimum Platinum Loop Atomizer Parameters

becomes extremely complex. Several local maxima exist for the variation of S/N with the experimental variables, and care must be taken to ensure that the optimization procedure does not stop at the local maximum, but instead searches for the unique global maximum.

It should be noted that the optimization study reported here required approximately 20,000 AF analyses of cadmium. Only the extent of automation and computer control allowed this study to be completed in a reasonable length of time. The large number of data points, however, diminished the possibility of the optimization being incomplete.

## E. Analytical Results

#### 1. Stability

After the optimum parameters were chosen, a study of the longterm stability of the nonflame AF system was performed. The results of the study are shown in Figure 22. One hundred separate samples, each containing  $2\times10^{-8}$  g of cadmium, were analyzed by the fully optimized automated nonflame spectrometer. The analysis took one hour, and was performed entirely under the direction of a laboratory minicomputer. No operator adjustments were made during the duration of the analyses.

The relative standard deviation of the 100 samples was 9.1%. The instrument exhibits no long-term drift, but the results are less precise near the end of the analysis. This behavior points out the advantage of recording signal-to-noise ratios rather than signals. The signal remains constant, but the noise increases with time.

The increase in noise is due to several factors. The atomizer properties for example, change over long periods of time. Repetitive heating and cooling changes the metal's characteristics. After hundreds of samples, the loop size has generally changed from the starting size. The atomizer becomes weaker and starts to sag, so the overall shape of the atomizer changes with time.

The sampling precision also changes with time. The tubing in the peristaltic pump will lose resiliance as it is continuously compressed. Unless the loss is constant, a variance term will be introduced by the sampler.

The precision early in the analysis is excellent. The RSD



Figure 22. Long Term Stability of Nonflame Spectrometer Cadmium Under Fully Optimized Conditions.

of the first ten samples is less than 2%. The imprecision is close to random: 62% of the samples are within one standard deviation from the mean; 89% within  $\pm 2\sigma$ ; 100% within  $\pm 3\sigma$ . The distribution would be 68%; 95%; and 99.7% if the errors were truly random.

## 2. Calibration Plot

a. <u>Photocurrent integration</u>. The analyte concentration was varied, and the integrated signal was plotted as a function of concentration in Figure 23. The data are presented on logarithmic axes to illustrate the length of linearity of the plot. The standards varied from  $10^{-10}$  g to  $2x10^{-8}$  g if cadmium. This corresponds to concentrations in the range of 0.04 to 2 µg/ml.

The uncertainty in the experimental results is indicated by the length of the vertical bars on the signal axis. The relative standard deviations were approximately 9 to 7% and independent of the signal. This tends to indicate that the dominant noise source is flicker in the primary excitation source. Both the precision and minimum detectible concentration can be improved by using a light source more stable and more intense than the metal vapor discharge lamp. An electrodeless discharge lamp, for example, should substantially improve precision.

The slope of the log-log plot was determined to be unity within experimental errors. The slope was found by a least square fit which assumed the error in the signal to be much larger than the error in concentration. This assumption is probably better than any of the assumptions made in Chapter III.

b. Peak height measurements. The time duration of the AF

Figure 23. Integrated Fluorescence as a Function of Cadmium Concentration Under Fully Optimized Conditions.



signal varied from 0.08 sec to approximately 2 seconds over the concentration range studied. When peak heights were plotted against concentration, the calibration plot was markedly curved at high concentrations. These data are presented in Figure 24. The curvature is not bad enough so that the calibration plot can be considered unusable, but precision is generally less in curved regions of analytical working curves (101).

The signal at the limit of detection is presented in Figure 25. The signal can readily be seen above the baseline. If the noise can be considered to be 1/5 the peak-to-peak excursion of the background (93), then the S/N is approximately 20 for these signals. The computer-controlled integrator cannot discern the signal from the noise based on the reference voltage and time constant which have been given to it. At low signal levels it becomes advantageous to switch to a fixed time integration method.

c. <u>Photon Counting</u>. The sensitive integration method is used to perform photon counting measurements. The photon counting system shown in Figure 14 was used. The discriminator was the discriminator of the EU-805 Universal Digital Instrument. The UDI was modified by replacing the standard input transistors with high speed, low noise transistors and by adding a ten-turn potentiometer to the internal discriminator. The photon counting was performed for a 10 second period encompassing the moment of atomization. The results are shown in Figure 26.





Figure 25. The Signal at the Limit of Detection.

Vertical Axis: Fluorescence, Arbitrary Units.

Horizontal Axis: Time, 30 sec/div



The calibration plot is linear for a shorter concentration range and exhibits non-unity slope. The most probable reason for the lack of agreement with theory is pulse pile up effects in the photon counting system. If  $10^4$  counts are accumulated from a signal only 80 msec wide, the peak count rate would have to be greater than 250 kHz. Count rates above 10 kHz begin to give noticeable nonlinearity, so the experimental data cannot be expected to be linear. If a faster counter or one with mathematical correction for pulse overlap is used (102), then photon counting becomes the method of choice with low background nonflame atomizers.

## VI. CHARACTERIZATION OF THE ATOMIZATION PROCESS

The events leading to the atomization of the sample significantly affect the atomization process. If these events are known and understood, they can conceivably be controlled. In Chapter V, it was shown that if the instrumental parameters are controllable, they may be optimized so that the best precision may be obtained. If the atomization process can be controlled, then it may also be optimized. Both the events leading to atomization and the events following atomization must be elucidated if the overall atomization process is to be understood.

# A. Characterization of the Platinum Filament Atomizer

The repetitive sequence of heating the filament and then cooling it (by placing the sample on it) will cause changes in both the chemical and physical nature of the filament material. The constant heating and quenching cause the filament to become brittle, to lose strength, and to change electrical resistance. The latter effect is due to evaporation of filament material at the atomization temperature.

## 1. Evaporation of the Filament Material

The rate of evaporation of material from a filament is well known and may determine the useful life of the filament (103). The evaporation rate is known to be higher when alternating current is

used than when the same rms direct current is used. This is due to the fact that the rate of evaporation is an exponential function of temperature (103). If temperature varies sinusoidally with time, as in the case of a filament heated by AC, the average rate of evaporation over one period is greater than the rate of atomization at the mean temperature. For a tungsten filament heated to 2,000 K with an alternating current, the temperature varies over a 157 K range, and the evaporation rate is 9.53 times the rate calculated for the same direct current (104).

The evaporation will affect the platinum loop atomizer by decreasing the diameter of the filament and increasing the resistance. The steady-state temperature of the loop will then decrease if the applied voltage is kept constant. The extent of the evaporation of tungsten filaments is small; only about 0.02% per hour (104). Platinum, however, is considerably more volatile than tungsten, so the evaporation rate should be higher than for tungsten. Since no data are available which describe evaporation from a platinum filament, the evaporation losses were measured experimentally. Unfortunately the variance in weighing the filament (total weight of about 20 mg) was about 0.1 mg; the measured loss due to the evaporation after about 1,000 analyses was approximately 0.1 mg, so the results are inconclusive. Even if the variance were disregarded, an evaporation loss of 0.1 mg would change the electrical resistance only by 0.5%, and the steady state temperature would decrease by about 6 K. This change is probably insignificant to the experiment.

## 2. Changes in the Physicochemical Properties of the Atomizer

After several hundred analyses the properties of the platinum loop atomizer change enough to be readily detected. The loop becomes brittle and is easily broken. The tensile strength is decreased and there is little spring-type action from a coil. Since the changes in the loop are due to atomizing a series of samples, the changes must be analyzed as possibly being competitive reactions to atomization processes.

a. <u>Chemical composition</u>. A platinum loop used for approximately 450 analyses of 2 µg/ml cadmium solutions was analyzed to see if any cadmium has been leached into the platinum. The loop was taped directly to an aluminum x-ray target, and the x-ray fluorescence spectrum was scanned. A Philips vacuum x-ray fluorescence spectrometer was used in conjunction with an ethylenediamine *d*-tartrate (EDDT) analyzer crystal. The spectrum showed no lines other than platinum. An expanded scale scan over the angle where the Cd  $K_{\beta l}$  fluorescence would be expected showed only platinum lines.

An extraction was performed to eliminate the bulk of the matrix. The filament was dissolved in aqua regia and then the solution was neutralized with sodium carbonate. The pH was adjusted to 12 and then a solvent extraction was performed with a 0.1% dithizone solution (w/w in  $CHCl_3$ ). The dithizone quantitatively extracts any cadmium from a pH 12 aqueous solution. Drops of the dithizone extract were placed on an x-ray target and the solvent was evaporated with the aid of a heat lamp. The evaporation was repeated until the entire chloroform layer had been evaporated onto the target.

The analysis showed only a little platinum and traces of lead. The lead was probably a contaminant in the acid used to dissolve the filament. There was still no trace of cadmium. The limit of detection for cadmium was estimated to be 1  $\mu$ g. It is obvious that any change in the properties of the platinum were not due to the dissolution of cadmium into the platinum.

b. <u>Physical properties</u>. The surface of the loop was examined with an optical microscope. New loops were homogeneous and shiny whereas old loops showed occlusions. These appeared as white granules, 10 to 100  $\mu$ m in diameter, embedded in a gray matrix that appeared to be powdery. Since chemical analysis showed no major constituents other than platinum, these occlusions were thought to be various forms of platinum. A microtome capable of sectioning the material could not be found, so only the surface layer was examined.

Platinum is known to have several crystal structures (105). The occlusions may easily be platinum of a different crystalline form. The gray powdery like base is probably spongy platinum. This is the natural form of pure platinum prior to the annealing and extruding of the platinum into a thin wire.

c. <u>The platinum-rhodium alloy</u>. Some of the physical properties of the atomizer are improved if an alloy is used rather than the pure material. A platinum-rhodium alloy (90% Pt - 10% Rh) was found to be superior to pure platinum. The alloy has increased tensile strength, hardness, and has a higher melting point when compared to pure platinum (100). The differences in these parameters are minor for new loops, although the alloy appears to be stronger and more flexible.
The superiority of the alloy is more evident after many analyses. The Pt-Rh alloy stays flexible and strong for many more analyses than does pure platinum. The platinum loops could be used for several hundred analyses, but the Pt-Rh loops could be used several thousand times.

The continual heating and cooling affected the strength of the atomizer more than any of the other physical characteristics. The atomizers started to sag and if they were deformed slightly, they would not spring back to shape, but several thousand analyses were needed to see this effect in the Pt-Rh alloy. All data obtained with the "platinum" loop atomizer were actually obtained on a Pt-Rh loop atomizer. The loop was changed every 500 samples, so aging effects were minimal.

# B. Events at the Atomizer Surface

### 1. Desolvation

Several important steps must occur before atomization. First, a sample must be placed on the atomizer. As the atomizer is heated, the solvent will be driven off. During this step, the atomizer temperature will be fixed at the boiling point of the solvent if the applied power is chosen judiciously. If the heat gain by electrical heating is so high that the heat loss due to the latent heat of vaporization of the solvent, plus conductive, convection, and radiative losses, does not keep the temperature reasonably constant throughout the desolvation step, then other effects set in. The sample can explode off the loop as it is heated, for example. The precision is rather poor under these conditions.

After the sample is desolvated, it will be in the form of hydrated salt particles at the surface of the loop. The loop temperature then rises toward the steady-state value. As the temperature increases, the particles lose water of hydration. It is improbable that the heat loss in this step affects the loop temperature because the particles contribute about 2 ppm to the mass of the atomizer.

The atomizer temperature continues to rise and as it does, the particles at the surface may be changing crystalline form, or even chemical composition. The analyte salt will be in whatever form is thermodynamically favored, and the thermodynamics are obviously temperature dependent. All the reported experimental analyses done in this lab have been performed with cadmium in an aqueous chloride matrix. Cadmium chloride, CaCl<sub>2</sub>, does not decompose or form other compounds when heated.

### 2. Atomization

The anhydrous particle is ultimately vaporized. Since atomic absorption and atomic fluorescence clearly show the presence of cadmium atoms, the molecular CdCl<sub>2</sub> must be atomized. Unfortunately, the exact mechanism of atomization cannot be clearly identified at this time.

When CdCl<sub>2</sub> is heated, it simply boils. One would expect that an equilibrium is achieved at the boiling point, 1233 K. The molecular vapor is not heated in the volume directly above the atomizer, in fact, it is cooled, so dissociation of molecular vapor is an improbable atomization mechanism. The atom production must then take place at the atomizer surface. In other words, thermodynamic considerations

must make the reaction

$$CdC1_2 + Cd + 2C1$$

possible at a heated platinum surface.

#### 3. Time Resolution of Events Prior to Atomization

It is possible to study the desolvation process by recording the sample size as a function of time. This has been done only in a qualitative fashion, and the results show that even desolvation at a platinum surface is a complex process.

The history of a sample droplet on a platinum loop atomizer was recorded with high speed motion picture film. A Pathe camera body was used with a f/35 12-120 mm Angenieux zoom lens plus a series of macro lenses. The lens combination permitted 1:1 reproduction ratios. The film was Kodak 4-X Reversal Film (type 7277). The camera speed was adjusted to 80 fps and calibrated by photographing a digital clock. A sturdy tripod was used to support the camera throughout the study.

The enlargement necessary to photograph adequately the events at a loop only 2 mm in diameter will adversely affect the depth of field. The aperture had to be decreased so that the entire 2 mm diameter of the loop would be in focus. At f/22, the aperture used in the experiment, the depth of the field was less than 5 mm.

The small aperture obviously limits the light throughout and hence the S/N of the final print. The film had an ASA speed of 800, and even then, light sources using over 500 W had to be placed in close proximity to the atomizer to provide the proper exposure.

The last three paragraphs simply say that the images are necessarily fuzzy and grainy. The photographs are presented in Figure 27.

The first frame in the series, Figure 27A, shows the sample droplet on the loop. The electrical power has been turned on, but the droplet has not been noticeably affected. The top frame is considered time zero for the following discussion. The second photograph, Figure 27B, shows the droplet 1.44 seconds later. As it is heated, it starts to boil and expand. The droplet is originally in contact with the entire loop, but eventually looses total contact and becomes attached at only one point. This can be clearly seen in the sequence shown in Figure 27B. The frames are 12.5 msec apart; the bottom frame occurs the latest in time.

Figure 27C shows the situation after approximately 5 seconds. The droplet is becoming smaller and smaller. It is clearly migrating toward one spot on the loop rather than evenly coating the loop with salt particles. This is an important point that will be referred to in some of the following discussion. The point to which sample migrates is the coldest spot on the loop. It is also the lowest spot, because it is the closest to the source of the argon sheath. The top frame of Figure 27D shows the last step of the desolvation. This takes place 7.14 sec after time zero. The middle frame, 12.5 msec later, shows that the result of the desolvation is clearly a clump of salt particles, rather than an even film. The bottom frame shows the atomization. The salt is gone and a vapor cloud can be seen below the atomizer.



Figure 27. Time Resolution of Events at the Platinum Loop Atomizer.

Figure 27E, at time 11.20 sec, shows the loop glowing. The atomization is complete and the loop has reached a steady-state temperature of approximately 1500 K.

#### 4. Post Atomization Events

The events occurring after the atomization were monitored by following the atomic concentration as a function of time. The atomic concentration (as measured by AF) vs time profiles were recorded at various heights and various lateral positions above the loop. The data appear in Table 5.

The data cannot be represented adequately by a graphical presentation. There are no good ways to plot four parameters (AF radiance, time, lateral, and vertical position) as a function of each other. Some general comments about the data must precede a grossly inadequate attempt at presenting the data.

The time axis in the table has been arbitrarily set to zero just before the appearance of the AF signal. The lack of knowledge of the precise moment of atomization makes it impossible to reference the time axis against a standard. The inert gas sheath took the form of a column about 1 cm in diameter. This size had been found to be optimum in studies performed by Mr. Akbar Montaser in this laboratory (7). He chose this design on S/N criteria for integrated AF peaks. The optimal sheath design is detrimental to the spatial studies because sizable atomic concentrations were found outside the sheath. The sheath, in fact acted to create a toroidal atom population density as it tended to move atoms in the center of the atomic vapor cluster more quickly than atoms near the edge. The viewing area was restricted to a sphere approximately 5 mm<sup>2</sup> in area. The sheath gas source was 38 mm below the loop. This was the maximum distance that could be arranged. Hopefully the sheath gas would spread out in a laminar flow at this distance above the source.

Several interesting trends can be seen in the data of Table 5. First, when the observations are made directly above the loop, the atom population is spread out over the entire lateral measurement range. Second, the atomic concentration near the atomizer is still appreciable, although certainly decreasing, even seconds after atomization. These findings clearly show that the environment near the atomizer is very turbulent. This could be due to the atomizer itself, which obstructs the sheath gas flow, or due to thermal currents introduced by the high temperature of the atomizer, or due to rapid diffusion by the heated atomic vapor. The time duration of the AF peak is shorter at heights well above the atomizer than right at the atomizer.

The atoms clearly exhibit large lateral diffusion effects. With the observation height just above the atomizer, there is still appreciable concentrations of atomic vapor at the extreme horizontal positions. The concentration at the sides, for low observation heights is about the same as for high heights, but the concentration at the center is higher at points well above the atomizer. The atom cloud seems to have spread to its maximum width just above the atomizer.

An overall picture is difficult to obtain. The sheath gas affects the measurement (by allowing quenching collisions) as well as by changing the shape of the atom cloud. The results, which are tentative

Time
of
Function
Ø
as
Distribution
Atom
Temporal
and
Spatial
Table 5.

Lateral Position						c d						Pea	
Height 0 mm above loop	0	0.6	Pho 1.2	tocurr 1.8	•ent (♪ 2.4	(x10 <sup>3</sup> ) 3	at Tin 3.6	le T, s 4.2	sec. 4.8	5.4	6.0	Height (Ax10 <sup>9</sup> )	Time, sec.
0 0.35	00	0.2 0.8	1.7 2.1	2.6 3.3	2.5 3.0	1.8 1.9	1.4 1.4		1.0	1.0 0.8	0.9 0.6	3.1 3.4	2.0 2.0
0.70 1.05 1.40	000	0.1 0.5 0.3	2.3 2.3 2.4	3.2 3.2 3.2	3 8 8 7 8 7 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	2.3 3.0 2.5		1.3		1.0 0.8 0.8	0.9 0.7 0.7	3.9 3.1 6	2.2 2.2 2.5
l.4 mm Above loop													
0 0.35 0.70	000	1.5 0.8 0.6	4.1 3.4 3.4	<b>4</b> .0 <b>4</b> .3	1.9 3.4	1.3 2.0	1.0	0.9 0.9	0.7 0.7 0.8	0.7 0.7 0.7	6.7 0.7 0.7	4.9 6.0 4.6	1.4 1.4
1.05 1.40	00	0.4	3.3 3.3	5.1 4.2	3.2 2.6	2.0 1.6	1.4 1.1	0.9 0.9	0.8 0.7	0.7	0.7	5.3 4.4	1.5 1.9
2.8 mm above loop													
0 0.35 6.70 1.05 1.40	00000	0.1.3 0.8 0.4 1.7	.04 4.2 4.2 4.2 4.2	4.54.5 4.5 5.3	1.8 2.2 2.2 2.2	1.533.0	0.8 0.8 0.8 0.7	0.5 0.5 0.5 0.5	0.3 0.3 0.3	0.3 0.3 0.3 0.3	0.3 0.3 0.3 0.3	4 5 5 5 4 9 6 7 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9	

Table 5 - Continued

						c						Peak	
			РНО	tocurr	ent (A	x10 <sup>5</sup> )	at Tim	le T, S	ec.			Height	Time.
		0.6	1.2	1.8	2.4	e	3.6	4.2	4.8	5.4	6.0	(Axĭ0 <sup>9</sup> )	sec
-	0	0.4	4.0	4.5	2.1	1.0	0.7	0.5	0.4	0.3	0.3	5.1	1.5
-	0	0.4	3.2	4.1	2.3	1.2	0.8	0.5	0.4	0.3	0.5	4.4	1.7
0	~	0.8	4.2	4.6	2.2	1.0	0.5	0.4	0.4	0.3	0.3	4.2	1.6
<u> </u>	~	0.7	4.9	4.8	2.0		0.7	0.4	0.4	0.3	0.3	5.8	].5
		0.7	5.1	4.8	2.0	1.1	0.7	0.4	0.4	0.3	0.3	5.6	1.5
	0	0.4	3.5	4.4	1.9	1.0	0.5	0.3	0.2	0.2	0.2	9.8	1.6
	0	1.0	4.0	3.9	2.0	1.0	0.5]	0.3	0.2	0.2	0.2	4.7	1.6
	0	0.2	2.8	4.3	2.8	1.2	0.6	0.3	0.2	0.2	0.2	4.5	1.9
	0	0.7	2.6	3.6	1.7	0.9	0.5	0.3	0.2	0.2	0.2	3.6	
- 1	0	0.1	2.4	3.8	2.7	0.7	0.4	0.3	0.2	0.2	0.2	3.8	1.7
	0	1.4	3.5	1.6	0.7	0.4	0.2	0.2	0.1			3.5	1.1
	0	1.0	4.0	2.0	0.6	0.3	0.2	0.1				4.2	1.7
	0	0.9	2.7	2.9	0.7	0.4	0.1					3.8	1.4
	0	1.0	3.8	2.5	0.8	0.4	0.2					4.0	1.3
	0	1.2	3.7	2.3	0.8	0.4	0.2	0.1				3.7	2.3

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Table 5 - Cont	tinue	p											
8.4 mm above loop													
0	0	0.4	2.8	3.5	1.0	0.4	0.3	0.2	0.1			3.9	1.5
0.35	0	1.1	3.4	2.0	0.7	0.4	0.3	0.2	0.1			3.4	1.2
0.70	0	2.7	4.3	2.0	0.6	0.2	0.1	0				4.8	1.1
1.05													
1.40													
Lateral													
Position						c						Peal	
Height 9.8 mm			Pho	tocurr	ent (A	(( <sup>2</sup> 01×	at Ti	me T,	sec.			Height	Time.
above loop	0	0.6	1.2	1.8	2.4	m	3.6	4.2	4.8	5.4	6.0	$(Ax10^{9})$	sec
0	0	0.8	3.9	2.1	0.6	0.2	0.1	0.0				4.0	1.5
0.35	0	0.6	3.2	2.6	0.9	0.4	0.2	0.1				3.5	1.5
0.70	0	1.0	3.3	2.0	0.8	0.3	0.2	0.1	0.1	0.1	0.1	4.0	1.5
1.05	0	0.6	2.8	2.4	[.]	0.4	0.2	0.2	0.1	0.1	0.1	3.7	1.6
1.40	0	0.2	2.8	4.6	1.5	0.4	0.3	0.2	0.1	0.1	0.1	5.2	1.6

at best, seem to show that the atom cloud is quickly formed, and diffusion or turbulence effects determine the shape of the cloud. The cloud moves vertically, and the atom population now spreads out in the vertical direction and remains relatively constant in the horizontal direction. This effect could be caused if the sheath gas moves the atoms in the center of the cloud faster than it moves the atoms at the edges. At large distances (approximately 1 cm) above the atomizer the atom population sharply rises to a peak value, and then decays. The atomic vapor cloud is probably moving at the same velocity as the sheath gas at this point.

This hypothetical mechanism of atom cloud formation is shown diagrammatically in Figure 28. The shapes shown are approximate profiles of the atomic vapor cloud. The cloud almost instantly spreads to its maximum width, but whether this is due to turbulence or diffusion is not known. As it rises, the bottom of the cloud is pushed through the center. These effects eventually become smaller as the cloud rises. Obviously, much more work needs to be done in this area.



Figure 28. Peak Atom Population Profiles.

### VII. APPLICATION OF EXPERIMENTAL RESULTS

The results presented in Chapter V and Chapter VI cannot be treated as fully conclusive. These results merely guide the direction of future research. Even before the study was started, the platinum loop atomizer was known to be of little analytical utility. The simplicity and ease of automation, however, made it possible to perform a detailed study of the process of atomization and the effects of the instrumental parameters on the readout.

The general relationships presented in the previous two chapters can be expected to apply to any filament-type atomizer. From these relationships and from independent work performed by Mr. Akbar Montaser (7), a radical new atomizer has been developed. This atomizer, formed from a graphite braid, shows many of the advantages of the platinum loop atomizer, but the maximum temperature of the graphite braid is considerably higher than that of platinum loop.

In this section, a description of the modification to the instrumentation will be presented. These modifications are based on the knowledge gained from the initial studies of the platinum loop atomizer. The new spectrometer system is fully characterized by experimental and theoretical conditions.

The graphite braid atomizer (GBA) has been characterized by a study similar to that performed on the platinum loop atomizer. The experimental work, however, is not as detailed as for the platinum loop. The GBA has been applied to some difficult analytical problems and the results are critically compared to those achieved with the

platinum loop atomizer.

## A. Optical Considerations

The work described previously was performed with a "traditional" atomic fluorescence spectrometer. Tradition carries little weight in scientific investigations. The optical system that was used was especially suspect, and was thus re-examined.

#### 1. The Monochromator

The fluorescent radiance was rendered monochromatic by a Czerny-Turner mount grating monochromator. The monochromator (EU-700, Heath/ Schlumberger) has been characterized for spectral purity and transmission factors at the wavelength of interest.

a. <u>Slit transfer function</u>. The monochromator disperses the optical spectrum along a plane. As the exit slit moves across this plane, a portion of the dispersed spectrum appears at the output. The exit slit function is a rectangle; all light within the slit jaws is passed through and all other light is blocked. The entrance slit behaves in a similar manner. The total spectrometer response (slit function) is limited by the convolution of the two equal slits which produces a triangular slit function.

If the slits are perfect, and the smallest field stop in the monochromator is fully illuminated by a continuum source, then the output will be an isosceles triangle, with a width at half height equal to the spectral bandpass. The spectral bandpass is given by the product of the reciprocal linear dispersion and the slit width. These parameters are obviously important to measure.

An easy method of measuring the slit function is to scan the output of the monochromator with a second monochromator. The first monochromator, acts as a light source for the second monochromator. If the slit width of the second monochromator is much smaller than the slit width of the first monochromator, then little distortion will be introduced. The results of this experiment are shown in Figure 29.

The experimental relationship shows a width at half height of 1.75 nm. Since a 1 mm slit was used, this implies that the reciprocal linear dispersion is 1.75 nm/mm. This relationship, however, only holds if the slit function is triangular. That is clearly not the case. The slit function shows aberrations due to coma (106). The base of the observed relationship should be 3.5 nm; it is actually 4.30 nm implying that the reciprocal linear dispersion is 2.15 nm/mm. The "true" value is thus somewhere between 1.75 and 2.15 nm/mm. The model EU-700 monochromator is specified to have a reciprocal linear dispersion of 2.0 nm/mm (107).

b. <u>Monochromator transfer coefficient</u>. After the monochromator output was categorized for spectral purity, it was then analyzed for the transfer coefficient, the ratio of the output flux to input flux.

This was accomplished by recording the spectrum produced by a light source and one monochromator and then inserting a second monochromator between the first monochromator and the detector. Any perturbation would be due to the transfer function of the monochromator. The results were not too surprising: at 230 nm, the monochromator passes 5.64% of the light within the spectral bandpass. The transfer function rises to about 10% at 450 nm. A loss of 95%



Figure 29. The Slit Transfer Function.

of the fluorescent radiance cannot possibly help the S/N.

c. <u>Stray radiant energy</u>. Not all the radiation at the exit slit is monochromatic. A fraction of the output is not within the monochromator spectral bandpass. The methods most commonly proposed to determine the amount of non-monochromatic light are not directly applicable to monochromators that will be used with line sources. Stray light, or stray radiant energy (SRE) affects AA measurements to a greater extent than AF.

Stray radiant energy in monochromators is a prominent reason for deviation from Beer's law. Both atomic absorption (AA) and molecular absorption measurements are affected by SRE, which is often called stray light. Since stray radiant energy can determine the upper limit of absorbance which can be measured without significant error, it is important to have adequate methods for determining the stray light levels in monochromators under the actual conditions used for analysis.

For atomic absorption measurements, the stray light considerations are somewhat different than for molecular absorption, because AA spectrometers generally employ line sources, such as hollow cathode discharge tubes, while molecular absorption spectrometers employ continuum sources, such as tungsten or deuterium lamps. Thus, stray light levels cannot be directly compared for the methods. For AA spectrometry, it is desirable to determine stray radiant energy levels with a line source as the primary radiation source, under the experimental conditions (slit widths, wavelength, source intensity, etc.) to be used in actual AA analyses.

The problems caused by stray light in monochromators have been cited in the literature for many years (108, 109), and the design of monochromators has often centered around reducing SRE levels to a minimum (110). The SRE level is generally expressed as the ratio of the transducer response to radiation within the monochromator bandpass to the response to radiation outside the bandpass. A variety of methods has been proposed for the measurement of SRE levels with continuum radiation sources (108, 111-116). These methods are similar in that they generally attenuate the radiation within the monochromator bandpass until it becomes comparable to the stray light level. The ASTM method, for example, requires the attenuation of the reference beam of a double beam instrument as well as the attenuation of the radiation in the sample beam (108). Stray light levels measured in this manner cannot be easily extrapolated to AA spectrometers because the sources of radiation are different. The published methods also perform SRE measurements under low light level conditions, and hence low signal-to-noise ratios are obtained, which implies poor precision in the measurement.

A new method for the measurement of SRE levels has been developed. The method is directly applicable to AA spectrometers, and involves amplification of the SRE rather than attenuation of the radiation in the monochromator pass band. Hence, measurements of SRE levels are made under high signal-to-noise ratio conditions. The principles of the SRE measurement technique are presented, and the results of the proposed method are compared with experimental results obtained by the limiting absorbance method (111) in order to show the validity

of the proposed method.

(1). <u>Measurement principles</u>. When a line source is used for excitation, as is commonly done in AA, it is possible to amplify the SRE for measurement purposes, because the radiant power from a line source, impingent on the photomultiplier transducer, is directly proportional to the slit width of the monochromator, whereas the radiant power outside the monochromator pass band varies with the square of the slit width (108). Thus, if the line source in an AA spectrometer is passed through a monochromator to a photomultiplier detector (no flame present), the transducer readout R can be related to the slit width by

$$R = A + BW + CW^2$$
(70)

where W is the slit width, and A, B, and C are constants under conditions of constant photomultiplier supply voltage, line source intensity and wavelength.

When A, proportional to the photomultiplier dark current, is negligible compared to the observed photocurrent, the % SRE can be calculated by

$$% SRE = \frac{C}{B} W \times 100$$
 (71)

In the method proposed here, the parameters A, B, and C are experimentally determined by a curve fitting method which generates the best A, B, and C from an experimental plot of R vs. W.

(2). <u>Experimental measurements</u>. Measurements of the photomultiplier output as a function of slit width for a Cd hollow cathode

lamp were obtained with the instrumentation and parameters outlined in Table 6. A plot of readout vs. slit width was obtained, and the best A, B, and C parameters of Equation (70) were determined from a quadratic least square fit program written in BASIC R/T (real time BASIC) and executed on a PDP 8/e laboratory minicomputer. The individual data points were weighted according to their respective variances.

For comparison purposes, the limiting absorbance method (111) was used as an independent measure of the SRE level. A concentrated cadmium solution (1% by weight) was aspirated into an air-hydrogen flame and absorbance measurements were made as a function of slit width. The atomic vapor was considered to be sufficiently concentrated to absorb essentially all of the radiation at 228.8 nm, so that all the radiation which reached the detector was considered to be outside the absorption bandwidth. The observed absorbance under these conditions is then related to the SRE level.

(3). <u>Results and discussion</u>. The experimental conditions are given in Table 5. The curve fitting program yielded the following:

% SRE = 0.0108 W

where W is the slit width in  $\mu m$ . Thus, for the experimental apparatus and parameters used, which are realistic operating conditions, this relationship could be used to obtain the % SRE at any slit width.

The calculated SRE levels were converted to theoretical limiting absorbances and compared to the measured limiting absorbances. The results of this comparison are shown in Figure 30. The largest



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Experimental Conditions for the Determination of Stray Radiant Energy

A. Instrumentation	
Hollow Cathode Discharge Lamp	JA-45462 (Cd), Fisher Scientific, Waltham, MA.
Hollow Cathode Power Supply	EU-703-30, Heath Co., Benton Harbor, MI
Monochromator	EU-700, Heath Co., Benton Harbor, MI
Burner	"Tri-Flame," Fisher Scientific, Waltham, MA.
Photomultiplier	1P28A, RCA Electronic Components, Harrison, NJ.
Photomultiplier Power Supply	EU-701-30, Heath Co., Benton Harbor, MI
Current to Voltage Converter	Model 427, Keithley Instrument Co., Cleveland, OH.
Readout	EU-805 Universal Digital Instru- ment, Heath Co., Benton Harbor, MI.
B. Parameters	
Hollow Cathode Current	10 mA
Wavelength	228.8 nm
Photomultiplier Supply Voltage	-1000 V
Integration Period	10 sec.
Slit Widths	40 to 2000 μm.

single deviation of any measured absorbance from the calculated absorbance is 17%, and the mean deviation is 10.4%. The good agreement between results obtained with the varying slit width technique and the measured limiting absorbances is an indication of the general validity of the method.

The varying slit width technique should be very useful to the atomic spectroscopist for obtaining SRE levels in monochromators under actual experimental conditions used in analytical procedures. The % SRE is easily obtained from a plot of photocurrent  $v_{\mathcal{B}}$ . slit width. Measurements are made under high signal-to-noise ratio conditions, and therefore measurement precision is generally quite high.

### 2. Nondispersive Optical Systems.

a. <u>Advantages</u>. For many AF measurements, the transmission of the monochromator will limit the maximum S/N. Since the atomic fluorescence is already highly monochromatic, perhaps a monochromator isn't really needed. Jenkins (117) proposed that filters be used. Walsh suggested that a solar blind PMT could be used without filters (118). This type of PMT has a photocathodic surface which is insensitive to radiation of wavelengths longer than 320 nm. Such an instrument was built and characterized by Vickers *et al.* (119). An improvement of 700-fold was found for the AF signal from zinc when either a filter, or solar blind PMT was used in place of a dispersive monochromator.

b. <u>Experimental</u>. Atomic fluorescence data were obtained while using a monochromator, filter and just a solar blind PMT. The same PMT was used throughout the experiment. The filter-solar blind combination was found to be superior, probably because the background observed by the solar blind was high, and degraded the S/N. The background signal when just the solar blind PMT was used was  $10^{-4}$  A. This is largely due to scattering of the light source radiation (including nonresonance lines) from the reflective surfaces in the atomizer assembly.

The background signal with the monochromator was minimal, probably because the monochromator has well defined spatial resolution as well as wavelength resolution. One of the reasons that the background was so high when the solar blind PMT was used is that the solar blind "sees" a great deal more than just the atomic vapor. The monochromator also produced the smallest signal.

The filter was a compromise; it excluded the background to a far greater extent than the signal, thus increasing the S/N. The filter cannot be considered to be optimum. A much better method would be to limit the aperature of the solar blind PMT and/or design the atomizer chamber to contribute minimal scattering to the AF signal.

### **B.** Photocurrent Integration

The photocurrent was integrated by a computer-controlled fixedtime digital integrator. The software was kindly provided by Akbar Montaser (7). The computer was also used to supply timing signals to the sampler and to provide control over the electrical heating of the atomizer.

The fixed-time integrator summed a number of analog-to-digital conversions over the atomization time. The atomization time was actually set to be the product of the number of digitizations and the digitization period. The latter two parameters are set in an initial dialogue between the operator and the computer.

The integrated AF signal is printed out on a teletype in arbitrary units; these have been converted to coulombs for presentation in this work.

# C. The Sampling System

The sampling system described in Chapter IV was replaced by an adaptation of a commercial system. A micro-dispenser, capable of dispensing 0.25 to 20  $\mu$ l samples, (Model ULD-020, Hacker Machine, Dansville, MI) was used in conjunction with a syringe needle. To place the sample on the loop, the syringe needle was lowered to the atomizer and then the dispenser pumped a sample onto the atomizer. The syringe needle was withdrawn after the sample had been placed on the atomizer. The position of the syringe needle was determined by pneumatic cylinders. The sampler needed only one pulse to complete the entire sampling sequence; the timing was performed under computer control.

#### D. Temperature Programming

One of the largest limitations of the platinum loop system is inherent in the atomizer power control. The power setting is critical; the applied power must be low enough to gently desolvate the sample yet high enough to atomize it. Choosing the lower level is difficult, but not impossible for cadmium samples in aqueous matrices. It might, however, be truly impossible for other elements or other matrices. The obvious solution is to use a multi-step heating sequence. A low power may be used to desolvate the sample, followed by a higher power to ash the sample, and a still higher power to atomize the sample. The power applied in each step, and the length of time that the power is applied, must be easily varied.

A flexible, programmable power supply was fabricated by controlling a commercial dc supply (LK 350, Lambda Electronics, Melville, L.I., NY) by a computer. The computer was programmed to use a digitalto-analog converter (DAC) to produce any desired voltage in the range 0 - 10 V. This voltage was buffered and presented to the power supply. The power supply followed the input voltage, and was capable of controlling up to 35 A. The precise voltage applied to the atomizer, and the length of time this voltage would be applied, were established in an interactive dialogue between the computer and operator. The computer program was written by Mr. Akbar Montaser (7) and used with his kind consent.

The optimization procedure is actually easier with a three step program than without it. The temperature during the first step is adjusted slightly higher than the boiling point of the solvent. The temperature in the second step is adjusted so that the sample is heated hot enough to vaporize any organic material present, but not hot enough to vaporize the sample. The difference in the ashing and atomizing temperatures is usually 1000 K, so this step is not usually critical. The atomization step is also relatively noncritical. The integrated AA or AF signal was shown to be independent of atomization time by Equation (28). The time for each of the steps in the temperature program is easily optimized. The step should be terminated as soon as the desolvation (or ashing or atomization) has been accomplished. If the time selected is much longer than necessary, the lifetime of the loop may be affected adversely. There will be no effect on the signal.

The temperature of the atomization step can be expected to produce results similar to those in Figure 19 and 20. The effects of varying the ashing temperature are shown in Figure 31. The matrix, 6% bovine albumin, approximates a serum matrix. This matrix will be referred to as "serum" in the following discussion. The serum has approximately correct amounts of sodium, potassium, etc. added to the protein.

The ashing of a viscous, high organic content matrix would seem, at first glance, to be critical. In actuality, there is a wide range of temperatures which give acceptable results. The S/N does go through a maximum, however. The length of the vertical bars in Figure 31 represent the relative standard deviations of three measurements. The best precision (highest S/N) occurs at the same location as the peak signal. This is to be expected, because the ashing step will affect the signal far more than it will affect any noise source.

Note that the temperature axis in Figure 31 has no units. The "temperature" programmer actually controlled the *voltage* across the filament, rather than the temperature of the filament. Assuming only Ohmic heating, then the temperature T is given by

$$T = B \frac{V^2}{R}$$
(72)



where R is the filament resistance, and B is an experimental constant. Temperature, then, is directly proportional to voltage. The two will be used interchangeably in future discussion.

# E. Analytical Applications

The fully optimized nonflame spectrometer was used to determine the cadmium concentration in various matrices. The various matrices put a new element into the optimization procedure; not only must S/N be considered, but selectivity must also be optimized.

## 1. Optimization for Selectivity

The analytical chemist is seldom presented with an unknown quantity of analyte dissolved in distilled-deionized water. The bulk of the analytical samples can be expected to be in a matrix considerably different than pure water. The work of West and coworkers (46-58) has shown that the matrix can significantly affect the analytical results. The volatile metals, such as cadmium and zinc (47) are particularly prone to interferences from the matrix. The experimental matrix study was performed using cadmium as a test element, so the interferences would be maximized. Atomic fluorescence spectrometry was used to monitor the cadmium concentrations. West has also found AFS to be less selective than AAS above a filament atomizer, so the measurements can be expected to be a "worst case" representation of matrix effects. The temperature program was optimized for selectivity. Long, low temperature desolvation and ashing times (approximately 10 sec and 30 sec, respectively) were used to insure complete desolvation and ashing. These steps were found relatively easy to optimize. The atomizing temperature, however, was more difficult to optimize for the complex matrices. It was adjusted to produce a relative standard deviation of less than 10% and signal-to-blank ratios of greater than 100 for a 1  $\mu$ g/ml standard. These criteria were arbitrarily defined as "good precision" and "good" selectivity. The results and experimental conditions appear in Table 7.

# 2. Calibration Plot

Cadmium standard solutions were prepared in three matrices; high purity water, serum, and saline. The serum was a 1 to 100 dilution of a control serum (Cation-Cal. Scientific Products, Detroit, MI) in water. The saline solution was  $1.0 \mu g/l$  of NaCl in water. The data are presented in Table 7 and plotted in Figure 32. One can easily see that the matrix affects the integrated signal to an extent that cannot be ignored. These data are difficult to explain. The signal from the aqueous solution approaches the predicted unity slope, but the linear range has been compressed from 2 orders of magnitude to 1.5 orders of magnitude. No study has been performed on the effects of instrumental parameters on linearity; such a study might explain these data.

Α.	Atomizer P	arameters			
	Desolvatio Ashing Atomizatio	n	0.385 V, 2 0.525 V, 4 0.875 V, 3	0 sec 5 sec .67 sec	
Β.	Optimizati	on	Integrated	Fluorescen	ce, C x 10 <sup>7</sup>
	1 µg/ml Cd	in H <sub>2</sub> 0	4.07±3.8%		
	l µg∕ml Cd	in serum	4.04±5.9%		
	l μg/ml Cd 1000 μg/ml	in NaCl	3.35±4.8%		
C.	Calibratio	n Results			
Cad cen µg/	mium con- tration, ml	Absolute Value, g x 10 <sup>9</sup>	Integrated H <sub>2</sub> 0	Fluorescen Serum	ce, C x 10 <sup>7</sup> NaCl
0. 0. 0. 0. 1. 2. 5.	01 02 05 10 20 50 0 0 0	0.04 0.08 0.20 0.40 0.80 2.0 4.0 8.0 20	0.28±0.03 0.31±0.03 0.52±0.04 1.10±0.09 2.34±0.09 4.00±0.15 4.08±0.15	0.52±0.20 0.72±0.06 1.34±0.02 4.04±0.24 3.41±0.14 4.56±0.35	0.83±0.06 1.61±0.08 2.34±0.10 2.00±0.05 3.35±0.16 3.25±0.15 4.00±0.44 4 20±0 39

Table 7. Matrix Effects on Platinum Loop Atomization

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Figure 32. Calibration Plot for Cadmium in Several Matrices Obtained with Temperature Programmed Atomization.



Calibration Plot for Cadmium in Several Matrices Obtained with Temperature Programmed Atomization. Figure 32. explain these data.

The data from the AF of cadmium in the serum matrix are linear, but show log-log slopes that are less than unity. The same holds for the NaCl matrix. The possibility of condensation reactions in the vapor phase, as proposed by West (48), or quenching due to collisions cannot be clearly distinguished by this experiment. The atomization for cadmium at a platinum loop is highly efficient for aqueous solutions, but may be easily dependent on the matrix. The interference mechanism cannot, as yet, be determined exactly.

## F. The Graphite Braid Atomizer

In separate work in these laboratories Akbar Montaser (7) investigated the possibility of using a graphite braid as a nonflame atomizer. His initial investigations were quite promising, and a collaborative study ensued. The results of the collaborative study can be found elsewhere (8). The calibration plots for the integrated AF signals from cadmium and zinc were linear over 2-3 orders of magnitude and detection limits were approximately  $10^{-11}$  g. Copper and lead were measured by AAS and showed similar linearity and detection limits. These results were obtained without a rigorous optimization. The quality of the initial results indicate that the graphite braid atomizer (GBA) warrants further study.

### 1. Advantages

The atomizer is composed of thousands of fine graphite fibers woven into a braid about 1.5 mm in diameter. The braid is strong,

flexible, and can readily be heated to 2900 K with less than 300 W of applied power. The GBA has several interesting properties which contribute to its utility as an atomizer.

a. <u>Desolvation</u>. The largest difference between the GBA and other carbon or graphite atomizers is the ease with which samples may penetrate the GBA. As soon as a sample is placed onto the atomizer, it soaks into the braid. After the sample has soaked into the braid (less than 1 second after sampling) the spatial distribution is established and is independent of time. Varying the time between sampling and desolvation affects neither the mean nor standard deviation of the observed AA or AF signal (8).

Prior to the analysis, the sample resides in the volume between the thousands of graphite fibers. When heated, these fibers act to surround the sample with a highly reducing atmosphere. The possibility of sample explosion is minimized by the micro-furnace environment. The heating during the desolvation and ashing steps is much more efficient due to the large surface area of the GBA.

b. <u>Atomization</u>. The porous nature of the atomizer also makes significant changes in the atomization process. After the sample is atomized, the atoms remain in contact with the braid atomizer for a much longer time than for other filament atomizers. This obviously affords more complete atomization and should give more freedom from interelement effects. The atomic vapor must diffuse through the atomizer, and the diffusion rate will be different for vapors of different atomic weights. This effect, however, cannot be measured at this time.
# 2. Optimization of the Graphite Braid Atomizer

The same general procedure presented in Chapter IV was repeated for the GBA. The results will not be presented in detail, but reference will be made to some of the more important features. The argon sheath gas flow rate, sample size, and position of the viewing window were optimized for the largest signal-to-noise ratio. The results were quite similar to those obtained with the platinum loop atomizer.

The temperature  $v_{\mathcal{B}}$  power relationship was characterized. Temperatures were measured with an optical pyrometer. Only 50 W were needed to heat the atomizer to 2200 K. The relationship between applied power and optical temperature was approximately linear over the region 1100 to 2200 K. The power  $v_{\mathcal{B}}$  temperature relationship was not measured for temperatures less than 1100 K due to the lack of an acceptable temperature transducer.

The effects of atomization temperature on AF signal are presented in Figure 33. The temperature axis is in terms of voltage, the controlled parameter. The vertical bars represent the relative standard deviation of 3 samples. The best precision occurs when the applied voltage is 3.5 V; the maximum signal occurs when 3 V are applied across the atomizer. Thus the optimum S/N occurs when the atomizer is *hotter* than needed for maximum signal, whereas the opposite was true for the platinum loop atomizer. The micro-furnace environment of the braid allows greater heating without sample explosion. This can be expected to minimize matrix effects.

Figure 33. Dependence of Integrated Fluorescence on Atomization Temperature of GBA.



## 3. Analytical Applications

a. <u>Calibration plot</u>. The data taken with the optimized atomizer appear in Figure 34. The linearity is good, over 1.5-2 orders of magnitude and the slope is near unity. The relative standard deviations were typically 4-7%.

b. <u>Detection limit</u>. A modification to the nonflame spectrometer was made prior to the determination of the experimental limit of detection. The faithful cadmium metal vapor discharge lamp was replaced with a microwave excited electrodeless discharge lamp (120). The power supply (Scintillonics Interface, Fort Collins, Colo) was coupled to the discharge lamp by an "A" antenna. The lamp was a quartz tube containing a few mg of cadmium metal and argon at about 1 mm of mercury (121).

The lamp operating temperature was 200° C, and was kept constant by an oven. The applied power was approximately 60 W; the lamp radiance has been found nearly independent of power when properly thermostatted (120).

The data at the limit of detection are presented in Table 8. These data are in terms of integrated fluorescence, uncorrected for background. The mean (signal-background) and the standard deviation of the (signal-background) are calculated from these data. The mean (signal-background) from 3 x  $10^{-15}$  g of cadmium is greater than for water, but the standard deviations are approximately the same magnitude as the signal. Statistical tests are available, however, which will predict whether this difference between the cadmium and the blank is significant. One interesting point is that the variance



	Integra	Integrated Fluorescence, C x 10 <sup>9*</sup>				
Trial	3x10 <sup>-15</sup> cadmium <sup>9</sup>	H <sub>2</sub> 0	Background			
2 3 4 5	-3.18 -7.65 -2.00 -2.42 1.17	-2.10 -1.96 -1.13 -7.62 3.82	-5.19 -4. -4. -5.19 -4.71			
Background <sup>†</sup>	-5.30	-5.59				
Mean (signal-background)	3.67	4.52				
Standard deviation (signal-background)	0.88	1.18	0.22			

Table 8. The Signal at the Limit of Detection

\*The negative sign comes from a voltage offset in the ADC <sup>†</sup>Measured before each series of five samples.

in the background is much less than the variance in the signals. This is one of the major advantages of the low background nonflame atomizer. This was not the case when a metal vapor lamp was used as a source; background noise was higher in that case. The reason is that the stability of the EDL is much higher than that of the metal vapor discharge lamp. Thus the stray light from the EDL is less noisy, and makes minimal contribution to the total noise present at the limit of detection.

The blank (water - background) can be compared to the sample (sample - background) by Student's t test with t defined as

$$t = \sqrt{\frac{\bar{x}_1 - \bar{x}_2}{S}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$
(73)

where  $\bar{X}_1$  and  $\bar{X}_2$  are the mean values for the blank and sample and S is the pooled variance:

$$s^{2} = \frac{\Sigma(X_{11} - \bar{X}_{1})^{2} + \Sigma(X_{12} - \bar{X}_{2})^{2}}{n_{1} + n_{2} - 2}$$
(74)

The experimental value for t (neglecting the variance in the background) is

$$t_{exp} = 6.2$$

The theoretical value of t (8 degrees of freedom) is 5.041 at the 99.9% confidence level. This implies that the difference between the blank and the signal from a 3 x 10<sup>-15</sup> g cadmium sample is <u>highly</u> <u>significant</u>. The true detection limit is obviously less than 3 x 10<sup>-15</sup> g.

c. <u>Matrix effects</u>. The analytical signal from the graphite braid atomizer was examined as a function of the matrix. The atomizer parameters were varied in an attempt to find the best desolvation, ashing, and atomization temperatures. The porous nature of the GBA should make it possible to find one set of conditions that will produce acceptable results for most matrices. The results are shown in Table 9; they are, however, inconclusive.

If selectivity is to be optimized, then a rigorous optimization, as in Chapter IV, must be performed. The GBA should be as free from interferences as are the best furnace atomizers, but this could not be shown. The "optimization" for selectivity consisted of varying only the atomizer temperature; the results, considering the minimum time required for the optimization, were surprisingly good. The very

	Integrated Fluorescence, C x 10 <sup>7</sup> Voltage Across Atomizer (temperature)						
<u>Matrix</u>							
	2.25 V (3.8 sec)	2.45 V (0.4 sec)	3.5 V (0.4 sec)				
H <sub>2</sub> 0	6.86±7%	10.6±3%	2.18±12%				
serum	3.51±20%	9.39±13%	1.77±24%				
NaC1	2.70±30%	6.41±13%	1.97±15%				
Sample Desolvation Ashing	3 μl of l μg/ml Cd 0.70 V, 20 sec 1.40 V, 30 sec						

Table 9.	Effects	of	Atomization	Temperature	on	Cadmium	in	Several
	Matrices	5		·				

worst case, Cd in a 1000  $\mu$ g/ml NaCl, solution showed a depression of 40%. The work of West (46) showed that a 10  $\mu$ g/ml NaCl solution depressed the observed AF signal from cadmium by 10%. When a commercial furnace was investigated (30), a 1000  $\mu$ g/ml NaCl matrix depressed the AA signal for zinc by 100%. Since zinc normally behaves similarly to cadmium in both AAS and AFS, a similar depression is to be expected for cadmium. In the light of these investigations, the GBA appears to be superior in selectivity to either the graphite filament or heated graphite furnace.

#### VIII. SUMMARY

Nonflame atomization has been studied by two different approaches. First the processes occurring during atomization at a very simple nonflame atomizer have been analyzed. The effects of varying the instrumental parameters are elucidated; from a knowledge of how the ultimate readout varies with these parameters, the actual events occurring during atomization can be characterized. The complete characterization of atomization, however, was found to be beyond the scope of this work. If the actual atomization process could be fully characterized, then the analysis conditions could be adjusted to take full advantage of the events occurring during atomization.

Although the processes could not be completely elucidated, some qualitative relationships could be discerned. These relationships were then used to guide the construction of a new, second generation nonflame spectrometer. The second generation spectrometer was designed for maximum analytical utility. The performance of the new system has been compared to the original system and to the work of other researchers.

Nonflame atomization is much easier to study than atomization in a flame. The work performed on the platinum loop atomizer should be expanded in the future. Even though this atomizer has little use in the real world of hard-to-atomize samples, atomization at a heated platinum filament can be studied more easily than atomization at a more complex atomizer.

Among the projects that should be studied in detail is the matrix problem. A study of the mechanism of interelement effects would be a valuable contribution to the information known about nonflame atomization. Another interesting study would be to characterize the linearity of the system. The factors influencing linearity are not really known.

The nonflame atomizer has great potential in the area of elemental analysis. An instrument employing a flame atomizer, for the easily excited elements and a nonflame atomizer for the others could provide a method for quantitative analysis of all naturally occurring elements other than hydrogen, carbon, nitrogen, oxygen, fluorine, and the noble gases. Certainly the potential justifies more research into nonflame atomization.

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VITA

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