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SOME THEORETICAL AND EXPERIMENTAL STUDIES
IN
ATOMIC ABSORPTION SPECTROMETRY

by
JONATHAN CRAIG HUTTON, B. Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University
Ottawa-Carleton Chemistry Institute

Ottawa, Ontario

October 19, 1992

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ATOMIC ABSORPTION SPECTROMETRY"**

submitted by

JONATHAN CRAIG HUTTON, B. Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

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ABSTRACT

Cathodic sputtering in a glow discharge and electrothermal atomization are complementary techniques for producing atoms for measurement by atomic absorption spectrometry. Although both techniques are used routinely by the analyst, a comprehensive understanding of these techniques still eludes the researcher. Fundamental and applied studies of cathodic sputtering in a glow discharge and electrothermal atomization for atomic absorption spectrometry have been conducted. The investigations of cathodic sputtering in a glow discharge have revolved around the development of the techniques of pulsed and transient atomization of solution residues. Cathodic sputtering in a glow discharge is a technique that is traditionally employed for the analysis of solid, bulk samples by atomic emission spectrometry. Atomization of solution residues avoids the limitations that are inherent in the kinetics of production of the steady-state signal that is associated with the atomization of solid, bulk samples. The atomization of solution residues has led to a better understanding of the processes involved in the supply to and removal of atoms from the analysis volume. These studies have enabled the design and construction of an improved cathodic sputtering atomizer for atomic absorption spectrometry. For electrothermal atomization, it has been shown that both the lateral and longitudinal distribution of atomic and molecular species within an electrothermal atomizer can be highly non-homogeneous. The investigation of these non-homogeneous distributions provides a wealth of information for fundamental investigations of the processes involved in the formation and dissipation of species within the atomizer. A charge-coupled device (CCD) imaging apparatus has been constructed to provide both spatial and temporal distributions of atomic and molecular species in the

analysis volume. The ability to compare the experimentally-determined distributions, measured using the CCD-system, with computer-modelled theoretical distributions will lead to a better understanding of the processes that are occurring. The first step in the construction of a comprehensive set of computer models for the description of fundamental processes in electrothermal atomization is presented. The model that is presented predicts the three-dimensional distribution of oxygen molecules within the atomizer. These results provide the foundation upon which further models can be constructed.

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TABLE OF CONTENTS

ACCEPTANCE SHEET	ii
ABSTRACT	iii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xi
LIST OF FIGURES	xiii
INTRODUCTION	1
 CHAPTER 1. TRANSIENT ATOMIZATION BY CATHODIC SPUTTERING IN A GLOW DISCHARGE FOR ATOMIC ABSORPTION	
SPECTROMETRY	6
INTRODUCTION	6
Glow discharge	6
Cathodic sputtering	11
The Atomsource atomizer	15
Transient atomization by cathodic sputtering in a glow discharge	18

THEORY	20
EXPERIMENTAL	22
Apparatus	22
Test Solutions and Reagents	24
Gas	25
Procedure	25
Experimental Conditions	26
RESULTS AND DISCUSSION	29
Kinetic Modelling	29
Analytical Studies	34
CONCLUSIONS	39

CHAPTER 2. PULSED ATOMIZATION BY CATHODIC SPUTTERING IN A

GLOW DISCHARGE FOR ATOMIC ABSORPTION SPECTROMETRY	41
INTRODUCTION	41
EXPERIMENTAL	42
Apparatus	42
Test Solutions and Reagents	43
Gas	43
Procedure	44
Experimental Conditions	44
RESULTS AND DISCUSSION	44
Analytical results	44

Kinetic Modelling	48
CONCLUSIONS	52

CHAPTER 3. THE CONSTRUCTION AND CHARACTERIZATION OF A NEW LABORATORY-CONSTRUCTED ATOMIZER FOR CATHODIC

SPUTTERING IN A GLOW DISCHARGE	53
INTRODUCTION	53
THEORY	55
EXPERIMENTAL	57
Instrumentation	57
Cathodic sputtering atomizer	57
Gas control system	59
Power supply	59
Measurement system	60
Atomic absorption measurements	60
Atomic emission measurements	60
Procedure	61
Steady-state atomization	61
Pulsed Atomization	64
RESULTS AND DISCUSSION	66
Steady-state measurements	66
Pulsed atomization	77
CONCLUSIONS	91

CHAPTER 4. THE SPATIAL AND TEMPORAL DISTRIBUTION OF	
ALUMINIUM SPECIES IN ELECTROTHERMAL ATOMIZATION FOR	
ATOMIC ABSORPTION SPECTROMETRY	94
INTRODUCTION	94
EXPERIMENTAL	99
Digital Imaging System	99
Graphite Furnace	102
RESULTS AND DISCUSSION	107
CCD-Imaging System	107
Distribution of Aluminium Atoms	108
Atomization from the Graphite Tube Wall	108
Atomization from the Graphite Platform	112
Distribution of Aluminium-Containing Molecules	118
Vaporization from the Graphite Tube Wall	120
Vaporization from the Graphite Platform	123
Mechanism of Atomization	123
CONCLUSIONS	127

CHAPTER 5. THREE-DIMENSIONAL DISTRIBUTIONS OF OXYGEN IN	
GRAPHITE AND METAL TUBE ATOMIZERS FOR ANALYTICAL	
ATOMIC SPECTROMETRY	129
INTRODUCTION	129
THEORY	133

Construction of the Kinetic Model	133
Temperature Dependence for Gas-Phase Diffusion Coefficients	141
Rate constants for oxidation processes	143
Oxygen - pyrolytic graphite	143
Oxygen - Tantalum	147
Oxygen - Tungsten	149
Flux of oxygen through the dosing hole	150
RESULTS AND DISCUSSION	160
Graphite Furnaces	160
Metal Tubes	168
Estimation of the total number of free oxygen molecules	176
CONCLUSIONS	178
SUGGESTIONS FOR FUTURE RESEARCH	179
APPENDIX	185
Calculation of the oxygen flux through the sample dosing hole	185
REFERENCES	190

LIST OF TABLES

Table 1	Hollow-cathode lamps and monochromator settings for the pulsed and transient mode of atomization.	27
Table 2	Discharge parameters for the transient mode of atomization	28
Table 3	Limits of detection and characteristic masses for the transient mode of atomization.	35
Table 4	Discharge parameters for the pulsed mode of atomization.	45
Table 5	Limits of detection and characteristic masses for the pulsed mode of atomization.	47
Table 6	Rate constants for the pulsed mode of atomization.	50
Table 7	Hollow-cathode lamps and monochromator settings for the steady-state mode of atomization.	62
Table 8	Experimental parameters for the determination of the limits of detection using the steady-state mode of atomization.	63
Table 9	Hollow-cathode lamps and monochromator settings for the pulsed mode of atomization.	65
Table 10	Experimental parameters for the pulsed mode of atomization.	67
Table 11	Limits of detection and characteristic concentrations for the steady-state mode of atomization.	78
Table 12	Peak-height limits of detection and characteristic mass for the pulsed mode of atomization.	89
Table 13	Peak-area limits of detection and characteristic mass for the pulsed mode of atomization.	90

Table 14	Experimental conditions for the atomization of aluminium from the graphite tube wall.	103
Table 15	Experimental conditions for the atomization of aluminium from the graphite platform.	104
Table 16	Experimental conditions for vaporization of aluminium-containing molecules.	105
Table 17	Diffusion parameters and diffusion coefficients for oxygen and carbon monoxide in argon.	142
Table 18	Rate constant parameters and first-order rate constants.	148
Table 19	Conditions used for the calculations of the imaged distributions of oxygen.	164

LIST OF FIGURES

Figure 1	Representation of the use of cathodic sputtering in a glow discharge.	7
Figure 2	Schematic diagram of a typical DC glow discharge.	9
Figure 3	A pictorial representation of cathodic sputtering in a glow discharge.	13
Figure 4	Schematic diagram of the Atomsources.	17
Figure 5	Transient atomization of gold.	30
Figure 6	Transient atomization of copper.	31
Figure 7	Pulsed atomization of nickel.	49
Figure 8	Modular diagram of the new, laboratory-constructed atomizer. . . .	58
Figure 9	Emission and absorbance vs. argon flow rate at constant power. . .	70
Figure 10	Discharge voltage vs. argon flow rate at constant power.	72
Figure 11	Emission and absorbance vs. argon flow rate at constant voltage. . .	73
Figure 12	Power vs. argon flow rate at constant voltage.	74
Figure 13	Peak-height and peak-area absorbance vs. power at constant argon flow rate and pressure.	79
Figure 14	Rate constants vs. power at constant argon flow rate and pressure. .	80
Figure 15	Peak-height and peak-area absorbance vs. argon flow rate at constant pressure and power.	82
Figure 16	Rate constants vs. argon flow rate at constant pressure and power. .	83
Figure 17	Peak-height and peak-area absorbance vs. argon pressure at constant flow rate and power.	85
Figure 18	Rate constants vs. argon pressure at constant flow rate and power. .	86
Figure 19	Schematic diagram of the imaging apparatus.	100

Figure 20	Absorbance of aluminium vs. time for the atomization from the graphite tube wall with the associated temperature profile.	109
Figure 21	Images of the atomization of aluminium from the graphite tube wall.	111
Figure 22	Contour maps for the atomization of aluminium from the graphite tube wall.	113
Figure 23	Absorbance vs. time for the atomization of aluminium from the graphite platform.	114
Figure 24	Images of the atomization of aluminium from the graphite platform.	117
Figure 25	Contour maps for the atomization of aluminium from the graphite platform.	119
Figure 26	Images of the vaporization of aluminium-containing molecules from the graphite tube wall.	121
Figure 27	Contour maps for the vaporization of aluminium-containing molecules from the graphite tube wall.	122
Figure 28	Images of the vaporization of aluminium-containing molecules from the graphite platform.	124
Figure 29	Contour maps for the vaporization of aluminium-containing molecules from the graphite platform.	125
Figure 30	Tube atomizer geometry in longitudinal section and cross section.	135
Figure 31	Tube atomizer geometry in normalized, cylindrical coordinates. . .	140
Figure 32	Rate constant vs. temperature vs. log(pressure).	145
Figure 33	Schematic diagram of a Perkin-Elmer HGA-type furnace.	151
Figure 34	Protection coefficient vs. protection parameter.	157

Figure 35	One-dimensional distribution of oxygen concentration along the line "furnace bottom - dosing hole - environment".	159
Figure 36	Distribution of oxygen in the central cross-section of a graphite tube.	161
Figure 37	Distribution of oxygen in the longitudinal section of a graphite tube.	162
Figure 38	Imaged distribution of oxygen in an isothermal graphite tube. . . .	165
Figure 39	Imaged distribution of oxygen in a non-isothermal graphite tube. .	167
Figure 40	Imaged distribution of oxygen in an isothermal graphite tube with impurities in the argon	169
Figure 41	Distribution of oxygen in the central cross-section of a non-isothermal tantalum-lined furnace.	170
Figure 42	Distribution of oxygen in the longitudinal section of a non-isothermal tantalum-lined furnace.	171
Figure 43	Imaged distribution of oxygen in a non-isothermal tantalum-lined graphite furnace.	173
Figure 44	Imaged distribution of oxygen in an isothermal tantalum-lined furnace with impurities in the argon.	174
Figure 45	Imaged distribution of oxygen in an isothermal tungsten-lined furnace with impurities in the argon.	175
Figure 46	Preliminary correlation between computer modelling and CCD-SSF contour maps.	183
Figure 47	Model of the dosing hole area.	186

INTRODUCTION

A goal in the development of any analytical technique is to be able to perform standardless (or absolute) analysis [1-4]. While many researchers [5-7] have speculated on the potential of electrothermal atomization atomic absorption spectrometry (AAS) as a technique for absolute analysis, this technique still requires the use of an analytical calibration curve. Absolute analysis will require that the following is available: 1) excellent and reliable information about all processes involved in the generation of the analytical signal, 2) correct values for the physical constants related to the formation and dissipation of analyte, and 3) spectroscopic constants that relate the measured absorbance to the number of atoms in the gas phase through a proportionality constant (atomization efficiency - a temperature-dependent, dimensionless constant). Since the above requirements for standardless analysis are difficult to fulfil because of the lack of reliable values for the physical and spectroscopic constants, and the experimental difficulties involved in maintaining 100% atomization efficiency, absolute analysis by electrothermal atomization AAS remains elusive. However, even if absolute analysis is not possible, controllable and predictable atomization can be achieved, making electrothermal atomization AAS a much-used analytical technique.

Atomic absorption spectrometry can be broken down into two simplified steps: 1) the production of atoms from the sample and, 2) the measurement of the absorption of radiation by the atoms. The absorption of radiation by atoms is well understood although there still exist uncertainties in the physical constants relating the number of atoms in the analysis volume to the signal measured. It is the atomization step that is not adequately understood. This is especially true about the knowledge of the mechanisms

of electrothermal atomization. There is considerable controversy about this subject and many contradictory mechanisms for atomization have been published [8].

The inherent limitation of all analytical techniques based on thermal atomization is that the rate of atomization is controlled by the temperature-dependent vapour pressure of the individual components of a sample [9]. This means that the measured analytical signal will represent the composition of the sample only if the sample is completely vaporized and atomized at the time the signal is measured. However, if the process of vaporization and atomization of the sample is rate-limited, the number density of vapour-phase analyte atom will depend not only on the composition of the sample, but also on the rates by which the individual components of the sample are atomized. In such cases, therefore, there can be no conformity between the composition of the vapour and the sample. In a retrospective survey of the first 25 years of atomic absorption analysis [10], Sir Alan Walsh recognized this limitation and concluded, "If atomic absorption methods are to be substantially improved it seems inescapable that the advances can only result from improved methods of atomization." Such improved methods of atomization can grow beyond their present empirical development only when the fundamental processes of atom formation and dissipation in thermal atomizers (*i.e.*, mechanisms of atomization) are fully known and are well understood.

This thesis presents an attempt to meet the challenge of Sir Alan Walsh using two approaches: 1) the development of a new analytical technique - the analysis of solution residues by cathodic sputtering, and 2) the development of diagnostic techniques that will enable a better understanding of the fundamental processes involved in electrothermal atomization to be achieved.

Sir Alan Walsh also made the following comment [10] “.... I believe cathodic sputtering merits further study, since it is a method of atomization which is different in principle to the thermal processes occurring in flames and furnaces. To date all sputtering work has been concerned with steady-state systems. Would it not be worthwhile considering the use of cathodic sputtering in association with the ‘total vaporization’ method evolved by L’vov?” This comment has inspired the study of the atomization of solution residues by cathodic sputtering in a glow discharge. Towards this end two new techniques of atomization have been developed in this laboratory [11]: the pulsed technique and the transient technique of atomization by cathodic sputtering in a glow discharge. During the initial development of these techniques [12-14], the only commercially-available cathodic sputtering atomizer for atomic absorption spectrometry, the Atomsources [15] manufactured by Analyte Co. (Grants Pass, Oregon), was used. Since this atomizer was designed to be used with the conventional steady-state mode of atomization (which has relatively poor sensitivity because of the inherent limitation of the kinetics involved in the generation of a steady-state atom population), a large part of the work involved the identification of limitations of the Atomsources design, and then making modifications for fast kinetics of the pulsed and the transient atomization technique. This was followed by subsequent re-design and fabrication of various components of a new atomizer [16, 17]. In its current state of design, the new atomizer has no components in common with the Atomsources. The first half of this thesis explores and analyzes the evolution of the new atomizer and the concurrent evolution of the understanding of the processes involved in atomization by cathodic sputtering in a glow discharge.

The second half of this thesis is concerned with the development of new techniques for the investigation of electrothermal atomization. The recent introduction of the shadow spectral filming (SSF) technique by Gilmudtinov *et al.* [18, 19] has provided researchers with an excellent tool for probing into electrothermal atomizers and getting unique insights into the processes that are occurring within these atomizers. The SSF technique consists of obtaining a time-resolved, monochromatic image of the interior of a furnace that is illuminated by the radiation from the resonance line of the element being studied. Therefore, the SSF technique provides both temporal resolution and two-dimensional spatial resolution. The original design of the SSF technique uses a conventional movie camera as the detector, and film to record the images. The SSF technique has been modified by employing a charge-coupled device (CCD) camera system as the combined detector and recorder. The digital CCD results are processed, stored, and displayed on a personal computer. The digital results provided by the CCD detector represent a significant improvement in the SSF technique. Properties of CCDs that make them superior to film for recording and storing of images will be described later.

In the study of mechanisms of atom formation and dissipation, three important questions must be addressed: 1) Which species are involved in the atom formation and dissipation process? 2) What is the dynamics of formation and decay of these species? 3) What is the temporal and the spatial distribution of these species? Mass spectrometry can answer Questions 1) and 2), but not 3), whereas the SSF technique can answer all three questions. The significance of using the CCD imaging system to record the SSF images is that it will enable, for the first time, complete understanding of atomization

mechanisms. This understanding is essential for: (I) optimum design of atomizers, and (II) rational development of analytical procedures.

The spatially-resolved distributions obtained by the SSF technique can get support and sustenance from the development of a theoretical framework, enabling one to predict and to correlate the theoretical predictions with the experimental observations. Therefore, a two-pronged research strategy has been initiated: 1) the measurement of the distribution of species within electrothermal atomizers using the SSF technique, and 2) the construction of computer models to simulate the distribution of species within electrothermal atomizers. Although computer models have been used before in the development of the theory of graphite furnace AAS [20-25], their results could only be compared with the spatially-integrated results of conventional graphite furnace AAS. With the availability of the spatially-resolved results of the SSF-CCD technique the comparison between computer-generated prediction and experimentally-determined fact becomes more productive of further development. The comparison of the theoretical prediction (computer modelling) with the experimental observation (SSF-CCD) will enable superior computer models to be constructed for the description of graphite furnace AAS. The first steps in the development of this research program are described in this thesis.

CHAPTER 1

TRANSIENT ATOMIZATION BY CATHODIC SPUTTERING IN A GLOW DISCHARGE FOR ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Cathodic sputtering in a glow discharge is an established technique for producing atoms and/or ions that can be sampled by a variety of atomic spectrometric techniques. The use of several of the more common of these techniques is illustrated in Fig. 1. A description of some of the major features of glow discharges and cathodic sputtering that are important for this thesis are described below. A comprehensive review of theoretical and experimental aspects of glow discharge processes has been written by Chapman [26]. As well, there are a number of well-written review articles [27-30] that are concerned with the use of the glow discharge as an analytical tool. Figure 1 shows that a glow discharge is a versatile tool for producing atoms to be measured by atomic spectrometric techniques. Its versatility comes from the fact that cathodic sputtering provides an atom source while the glow discharge provides an excitation/ionization source. Investigations of glow discharge and cathodic sputtering phenomena have been mostly empirical in nature. Fundamental investigations will lead to a better understanding of the processes that are occurring and this, in turn, will lead to better analytical results.

Glow discharge. A glow discharge is one type of gas discharge. The term "gas discharge" refers to the flow of electrical current through a gas. For this to occur requires both that the gas is ionized and an electrical field is present. Typically, the gas is situated between two electrodes to which a DC potential is applied. There are three

Figure 1. Representation of several frequently-used analytical atomic spectrometric techniques that can be employed with cathodic sputtering in a glow discharge.

types of gas discharges: 1)) a Townsend discharge, characterized by a very low current (nA - μ A), 2) an arc discharge, a high current discharge in which the source of electrons is from thermionic emission from the cathode, and 3) a glow discharge. The current in a glow discharge is intermediate between the other two discharges and is in the range from a few milliamps to close to one amp. A glow discharge is a plasma, which is a partially ionized gas consisting of approximately equal number of positively and negatively charged species with a large majority of neutral species. The low-pressure DC glow discharge is easy to produce and maintain. It also has the added benefit that it is self-sustaining. Therefore, a glow discharge does not require an external source for ionization.

A glow discharge is made by applying a high voltage to a reduced-pressure inert gas that is situated between two electrodes. The electrons necessary to sustain a glow discharge are produced by emission from the cathode surface as a consequence of bombardment by positive ions. It is thought that the incoming positive ion is neutralized by an electron that is ejected from the surface before the ion collides with the surface [31]. This neutralization energy is transferred to the lattice where it may cause ejection of secondary electrons.

There are many different zones in a glow discharge. The number and type of the zones present is dependent on the cell configuration. A few of these zones are illustrated in Fig. 2 which is a schematic diagram of a typical glow discharge. The two most important regions of a glow discharge for quantitative determination are the cathode dark space and the negative glow. A glow discharge can exist without all zones except the cathode dark space [32]. As the name implies, the cathode dark space is situated

Figure 2. A schematic diagram of a typical DC glow discharge showing the location of the cathode dark space and the negative glow.

adjacent to the cathode surface. The secondary electrons that escape from the cathode surface are accelerated into the dark space where they may cause ionization. This ionization leads to a multiplication in the number of electrons and at the same time an equal number of positive ions are created. Since the electrons continue to traverse the glow discharge and do not remain in the cathode dark space, a region of positive space charge is created in front of the cathode which leads to a large potential gradient. The majority of the discharge potential is consumed in the cathode dark space and this voltage drop is known as the cathode fall potential [28]. As the distance from the cathode is further increased, further electron multiplication leads to a decrease in the positive space charge and at the boundary between the cathode dark space and the negative glow nearly all the current is carried by electrons. There are two types of electrons present in the glow discharge; fast electrons and slow electrons. As the fast electrons slow down their ability to ionize diminishes, but, at the same time their ability to cause excitation increases. Therefore, the most intensely glowing region is at the cathode dark space / negative glow interface. There remains only a slight electric field in the negative glow, and positive and negatively charged species are present in nearly equal numbers in this region.

There are two broad classifications of glow discharges based on their current/voltage behaviour. These two types of glow discharges are called normal and abnormal glow discharges. The normal glow discharge is characterized by a constant current density and a constant voltage. In this type of discharge the glow covers only a fraction of the cathode surface. Therefore, as the applied current is increased the fraction of surface coverage also increases in order to maintain the constant current

density. As soon as the cathode surface is completely covered by the glow discharge, further increases in the current require a greater current density. This requires more electrons which in turn requires a greater cathode fall potential (*i.e.*, as current increases, voltage increases). These are the characteristics of the abnormal glow discharge. Since there is complete surface coverage by the glow in the abnormal discharge there is more homogeneous sampling of the surface. Therefore, it is the abnormal glow discharge that is used in analytical applications.

The interaction of the gas-phase ions with the solid surface of the electrodes is a complex physico-chemical process known as cathodic sputtering. At first this process was considered a nuisance because it interfered with studies of the glow discharge. However, when it was realized that the process of cathodic sputtering can be exploited to give compositional analysis of the cathode surface, its benefits far outweighed its disadvantages. Usage of the glow discharge in analytical chemistry relies on the process of cathodic sputtering since it is this process that provides the atom population for measurement. Sputtering occurs on the cathode surface only. The anode does not emit particles and only serves to collect electrons. Cathodic sputtering appears to be a simple technique for producing an atomic vapour. However, the processes involved are quite complex and are not yet fully understood.

Cathodic sputtering. Cathodic sputtering in a glow discharge is an electrical means of atomization in which atoms of the cathode are ejected from the cathode into the vapour phase as a result of bombardment by and subsequent momentum transfer from accelerated discharge-gas ions to the target cathode material. Positive gas-phase ions that enter the cathode dark space / negative glow interface are accelerated across the cathode dark

space by the cathode fall potential. The highly energetic ion collides with the cathode surface, penetrates the surface, and then dissipates its energy to the surface atoms. The remaining potential energy of the ion leads to the ejection of secondary electrons. The kinetic energy of the bombarding ion is transferred to lattice atoms through collisions that are both elastic and inelastic. The resultant billiard ball-type collisional cascade propagates in random directions. If a surface atom receives energy that exceeds its surface binding energy and if the collision occurs in the right direction then the surface atom is ejected from the cathode. This process is known as physical sputtering.

There are numerous types of species that are sputtered from the cathode surface. The majority of the sputtered flux consists of neutral particles. Most of these neutral particles are atoms, although molecules, dimers and clusters have also been reported [28, 33, 34]. A significantly fewer number of the species are sputtered as positive and negative ions. However, any positive ions that leave the surface do so only briefly and they are quickly re-accelerated towards the cathode. Secondary electrons and photons are also emitted from the cathode surface. This whole process is represented pictorially in Fig. 3. The sputtered neutral particles exist mostly as ground-state species. The estimated fraction of excited state species is approximately 1% [35]. In a glow discharge, electron impact ionization accounts for another 1% of the total population, while Penning ionization (collision with metastable discharge gas atoms) can account for up to another 10% [36]. Nonetheless, the particles present in a glow discharge are mostly ground-state neutral atoms, which is the ideal situation for atomic absorption spectrometry.

An important characteristic parameter of the cathodic sputtering process is the

Figure 3. A pictorial representation of cathodic sputtering in a glow discharge showing different species that are present and different processes that are occurring.

sputtering yield. The sputtering yield is defined as the number of particles ejected from the cathode surface per primary ion collision. The sputtering yield is dependent on both the projectile (flux, type and energy) and the target (crystal structure and surface binding energy) [27]. The sputtering yield is also dependent on both the state of surface roughness as well as the presence of surface impurities. Therefore, pre-sputtering, or sputter-cleaning, gives the most reproducible surface for sputtering. For a given projectile/target combination, the sputtering yield increases with the energy of the projectile. Since the sputtering rate is the product of both the sputtering yield and the flux of bombarding particles that collide with the surface, the sputtering rate increases with both the ion energy (which is proportional to the cathode fall potential) and the electrical current [27]. Argon produces the highest sputtering yields for copper [37] and copper, silver, and gold have highest sputtering yields among transition metals. Most of the studies that have been conducted have used argon bombardment of copper cathodes.

As mentioned above, the sputtering yield is dependent on the cathode material and all materials do not have identical sputtering yields. Luckily, sputtering yields rarely differ by more than a factor of 10, whereas evaporation rates for metals can be different by many orders of magnitude. For example, the sputtering yields for aluminium and tungsten differ by only a factor of 2. Yet, the rates of evaporation of these two metals differ by nine orders of magnitude at 2000 °C [31]. Therefore, the relative amounts of aluminium and tungsten in the gas phase will be more representative of the original matrix in the case of cathodic sputtering as opposed to the situation that would exist if aluminium and tungsten were atomized by a thermal means of atomization.

Cathodic sputtering in a glow discharge was recognized as a promising technique for atomization for atomic absorption spectrometry as early as 1959 by Russell and Walsh [38]. So far, however, its application has been limited mostly to the direct, emission-spectrometric analysis of solid, conducting samples to generate a steady-state atomic vapour. The main reason that cathodic sputtering in a glow discharge for atomic absorption spectrometry has never become established as a much-used technique is that it has only given relatively poor sensitivity [39]. Cathodic sputtering in a glow discharge is nonetheless an electrical means of atomization that is a potential solution to the thermal atomization problem.

One of the main problems with cathodic sputtering in a glow discharge for atomic absorption spectrometry is the transport of the sputtered atoms from the cathode surface to the analysis volume. The sputtered neutral particles leave the surface and enter the analysis volume by concentration diffusion. Therefore, there exists the probability that the atoms will redeposit on the cathode surface. The redeposition of neutral particles is an extremely undesirable side-effect of the cathodic sputtering process. At an argon pressure of 1.5 Torr it has been estimated that as much as 95% of the sputtered atoms are redeposited [40]. At higher pressures the amount of redeposition increases. This leads to only a small fraction of the sputtered atoms being available to produce the analytical signal. Therefore, the atomizer must be designed to reduce the problem of redeposition.

The Atomsource atomizer. The Atomsource atomizer, manufactured by Analyte Corporation (Grant's Pass, Oregon), was introduced in 1986, and is the first commercially-available cathodic sputtering atomizer designed for atomic absorption

spectrometry [15]. Figure 4 is a schematic diagram of the Atomsources. The anode/cathode geometry of the Atomsources produces a Grimm-type discharge [41]. A Grimm discharge refers to a discharge that is both abnormal and obstructed. An obstructed discharge is designed with the anode close enough to cathode to be in cathode dark space. The fact that the discharge is abnormal means that the whole cathode surface is subject to cathodic sputtering. The Atomsources are designed with a T-shaped geometry to avoid the background emission that is reported to be a limiting factor [42]. Therefore, there is a spatial separation between the cathode surface which is a source of intense emission, and the analysis volume (defined by the beam of radiation from the hollow-cathode lamp). The vacuum ports that are shown in Fig. 4 serve to pull sputtered atoms along the light path. This increase in path length leads to a corresponding increase in sensitivity. However, the main feature of the Atomsources design is the gas jets. The gas jets, first employed by Gough [39], significantly reduce redeposition of sputtered material by sweeping atoms away from the cathode surface and into the analysis volume. In the Atomsources design there are six concentric jets focused on the cathode surface. These jets produce a distinctive six-cavity depression on the cathode surface that indicate that either sputtering is more intense or redeposition less where the jets strike the surface. Kim and Piepmeier [43] have shown that the use of six gas jets (as in the Atomsources) significantly increases the rate of sputtering over that provided by either a static system (*i.e.*, with no gas flow) or the use of a single gas jet, such as that used by Gough [39]. In a review article [30] it was predicted that the Atomsources would lead to a renewed interest in atomic absorption spectrometry using cathodic sputtering in a glow discharge. The first published work using the Atomsources atomizer demonstrated the capability of

Figure 4. A schematic diagram of the Atomsource. Shown in this diagram are: (a) sample cathode; (b) atomizer body; (c) vacuum port; (d) gas jets; (e) quartz windows; (f) water cooling jackets; (g) cathode plate; and (h) sample clamp.

the Atomsource for direct analysis of solid conducting samples by atomic absorption spectrometry [15].

Analytical applications of cathodic sputtering in a glow discharge have almost wholly involved the production of a steady-state atomic vapour from a bulk solid. Limitations of the kinetics inherent in the production of a steady-state atomic vapour result in relatively poor sensitivity and limits of detection for the steady-state mode of atomization. A method that overcomes these limitations, using the rapid generation of analyte atoms from the atomization of solution residues to produce a greater transient concentration of atoms in the analysis volume than is possible for the steady-state mode of atomization, has been described [12]. Transient atomization of solution residues (involving rapid kinetics of atom formation) by cathodic sputtering (which has none of thermal atomization's vapour-pressure dependence) in a glow discharge is a promising new technique for atomic absorption spectrometry.

Transient atomization by cathodic sputtering in a glow discharge. The sensitivity of the steady-state technique is relatively poor because of the inherent limitation in the analytical sensitivity of all techniques based on a steady-state population, and because in the solid, bulk samples the analyte is more strongly bound in the three-dimensional lattice of the sample matrix than for a solution residue on the cathode surface. An increase in the sensitivity can be obtained by basing the analytical determination on the transient atomization of solution residues of samples. The transient mode of atomization uses a high-power discharge for rapid production of analyte atoms. An important factor leading to the rapid production of analyte atoms is the difference in bonding between analyte in the solution residues and the analyte in the solid, bulk samples. The faster kinetics of

atom formation for the transient mode of atomization result in better sensitivity for this mode of atomization compared to the steady-state mode of atomization.

Glow discharge atomic emission spectrometry has been applied to the analysis of microlitre solution samples [44] and to the analysis of microsamples [45]. Ultra-trace analysis of aqueous solution residues using atomic absorption spectrometry has been reported by Bruhn and Harrison [40], and more recently, using the commercial Atomsorce, by Ohls [46]. Ohls [46] has demonstrated atomic absorption analysis of solution residues of refractory elements, lanthanum and zirconium, using the Atomsorce. However, the most extensive examinations of the atomization of solution residues by cathodic sputtering in a glow discharge have been conducted in our laboratories [11-14, 16].

For the initial investigations of the atomization of solution residues by cathodic sputtering in a glow discharge for atomic absorption spectrometry [12], the Atomsorce was set-up as the manufacturer (Analyte Corporation) intended. The atomizer was used as a replacement for the flame attachment in a conventional spectrophotometer. Preliminary fundamental investigations as well as the determination of analytical figures of merit were performed with the Atomsorce being used in this configuration [12].

This thesis begins with an investigation of analyte introduction and removal from the analysis volume by kinetic analysis using the atomizer in a conventional spectrophotometer. The kinetic analysis revealed limitations associated with the use of the conventional spectrophotometer. The spectrophotometer was subsequently replaced and the improvement in the new analytical technique in terms of sensitivity and limits of detection over previously obtained results is shown.

THEORY

For simplicity, the kinetic analysis is confined to the introduction of atoms into and the removal of atoms from the analysis volume. If the atoms are sputtered direct from the surface of the cathode without the formation of any condensed-phase or gas-phase intermediates, and the convection/diffusion of the atoms out of the analysis volume is a first-order process, then atom introduction and atom loss can be represented by the following consecutive, first-order reactions:

where A represents the analyte atoms entering the analysis volume, B the analyte atomic species within the analysis volume, C the analyte atomic vapour that has been lost from the analysis volume by diffusion/convection, and k_1 and k_2 are first-order rate constants for the introduction of atoms into and their subsequent loss from the analysis volume, respectively. It should be stressed at this point that the geometry of the atomizer has a spatial separation between the location of atom formation (the cathode surface) and the analysis volume (defined by the geometry of the beam of radiation from the hollow-cathode lamp), as seen in Figure 4. Therefore, the rate of analyte atom formation at the cathode surface cannot be measured directly, and may be different from the rate of introduction of the analyte atoms into the analysis volume.

When there are no analyte atoms initially present in the analysis volume, the mechanism shown above yields the following equation for the time-dependent concentration of analyte atoms within the analysis volume, B_t :

$$B_t = A_0 \frac{k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \quad (2)$$

The form of this equation requires that the concentration of B, initially zero, increases to a maximum and then decays at a rate that is controlled by the smaller of the two rate constants.

When one of the rate constants is smaller than the other the tail of the absorbance profile decays exponentially at a rate controlled by the smaller of the two rate constants as follows:

$$B_t' = C A_0 e^{-k_a t} \quad (3)$$

where B_t' is the concentration of B at later times, C is a constant dependent upon which of the two rate constants is smaller, and k_a is the smaller of the two rate constants. Therefore, a plot of $\ln(B_t')$ vs. t has a slope = $-k_a$ and an intercept = $\ln(C A_0)$. The value of the intercept, and therefore also of the peak-height absorbance depends on C, the value of which depends on which of the rate constants is larger than the other. From Eqn. 2, if $k_1 > k_2$, then $C \approx 1$; whereas if $k_2 > k_1$, then $C \approx k_1/k_2$, which is less than 1 since $k_2 > k_1$. The maximum sensitivity can therefore be predicted when $k_1 > k_2$, i.e., when the atomization is rapid.

To get the larger of the two rate constants, first the difference between Eqns. 2 and 3 is taken:

$$B_t' - B_t = \Delta B = C A_0 e^{-k_b t} \quad (4)$$

where ΔB is the difference between the measured absorbance due to B and the extrapolation of Eqn. 3, C is as previously defined, and k_b is the larger of the two rate constants. It can be seen that a plot of $\ln(\Delta B)$ vs. t has a slope = $-k_b$ and an intercept

$= \ln(C A_0)$. The two kinetic plots, $\ln(B_1')$ vs. t and $\ln(\Delta B)$ vs. t , are used to determine the magnitude of the two rate constants.

The above method (to be called the "kinetic plot" method) requires lengthy data treatment and is used only to check that the plots generated are indeed linear. In practice, k_a is determined from the half-life of the signal decay (*i.e.*, $k_a = \ln 2/t_{1/2}$). This value for k_a and the time required for the signal to reach its maximum value, $t_{\max}$, is then used to determine k_b using the following equation;

$$t_{\max} = \frac{\ln k_a - \ln k_b}{k_a - k_b} \quad (5)$$

The values obtained in this manner can be easily checked against those obtained using the "kinetic plot" method, and this was done frequently.

The validity of the above model can be tested by determining the rate constants from an experimental absorbance profile and then using these values to calculate a theoretical absorbance profile using Eqn. 2. The shape of the transient absorbance profile can be used to determine the magnitude of the two rate constants, k_a and k_b , but an unambiguous assignment of these two rate constants to the processes defined by the rate constants, k_1 and k_2 , requires additional experiments to be performed.

EXPERIMENTAL

Apparatus. The experiments were performed using the Atomsources manufactured by Analyte Corporation (Grants Pass Oregon, USA). Software versions 3.14 and 3.15 were used for all experiments. The Atomsources sputtering cell is shown schematically in Figure 4. The Atomsources consists of a sputtering cell with a power supply, gas

regulation equipment, operator interface and supporting software, and is designed to replace the flame or graphite furnace of a commercial atomic absorption spectrophotometer. For the analysis of solution residues it is necessary to be able to clamp the removable cathodes to the atomizer in a reproducible position. Therefore, two L-brackets were mounted perpendicular to one another on the cathode plate of the Atomsources. One corner of the square, removable cathode could then be positioned reproducibly at the intersection of these two L-brackets.

The Atomsources was used with one of two atomic absorption spectrophotometers. For the preliminary modelling the Atomsources was mounted in the usual place of the burner assembly in the Perkin-Elmer Atomic Absorption Spectrophotometer, model 5000, equipped with a deuterium-arc background corrector, and was operated as a part of the spectrophotometer. The Atomsources was used in the current regulation mode. The time constant of the above spectrophotometer is ~ 17 ms. The experimental absorbance profiles were recorded with a Perkin-Elmer professional computer, model 7500, and hard copies of the plots were obtained with a dot-matrix printer, Prism 132 (Integral Data Systems, Milford, New Hampshire, U.S.A.).

After it had been determined that the relatively slow detection system of the Perkin-Elmer spectrophotometer was insufficient for the recording of the rapid signals generated by the transient mode of operation, the Atomsources was used with a fast detection system [47]. This fast detection system consisted of a Varian-Techtron Atomic Absorption Spectrophotometer, model AA-5, with a laboratory-built power supply for the hollow-cathode lamp modulated at 843 Hz and a synchronous detection system with a laboratory-built lock-in amplifier having a time constant variable from 2-104 ms. The

fastest time constant, 2 ms, was used for all experiments. The absorbance and the discharge voltage were recorded simultaneously using a Nicolet model 2090-III, two-channel digital oscilloscope.

The Atomsources power supply is capable of either direct current or voltage regulation. The power supply has a maximum output of 300 mA at 1500 V, giving a maximum output of 450 W. The microprocessor controlling the power supply allows for discharges of one second and multiples thereof.

The following hollow-cathode lamps were used: silver, gold, iron, magnesium, manganese, molybdenum, nickel and lead, manufactured by Westinghouse, aluminium, cobalt, chromium and copper by Varian, gold, copper, molybdenum and vanadium by Perkin-Elmer, cadmium by Cathodeon, and molybdenum by Analyte Corporation.

Test Solutions and Reagents. Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions containing 1000 $\mu\text{g/mL}$ were prepared as follows. For aluminium, the metal was dissolved in 50% (v/v) HCl (ULTREX) with heating and the solution was diluted with ultrapure water. For gold, the stock solution was supplied by Harleco (Philadelphia, Pennsylvania, U.S.A.) - the solution was prepared by dissolving the metal in aqua regia and subsequent dilution with ultrapure water. For molybdenum and vanadium, the stock solution of each metal was prepared separately by dissolving MoO_3 or V_2O_5 in ammonium hydroxide (ACS reagent grade) and diluting the solution with ultrapure water. For cadmium, CdO was dissolved in 50% (v/v) nitric acid (ULTREX) with heating and the solution diluted with ultrapure water. For magnesium, MgO was dissolved in 10% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. For lead, $\text{Pb}(\text{NO}_3)_2$ was dissolved in 2% (v/v) nitric acid

(ULTREX) and the solution diluted with ultrapure water. For chromium, $K_2Cr_2O_7$ was dissolved in 1% (v/v) nitric acid (ULTREX). For cobalt and nickel, each metal was separately dissolved in concentrated nitric acid (ULTREX) with heating and the solution diluted with ultrapure water. For silver, copper, iron and manganese, each metal was separately dissolved in 50% (v/v) nitric acid with heating and the solution diluted with ultrapure water. All stock solutions were made to contain 1% (v/v) of the acids or the ammonium hydroxide used to dissolve the metals or their salts except aluminium, which contained 2% (v/v) HCl. The ULTREX brand acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 Water Purification System (Millipore Corporation). All test solutions were prepared by serial dilution of the above stock solutions immediately prior to determination. The test solutions made up in HNO_3 were made up to contain the minimum amount of acid that was necessary to prevent hydrolysis. The presence of an excess amount of HNO_3 in the test solutions caused oxidation of the copper cathode surface. This was found to interfere with the analysis which resulted in a reduction in sensitivity.

Gas. Argon gas (99.997% pure) was used as the discharge gas. A molecular sieve trap (Matheson) was used to remove water vapour from the argon gas.

Procedure. Cathodes of copper (99% pure) or tantalum (99.99% pure), as described below, were used. The tantalum cathodes were cut from a polished sheet of metal that was supplied by the manufacturer. The copper cathodes were polished (working surface only) with 400 grit emery paper on an electric polishing machine, then cleaned with

ethanol and air-dried. The clean, dry cathode was then clamped to the atomizer. Before every atomization cycle, the cathodes were sputter-cleaned to ensure a reproducible atomization surface and to prepare a circular depression into which the sample solution was deposited. The depth of the cavity was found to have no effect on the results; however, the cavity must be of sufficient depth to contain the sample solution. For copper and tantalum, about 5-10 s sputtering at the optimum operating conditions for the particular experiment was sufficient.

The cathode was then detached from the atomizer and laid flat with the prepared surface facing up. A 1 μ L volume of the test solution was then deposited in the centre of the cavity with a Hamilton microsyringe that was fitted with a Chaney adaptor, model 7105 NCH, part No. H88004 (Chromatographic Specialties). The test solution was then air-dried outside the atomizer and the cathode was resealed to the atomizer. The following gas flushing sequence was used as a part of the run mode. The atomizer pressure was maintained at 10 torr of argon for 10 s; the atomizer was evacuated to 0.3 torr, then repressurized to the pre-selected operating pressure. When the atomizer reached the operating pressure, the electric discharge was automatically initiated. The Nicolet oscilloscope, or the Perkin-Elmer spectrophotometer, was triggered manually just before the initiation of the discharge. In all cases, blanks were run to ensure that there was no sample carryover from run to run, and to determine blanks and background absorbances.

Experimental Conditions. The hollow-cathode lamp and the monochromator settings used are given in Table 1. The discharge parameters used for the analytical studies are given in Table 2. The discharge conditions for each element were optimized

Table 1. Hollow-cathode lamps and monochromator settings for the pulsed and the transient mode of atomization.

Element	Wavelength / nm	Hollow-Cathode Lamp		Spectral Bandpass / nm
		Manufacturer	Current / mA	
Al	309.3	Varian	4	0.2
Ag	328.1	Westinghouse	5	0.08
Au	242.8	Westinghouse	6	1.0
Cd	228.8	Cathodeon	6	0.1
Co	240.7	Varian	11	0.08
Cr	357.9	Varian	2	1.0
Cu	324.8	Varian	4	0.3
Fe	248.3	Westinghouse	6	0.5
Mg	285.2	Westinghouse	1	1.0
Mn	279.5	Westinghouse	3	1.0
Mo	313.3	Westinghouse	3	1.0
Ni	232.0	Westinghouse	11	0.1
Pb	283.3	Westinghouse	3	0.5
V	318.5	Perkin-Elmer	4	0.8

Table 2. Discharge parameters for the transient mode of atomization

Element	Instrumental Setting of		Measured Voltage	Calculated Power
	Pressure / Torr	Current / mA	/ V	/ W
Al	8	260	1300	338
Ag	8	230	1000	230
Au	8	220	750	165
Cd	10	260	1270	330
Co	8	250	1290	323
Cr	12	260	940	244
Cu	10	250	1180	295
Fe	8	150	613	92
Mg	8	280	560	157
Mn	12	250	723	157
Mo	8	250	640	181
Ni	8	260	1240	322
Pb	8	250	1100	275
V	8	250	1144	286

Copper was used as the cathode for all elements except Cu, for which tantalum was used.

individually. The optimum conditions were those that provided the best signal-to-noise ratio.

RESULTS AND DISCUSSION

Kinetic Modelling. Figures 5 and 6 present typical results for the kinetic analysis of the atomization of solution residues by cathodic sputtering in a glow discharge. Figures 5 and 6 are for the atomization of gold and copper, respectively. Figures 5a and 6a are the kinetic plots of $\ln(\text{absorbance})$ vs. time and of $\ln(\Delta B)$ vs. time as described by Eqns. 3 and 4 in the Theory. The filled-in circles are the experimental data points. The filled-in squares are the calculated values of ΔB , and the straight lines are the least squares fits to the data. Figures 5b and 6b compare the theoretical absorbance profiles (calculated using Eqn. 2 and the rate constants obtained by the above least squares fit) with the experimental absorbance profiles. The conditions under which the experimental absorbance profiles were obtained are the following. For gold, 50 ng of the metal (taken as the chloride in aqueous solution) was sputtered from a copper cathode at an atomizer pressure of 6 Torr using a regulated sputtering current of 150 mA. The 242.8 nm analysis line was used with a 12 mA hollow-cathode lamp current. For copper, 250 ng of the metal (taken as the nitrate in aqueous solution) was sputtered from a tantalum cathode at an atomizer pressure of 15 Torr using a regulated sputtering current of 200 mA. The 324.8 nm analysis line was used with a 15 mA hollow-cathode lamp current. Perkin-Elmer hollow-cathode lamps were used for both gold and copper.

It was assumed there was no change in the temperature in the sputtering cell while the signals were being measured. This assumption was based on the fact that the cathodes were water-cooled and the sputtering times necessary to completely atomize the

Figure 5. Transient atomization of Au (as the chloride in aqueous solution) by cathodic sputtering in a glow discharge from a copper cathode.

(A) Kinetic plots of (i) $\ln(\text{absorbance})$ vs. time and (ii) $\ln(\Delta B)$ vs. time.

(B) Theoretical fit (solid line) to the experimental absorbance values (●).

Figure 6. Transient atomization of Cu (as the nitrate in aqueous solution) by cathodic sputtering in a glow discharge from a tantalum cathode.

(A) Kinetic plots of (i) $\ln(\text{absorbance})$ vs. time and (ii) $\ln(\Delta B)$ vs. time.

(B) Theoretical fit (solid line) to the experimental absorbance values (●).

solution residues were short. If there were a change in temperature, it could affect both the sputtering yield and the rate constants. However, this was not the case.

The rate constants used to generate the theoretical absorbance profiles in Figs. 5b and 6b are the following: for gold, $k_b = 100 \text{ s}^{-1}$ and $k_a = 22 \text{ s}^{-1}$, for copper, $k_b = 130 \text{ s}^{-1}$ and $k_a = 6.3 \text{ s}^{-1}$. For this modelling, the k_a 's are similar to the k_2 's found earlier [12], whereas the k_b 's are different from any rate constants found previously. The present fitting is based on two consecutive first-order reactions as shown in Eqn. 1. Previously, it was found necessary to use two sets of two consecutive first-order reactions, with an abrupt stop between where one set of reactions finished and the next set of reactions started [12]. This more complicated model was found to be necessary as a result of a serious systematic error caused by the sampling rate of the Perkin-Elmer 5000 spectrophotometer. Previously [12], it was assumed that the last data point on the baseline before the signal started to rise occurred at the initial time, t_0 . Subsequently, it was realized that t_0 could be anywhere between the last data point on the baseline and the first data point on the rising portion of the transient absorbance signal. This realization led to the conclusion that one of the two sets of consecutive, first-order equations was unnecessary.

In the theory it was mentioned that the rate constants could be obtained from the shape of the absorbance profile, but assigning the obtained rate constants to either k_1 or k_2 would require additional information. At this point, the information required to make an unambiguous assignment was not yet available. The experiments necessary to carry out the assignment of the rate constants are described in Chapter 3.

It can be seen from the fit of the theoretical curves to the experimental data points

in Figs. 5 and 6 that the model correctly describes the processes that are occurring. The fitting was performed for many elements and all the fitting results showed the sequence of consecutive first-order reactions to be correct. However, the rate constants derived for these fits will not be reported since they were not obtained under what are now known to be the optimum conditions. A complete set of rate constants, obtained under the optimum conditions, will be given in Chapter 2.

Upon closer inspection of Figs. 5b and 6b, it can be seen that the model predicts a greater peak height than what has been measured. Therefore, not only does the relatively large time constant of the Perkin-Elmer 5000 spectrophotometer require that greater care is taken when fitting the data, it also may lead to a reduction in the sensitivity. The need for a faster detection system is evident from the above results. Also, it can be seen that there are very few data points on the rising portion of the transient absorbance profiles. The availability of more data points will lead to a more precise determination of the rate constants.

Although the rate of formation of atoms by cathodic sputtering at the cathode surface cannot be measured directly, the rate of entry of the atoms into the analysis volume must depend on the formation process. Therefore, the rate of entry of atoms into the analysis volume is used to give an insight into the processes that are occurring at the cathode surface. The results of the kinetic modelling are consistent with a mechanism whereby atoms are sputtered direct into the vapour phase from the solution residue on the cathode surface without significant formation of an intermediate. This agrees with the findings of other workers, that most of the sputtered particles are ground-state neutral atoms that have been sputtered direct into the vapour phase [27], mostly as atomic rather

than molecular species [33, 48, 49], and excited atoms or ions constitute only a small fraction of sputtered species [27, 35].

Analytical Studies. The experimental conditions shown in Tables 1 and 2 were the conditions found to give the maximum analytical sensitivity and were used to determine the characteristic masses and limits of detection. The characteristic masses and the limits of detection are given in Table 3 for the transient mode of atomization. The transient mode of atomization is a new technique, still in its infancy, and there is still a lot of room for improvement in these values, as will be discussed later.

It can be seen from the values presented in Table 3 that there has been an improvement by at least an order of magnitude over the previously reported values for the characteristic mass and there are similar improvements in most limits of detection for the transient mode of atomization. There are several reasons for the increase in sensitivity. These reasons are discussed in detail below, and include: the time constant of the detection system, the hollow-cathode lamp current, the design of the hollow-cathode lamp used, the method of lamp modulation, and the discharge power.

One reason for the above-mentioned improvement in the characteristic mass is that the previous values were obtained using a Perkin-Elmer 5000 spectrophotometer. This spectrophotometer records a datum point every ~ 17 ms, which is too slow to define accurately the peak of the rapidly changing transients. The values in Table 3 were all obtained using the fast detection system described in the Experimental section. A time constant of 2 ms was used for all the determinations.

Another reason for the improvement in both the characteristic mass and the limits of detection comes from the realization of the importance of the hollow-cathode lamp

Table 3. Limits of detection and characteristic masses for the transient mode of atomization. The limits of detection and characteristic masses were obtained using the experimental conditions given in Tables 1 and 2. The previously reported [12] values were those obtained before optimization of the experimental set-up.

Element	Limits of Detection*		Characteristic Mass†	
	This work / pg	Previous[12] / pg	This work / pg	Previous[12] / pg
Al	7.0	1340	2.9	1140
Ag	140		26	
Au	550		47	
Cd	27	40	4.9	31
Co	3000	716	130	525
Cr	0.5		0.25	
Cu	43	740	8.0	183
Fe	210	1670	30	524
Mg	0.5		0.11	
Mn	68	650	25	724
Mo	0.34	164	0.11	63
Ni	1500	3700	210	2100
Pb	1600		210	
V	185	723	68	723

*Mass giving a signal = 3σ /slope of the analytical calibration curve.

†Mass required to give an absorbance value of 0.0044 (1% absorption).

current. Piepmeier [50] has reported on the influence of the spectral profile of the source lamp on the analytical results for low pressure, cathodic sputtering cells for atomic absorption spectrometry. One of the assumptions of the Walsh method for atomic absorption spectrometry is that the emission line from the hollow-cathode lamp is much narrower than the absorption line. One would expect that this condition would be at least approximately fulfilled for a flame or a graphite furnace, since the atomizer is at atmospheric pressure and at a high temperature, whereas the hollow-cathode lamp is at a low pressure and a lower temperature, and therefore the absorption line is much more broadened by Lorentz and Doppler broadening than is the emission line from the hollow-cathode lamp. However, for a cathodic sputtering atomizer this is not the case. The atomizer pressure is only slightly greater than that of the hollow-cathode lamp, whereas the temperature of the atomizer is much less than that of the hollow-cathode lamp because the cathode of the atomizer is water-cooled and short sputtering times were used, thereby preventing any temperature change for the cathode of the atomizer. The absorption and emission line widths are, therefore, probably not very different. It has been found that the highest sensitivity is obtained when the lowest possible lamp current is used, in agreement with the findings of Bernhard [15]. A low current for the hollow-cathode lamp means a lower hollow-cathode lamp temperature and therefore, a narrower emission line. Of course, using a low current for the hollow-cathode lamp means a decrease in the intensity of radiation, and a resulting increase in the signal noise. The conditions that have been employed are those which have been found to give the best compromise between high sensitivity (low characteristic mass), and low limit of detection (*i.e.*, best signal-to-noise ratio). It is also important to use electronic, rather than

mechanical modulation of the radiation from the hollow-cathode lamp (the Perkin-Elmer spectrophotometer is mechanically modulated), since for electronic modulation the average power dissipated in the cathode is less than that when the current is DC and the radiation is mechanically modulated. The former results in a lower temperature for the hollow-cathode lamp, a narrower width for the emission line, and therefore, a lower characteristic mass than if the radiation from the hollow-cathode lamp were mechanically modulated. Another advantage of electronic modulation is, of course, an increase in the useful life of the hollow-cathode lamp.

The design of hollow-cathode lamp used was found to have a large effect on the characteristic mass. In the initial studies of the atomization of solution residues by cathodic sputtering in a glow discharge with the Perkin-Elmer 5000 spectrophotometer, the Perkin-Elmer hollow-cathode lamps were most frequently used. The Perkin-Elmer hollow-cathode lamp gave a characteristic mass of 4.8 pg for the determination of molybdenum. When a Westinghouse lamp for molybdenum was used the sensitivity was much better than that given by the Perkin-Elmer lamp. The characteristic mass decreased to 0.11 pg. A hollow-cathode lamp marketed by Analyte Corporation, the manufacturer of the Atomsource, was also tested and gave a characteristic mass of 17 pg, the highest characteristic mass (*i.e.*, lowest sensitivity) for all the molybdenum hollow-cathode lamps tested. It should be kept in mind that these hollow-cathode lamps (and the rest of the apparatus for that matter) were not used as advised by the manufacturers. The Perkin-Elmer molybdenum lamp, for example, had a continuous current rating of 30-40 mA; the lamp current that was used was 3 mA.

The above observations can be explained by considering the work of Wagenaar

et al. [51], who studied the emission line profiles and intensities of various hollow-cathode lamps as a function of lamp current. These authors [51] found that the 423 nm calcium line from the Perkin-Elmer lamp was strongly self-reversed at 15 mA lamp current, whereas the same line from a Varian lamp showed no self-reversal up to 25 mA lamp current. They also found that the intensity of the line of the Perkin-Elmer lamp at 15 mA lamp current was equal to the intensity of the line of the Varian lamp at 25 mA lamp current, and that self-reversal for both lamps began at the same intensity, although the current densities were different. Thus, for a given lamp current, the Perkin-Elmer lamps produce broader, more intense lines than the Varian lamps because of differences in the filler gas or the cathode material [51], as well as in the geometry and size. For atomic absorption spectrometry with flame or graphite furnace atomization, the width of the emission line usually does not have too large an effect on the sensitivity. This is not the case for cathodic sputtering atomizers for atomic absorption spectrometry. The results that have been obtained indicate that the increase in the noise due to the decrease in the intensity of the emission line with decreasing lamp current is more than offset by the increase in sensitivity due to the better overlap between the emission and the absorption line as the emission line becomes narrower. At present, manufacturers of hollow-cathode lamps for atomic absorption spectrometry make their lamps as intense as possible, as evidenced by several hollow-cathode lamps that bear labels stating "high spectral output" on the lamp. Results that have been obtained indicate that for the cathodic sputtering atomizers, the highest sensitivity is obtained with lamps that have the narrowest emission line, and that the intensity of the lamp is of secondary importance. Therefore, for all further work, hollow-cathode lamps of the type manufactured by either

Varian or Westinghouse will be used.

Previous results [12] obtained using the Atomsources and a pyrolytic graphite cathode reported that for the transient atomization of cobalt (taken as an aqueous solution of the nitrate), the peak-height absorbance shows a linear relationship to both power and discharge current. Fang and Marcus [52], using preliminary factor analysis of their experimental results, found that for oxygen-free hard copper the weight loss was directly proportional to the applied power. These results suggest that the power applied to the discharge is the key to increasing the analytical sensitivity of the atomization of solution residues by cathodic sputtering in a glow discharge for atomic absorption spectrometry. Therefore, the highest power that the Atomsources power supply is capable of giving has been used to provide a stable glow discharge using the transient mode of atomization. Application of even greater power is likely to improve the sensitivity and limits of detection still further.

CONCLUSIONS

The kinetic modelling showed that the data fit a mechanism of two consecutive, first-order reactions. This was interpreted to mean that the atoms were sputtered direct from the cathode surface, without significant formation of any intermediates. The kinetic modelling also revealed limitations associated with using a commercially-available spectrophotometer having a relatively large time constant in its detection system. When the Perkin-Elmer spectrophotometer was replaced with a faster, laboratory-constructed detection system, and when the influence of the type of hollow-cathode lamps and their operating current were optimized, the characteristic masses and limits of detection

obtained using transient atomization by cathodic sputtering in a glow discharge for atomic absorption spectrometry improved by more than one order of magnitude. The optimum sputtering conditions for some elements require that the Atomsources power supply delivers the maximum power that it is capable of. Further improvements to the technique can be expected by replacing the Atomsources power supply by a larger, more robust power supply.

CHAPTER 2

PULSED ATOMIZATION BY CATHODIC SPUTTERING IN A GLOW DISCHARGE FOR ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

A steady-state population of analyte vapour represents an inherent kinetic limitation in the number of analyte atoms, and hence, in the analytical sensitivity of all techniques based on a steady-state population. Also, the kinetics of steady-state atomization by cathodic sputtering of solid, bulk samples in a glow discharge is slower than for the atomization of solution residues because in the solid, bulk samples the analyte is more strongly bound in the three-dimensional lattice of the cathode atoms than for a solution residue on the cathode surface. Hence, a significant increase in the sensitivity can be obtained by basing the analytical determination on the atomization of solution residues. The previous chapter described the development of the transient mode of atomization by cathodic sputtering in a glow discharge for analytical atomic spectrometry.

In Chapter 1, it was experimentally observed that the sensitivity of the transient mode of atomization was limited by the power available from the Atomsources power supply. A higher effective power (and a higher sensitivity) can be obtained by concentrating a larger amount of power into short pulses rather than using the long-duration, low-power output of the Atomsources power supply. The pulsed mode of operation uses a single positive-going square-wave pulse having a duration of a few milliseconds and of higher amplitude (compared to the transient mode of atomization).

The pulsed mode of operation offers the capability of high power (which is required for a fast rate of atomization and therefore, for maximizing the sensitivity), whereas the transient mode of atomization uses limited current at the maximum available voltage. It should be emphasized that the difference between the pulsed and the transient mode of atomization is the much shorter duration of the discharge and the higher power capability of the Advanced Energy power supply used for the pulsed mode of atomization compared with the Atomsource power supply used for the transient mode of atomization. The pulsed mode of atomization is similar to the transient mode of atomization and can be expected to give similar results for similar experimental conditions; it is, however, easier to achieve high-power discharges (and therefore, higher sensitivity) for the pulsed mode of atomization than for the transient mode of atomization.

EXPERIMENTAL

Apparatus. The experiments were performed using an Atomsource cathodic sputtering atomizer [15] (for atomic absorption spectrometry) manufactured by Analyte Corporation (Grants Pass, Oregon). Software version 3.15 was used for all experiments. The Atomsource sputtering cell is shown schematically in Figure 4. The Atomsource was used with the fast detection system described in the previous chapter [47]. This fast detection system has a time constant that is variable from 2 to 104 ms. A time constant of 2 ms was used for all determinations. The absorbance and the discharge voltage were recorded simultaneously using a Nicolet, model no. 2090-III, two-channel digital oscilloscope.

For the pulsed mode of atomization, discharges of high power and short duration were required. For the pulsed mode of atomization the Atomsource power supply was

disconnected from the atomizer and replaced with another power supply that was capable of providing fine control of the discharge duration and higher powers than the Atomsources power supply is capable of. The power supply used for these experiments was a 1 kW High Z DC Magnetron, model MDX-1K, manufactured by Advanced Energy Industries Inc. (Fort Collins, Colorado). The MDX power supply has a rated output of 1 A at 1000 V for a maximum power output of 1000 W. This power supply was used in conjunction with a Wavetek function generator, model no. 164 (San Diego, California). This combination allows for single or multiple positive-going square-wave pulses of variable duration (frequency) and amplitude. Typically, a single pulse of 50-500 ms duration was used. The power supply permits current, voltage or power regulation. Power regulation was used for these studies as it was found to give more reproducible results than current or voltage regulation.

Test Solutions and Reagents. Chemically pure metals or their salts were used to prepare the standard solutions. The same 1000 $\mu\text{g/mL}$ stock solutions as described earlier were used for both the transient and the pulsed mode of operation. The preparation of these standard solutions is described in the Chapter 1. All test solutions were prepared by serial dilution of the stock solutions with ultrapure water immediately prior to determination. Ultrapure water of 18.3 megohm-cm resistivity was obtained direct from a Milli-Q2 Water Purification System (Millipore Corporation).

Gas. Argon gas (99.997% pure) was used as the discharge gas. A molecular-sieve trap (Chromatographic Specialties, model no. MT120-4) was used to remove water vapour from the argon discharge gas. A particulate filter (Matheson Gas Products) was used to

remove any particulate matter from the discharge gas.

Procedure. The same cathodes were used for both the transient and the pulsed mode of atomization. The same sputter-cleaning and sample introduction procedure were also used. These procedures are described in Chapter 1.

The following measurement procedure was used for the pulsed mode of operation. The Atomsource standby-flush-pressure mode was used to flush the atomizer at the desired operating pressure. Once the pre-chosen operating pressure was reached, the discharge could be initiated whenever desired. The Nicolet oscilloscope was triggered manually prior to the initiation of the discharge. For the low concentrations of the aqueous standard solutions used for most of the experiments, a discharge of 50 ms duration was sufficient to insure complete atomization of the sample. In all cases, blanks were run to ensure there was no sample carryover from run to run, and to determine blanks and background absorbances.

Experimental Conditions. The hollow-cathode lamp and monochromator settings used for the pulsed mode of operation were the same optimum values that were determined for the transient mode of operation. The hollow-cathode lamp currents, lamp manufacturers and monochromator settings are given in Table 1. The discharge parameters used for the pulsed mode of operation are given in Table 4. The discharge conditions for each element were optimized individually. The optimum conditions were those conditions that gave the best signal-to-noise ratios.

RESULTS AND DISCUSSION

Analytical results. The experimental conditions shown in Table 4 were the conditions

Table 4. Discharge parameters for the pulsed mode of operation

Element	Instrumental Setting of		Measured	
	Pressure / Torr	Power / W	Current / mA	Voltage / V
Al	8	229	250	920
Ag	8	400	287	1400
Au	8	410	284	1410
Cd	10	250	305	820
Co	8	200	227	880
Cr	8	301	251	1200
Cu	10	149	198	750
Fe	8	200	240	830
Mg	8	299	262	1140
Mn	10	300	310	970
Mo	8	203	285	810
Ni	10	200	227	880
Pb	10	249	312	800
V	8	250	250	1000

Copper was used as the cathode for all elements except Cu, for which tantalum was used.

found to give the maximum analytical sensitivity and were used to determine the characteristic masses and limits of detection. The characteristic masses and the limits of detection are given in Table 5. The characteristic mass for the pulsed mode of operation is smaller than or equal to that of the transient mode of operation for ten of the fourteen elements listed in Table 5. Of the other four elements, three are within a factor of about 2 of the characteristic mass obtained for the transient mode of operation. The characteristic masses obtained for the pulsed mode of atomization are higher than expected. This has been attributed to the low voltage rating of the MDX power supply. Tables 3 (in Chapter 1) and 4 show that the experimental conditions for the pulsed mode of operation are not very different from those used for the transient mode of operation. The MDX power supply is rated at only 1000 V, and although it was possible to draw up to 1400 V, the maximum useable voltage was approximately 900 V. Above this voltage, the rise time of the power supply output increased and multiple bursts of variable power were often seen, usually producing several small absorbance peaks instead of one large peak.

To use more of the power that is available from the MDX power supply, it is necessary to decrease the operating voltage and increase the discharge current. With the Atomsource gas control unit, and using power regulation of the MDX power supply, it is possible to decrease the operating voltage by increasing the discharge gas pressure in the atomizer. Unfortunately, when the discharge gas pressure is increased in the Atomsource atomizer the gas flow rate is also increased. This occurs because the Atomsource controls the gas pressure by varying the flow rate of the gas. The reason that this is undesirable is that an increase in the argon gas flow rate beyond the optimum

Table 5. Limits of detection and characteristic masses for the pulsed mode of operation

Element	Limit of Detection / pg	Characteristic Mass / pg
Al	7.0	2.6
Ag	280	46
Au	260	48
Cd	5.6	2.0
Co	260	38
Cr	0.23	0.17
Cu	31	7.5
Fe	140	53
Mg	6.5	1.1
Mn	71	27
Mo	0.32	0.08
Ni	410	100
Pb	560	190
V	140	84

*Mass giving a signal = 3σ /slope of the analytical calibration curve.

flow rate leads to a decrease in the analyte atom residence time. This, in turn, decreases both the peak height and the peak area sensitivity. Independent control of the gas pressure and the gas flow rate would make it possible to increase the gas pressure while the optimum gas flow rate is maintained. This would allow the MDX power supply to deliver higher powers. Also, the absorbance profiles obtained with the Atomsource by the pulsed mode of operation have a very short duration and therefore have a very small peak-area absorbance. An increase in the gas pressure without an increase in the gas flow rate would increase the atom residence time and lead to a substantial increase in the peak-area sensitivity. An atomizer that allows independent control of gas pressure and gas flow rate is essential to optimize fully the operating conditions.

Kinetic Modelling. In the previous chapter, it was concluded that the entry of atoms into and the loss of atoms from the analysis volume of the Atomsource could be described by Eqn. 1. The absorbance profiles of the pulsed mode of operation were also compared with the theoretical curves calculated using Eqn. 2. A representative result of this fitting is shown in Fig. 7, the fitting of an absorbance profile for the pulsed atomization of 10 ng of nickel. The rate constants used to generate the theoretical fit were: $k_b = 185 \text{ s}^{-1}$ and $k_a = 45 \text{ s}^{-1}$. The same fitting, with similar results, was performed for all of the elements using the optimum experimental conditions for the pulsed mode of atomization shown in Table 4. The rate constants for the pulsed mode of atomization are presented in Table 6.

Upon closer investigation of Fig. 7, it can be seen that the duration of the absorbance profile is 40 ms and the time to reach the maximum absorbance is 10 ms. With the 17 ms time constant of the Perkin-Elmer 5000 atomic absorption

Figure 7. Pulsed atomization of nickel (as the nitrate in aqueous solution) by cathodic sputtering in a glow discharge from a copper cathode. Theoretical fit (solid line) to the experimental absorbance values (●).

Table 6. Rate constants for the pulsed mode of atomization

Element	Mass / ng	A_0	k_1 / s ⁻¹	k_2 / s ⁻¹
Al	1	0.61	740	105
Ag	1	0.25	100	52
Au	10	0.60	90	26
Cd	0.1	0.59	170	110
Co	10	0.92	160	58
Cr	0.01	0.47	750	310
Cu	1	0.35	140	90
Fe	10	0.94	115	87
Mg	0.1	0.37	500	140
Mn	1	0.18	160	80
Mo	10	1.15	200	110
Ni	10	0.50	185	45
Pb	10	0.23	160	120
V	10	0.31	190	40

A_0 is defined by equation 2.

spectrophotometer, there would be a maximum of three data points recorded for this absorbance profile. The faster detection system used for this experiment has made it possible to fit absorbance profiles having faster rise times more precisely. Even a time constant of 2 ms is too large for some elements that have even faster rise times. For some elements, the absorbance peak near the limit of detection has a duration of approximately 5 ms. Therefore, a detection system with a time constant that is smaller than 2 ms is required.

In Chapter 1, in the Theory section, it was stated that it was not known which of the rate constants corresponded to k_1 , the rate constant for atom entry into the analysis volume, and which of the rate constants corresponded to k_2 , the rate constant for atom loss from the analysis volume. Evidence for assigning the rate constants can be obtained from an estimate of the theoretical residence time of the analyte atoms within the Atomsource. At an argon pressure of 8 Torr the residence time determined by convection alone (based on the atomizer volume and the flow rate of argon gas) was calculated to be 12 ms, which corresponds to $k_2 = 80 \text{ s}^{-1}$. The effect of diffusion was neglected in this calculation, so this residence time is a first approximation. Nevertheless, when the rate constants in Table 6 are averaged, the average values are; $k_b = (150 \pm 40) \text{ s}^{-1}$, and $k_a = (80 \pm 40) \text{ s}^{-1}$. These results indicate that the smaller of the two rate constants, k_a , corresponds to the rate constant for atom removal, and the larger rate constant, k_b , corresponds to the rate constant for atom introduction, k_1 . If $k_1 = k_b$ and $k_2 = k_a$, then $k_1 > k_2$. Further investigations, that will be reported in Chapter 3, confirm that $k_1 > k_2$. However, the best sensitivity is obtained when $k_1 \gg k_2$, a condition not generally achievable with the present equipment.

CONCLUSIONS

Greater sensitivities are given by the pulsed mode of atomization compared with the transient mode of atomization for most elements. The pulsed mode of atomization by cathodic sputtering in a glow discharge fits the model of consecutive, first-order reactions. Further deficiencies in the atomizer design were identified. Although the 2 ms time constant of the fast detection system was a significant improvement over that provided by the Perkin-Elmer 5000 atomic absorption spectrophotometer, an even faster time constant would be better. Also, a new gas control system that allows independent control of the gas pressure and the gas flow rate is required. Independent control of gas flow rate and pressure would allow: 1) the use of higher powers at lower voltages, 2) better optimization of experimental conditions, and 3) investigation of the effects of an independent variation of each variable: gas pressure and gas flow rate, on the analytical sensitivity.

CHAPTER 3
THE CONSTRUCTION AND CHARACTERIZATION OF A NEW
LABORATORY-CONSTRUCTED ATOMIZER FOR CATHODIC
SPUTTERING IN A GLOW DISCHARGE

INTRODUCTION

The transient mode of atomization by cathodic sputtering in a glow discharge involves the application of relatively long-duration, moderate power, direct current to the atomizer to produce transient signals from aqueous solution residues. In the development of the transient mode of atomization, certain areas where it was felt that significant improvements could be achieved were identified. The first area that was investigated was the amount of power that was available from the power supply of the commercial Atomsource for atomizing the sample. The pulsed mode of atomization, which was developed subsequently, uses a large-capacity power supply to apply high power, short-duration (50 - 100 milliseconds), direct-current pulses to the atomizer to produce transient signals. This has resulted in enhanced sensitivity and improved limits of detection for the ultra-trace analysis of aqueous solution residues.

There are two other areas that have been identified as crucial for improvement. The first area is the speed of the detection system. The lifetime of the signals generated in the atomization of sub-nanogram amounts of samples was extremely short and difficulties were encountered when commercially available spectrophotometers were employed. The second area is the gas control apparatus of Atomsource. It has been found that a well-regulated gas flow is crucial for achieving reproducible transient

signals. It has also been found that to achieve maximum sensitivity both the flow rate and the pressure in the atomizer must be optimized individually. The commercial Atomsources does not provide the fine regulation of the gas flow rate required for transient signals and does not provide for independent control of flow rate and pressure. Therefore, an apparatus that addresses these problems has been constructed in our laboratory. The details of the apparatus will be described and results that have been obtained using the independent control of gas flow rate and of gas pressure that is provided by this apparatus will be discussed.

This new laboratory-constructed atomizer is an improvement over the commercially available Atomsources [15] in all respects. Although the atomizer was developed for the improvement of the technique of pulsed atomization by cathodic sputtering in a glow discharge, the new atomizer is also superior for steady-state measurements. The new atomizer has been used to study the atomization of both solid, bulk samples (steady-state atomization) and solution residues (pulsed atomization). Analytical studies of the atomization of solid, bulk samples and an evaluation of the independent effect of the gas flow rate on the steady-state signal have been made.

Studies of the independent effects of the gas flow rate on the atomic emission signal of copper have been made by Banks and Blades [53] using a similar apparatus. The results of these workers [53] confirmed the importance of the independent control of flow rate and pressure, but the measurement of emission alone could not explain why the emission signal of copper decreased while the sputtering yield increased with increasing flow rate of argon gas. In the present study, both absorption and emission studies have been made so that factors affecting the excited state population, and hence

the atomic emission signal, can be separated from factors that affect the ground state population, which are the sputtering efficiency and the transport efficiency. The sputtering efficiency is defined as the fraction of the total number of analyte atoms in the sample that are sputtered from the cathode surface and are not redeposited. The transport efficiency is defined as the fraction of the total number of analyte atoms sputtered from the cathode surface that reaches the analysis volume.

The new atomizer has also been used to study the pulsed mode of atomization by cathodic sputtering in a glow discharge. The independent control of argon flow rate and pressure allows a parametric evaluation of the effect of power, argon flow rate and pressure on the peak-height and the peak-area absorbance, and on the rate constants for the supply of atoms to and their removal from the analysis volume. This study allows the examination of how each of these factors affects the sensitivity of the new atomizer. The studies of the effects of different experimental parameters on the rate constants will allow the unambiguous assignment of the measured rate constants, k_a and k_b , to the rate constants associated with atom supply and atom removal, k_1 and k_2 , respectively. The sensitivity of the new atomizer has been determined for several elements and this sensitivity will be compared with that of the Atomsource.

THEORY

Integration of Eqn. 2 (in Chapter 1), which describes the time dependence of the absorbance signal, with respect to time yields the following equation that represents the theoretical peak-area absorbance:

$$\int_{t=0}^{t=\infty} B_t dt = \frac{A_o}{k_2} \quad (6)$$

Differentiating Eqn. 2 (in Chapter 1) with respect to time, and setting the result equal to zero, yields the following equation for the theoretical peak-height absorbance:

$$B_{peak} = A_o \frac{k_1}{k_2} \exp \left[\frac{k_1}{k_1 - k_2} \ln \left(\frac{k_2}{k_1} \right) \right] \quad (7)$$

where B_{peak} is the peak-height absorbance. From Eqns. 6 and 7 it is possible to predict the effect of a change in the first order rate constants upon the analytical signals. It can be seen that in order to maximize the peak-area absorbance signal it is necessary to make k_2 as small as possible. To maximize the peak-height absorbance it is necessary to make $k_1 \gg k_2$. If $k_1 \gg k_2$ then $B_{peak} \approx A_o$.

Other factors that will have an effect upon the analytical signals are the transport efficiency and sputtering efficiency. If either the sputtering or the transport efficiency is less than one, A_o will represent less than the total possible absorbance. It should be made clear that because the analysis volume is physically separated from the cathode surface where atoms are generated by cathodic sputtering, k_1 , the rate constant for the supply of analyte atoms to the analysis volume, is a measure of the rate of transport of the gas-phase analyte atoms to the analysis volume and not of the rate of sputtering, though k_1 also will reflect changes in the rate of sputtering. The rate constant k_2 is for the removal of analyte atoms from the analysis volume by whatever means, including diffusion of analyte atoms to and adsorption of the analyte atoms on to the walls of the analysis cell and convection of analyte atoms out of the analysis volume.

EXPERIMENTAL

Instrumentation. Figure 8 shows a modular diagram of the apparatus used in the investigation of cathodic sputtering for atomic emission and absorption spectrometry. The apparatus is composed of four basic systems: the cathodic sputtering atomizer, the gas control system, the power supply, and the measurement system. These systems are described below.

Cathodic sputtering atomizer. The new atomizer has been modelled after the Atomsources. Figure 4 (in Chapter 1) is a schematic diagram of the Atomsources atomizer. The atomizer that has been constructed has the same dimensions as the Atomsources. A six gas-jet configuration similar to that in the Atomsources has been employed but all the components have been manufactured in-house. The body of the atomizer is made of Delrin. The atomizer is designed so that the optical path is parallel to the cathode surface as in the Atomsources. The interior of the atomizer is lined with pyrex glass to protect the body of the atomizer from the glow discharge. Both the anode and the cathode plate are fabricated from brass. The cathode plate is water-cooled and is maintained at ground potential. Two L-brackets have been attached to the cathode surface. These L-brackets are positioned perpendicular to each other so one corner of the square, removable cathode can be placed at their intersection, making the position of the cathode reproducible. The atomizer is rigidly mounted on an XYZ Φ adjustable stage on the optical rail of an atomic absorption spectrophotometer (Varian Techtron, model AA5). All gas connections to the atomizer are made using Cajon Ultra-Torr fittings.

Figure 8. Modular diagram of the new, laboratory-constructed atomizer. A - Digital recording oscilloscope, B - Power supply for cathodic sputtering atomizer, C - Power supply for hollow-cathode lamps, D - Monochromator and detection system, E - Cathodic sputtering atomizer, F - Hollow-cathode lamp, G - Argon gas tank and regulator, H - Argon gas flow-rate control and measurement, I - Argon gas pressure control and measurement, J - Two-stage vacuum pump.

Gas control system. The sputtering gas used in this study was 99.997%-pure argon. A moisture trap (Chromatographic Specialties, model No. MT120-4) was used to remove water vapour from the sputtering gas as water vapour had been shown to have a detrimental effect when present in the discharge [54]. The sputtering gas was then passed through a particulate filter (Matheson Gas Products). The flow rate of the argon was regulated using a Nupro fine-regulating needle valve and was measured using the flow rate transducer of a mass flow controller (Sierra Instruments, model No. 740-05-2). This transducer was capable of measuring up to 5 standard litres per minute (SLPM) argon gas. The argon gas was admitted into the atomizer through the six gas jets. The pressure was monitored on the outlet side using a Pirani gauge (Granville-Phillips Convection Gauge, model No. 275). The gauge was calibrated for both nitrogen and argon gas. The pressure was controlled by throttling the vacuum line using a Whitey ball valve and a Whitey regulating valve in a parallel configuration. The ball valve was used for coarse control of the gas pressure while the regulating valve gave fine control. A two stage vacuum pump (Edwards High Vacuum, model 5) fitted with an oil mist filter (Edwards High Vacuum, model EMF10) provided the vacuum for all the studies.

Power supply. The power supply used for the sputtering studies was an Advanced Energy MDX 1K, which was capable of independent regulation of current, voltage, or power. The power supply was capable of supplying up to one kilowatt with up to 1400 volts at low currents. The maximum available current was one amp at 1000 volts. The power supply was controlled with a function generator that was constructed in our departmental electronics workshop. The function generator could deliver single or multiple positive-going square waves of variable amplitude and duration. A voltage

probe was situated between the power supply and the sputtering cell. The signal from this voltage probe was recorded on one channel of a dual-channel digital recording oscilloscope (Nicolet Instrument Corporation, model 201).

Measurement system

Atomic absorption measurements. A laboratory-constructed power supply for hollow cathode lamps that employed variable-frequency electronic modulation (from 400 Hz to 20 kHz) was used. This power supply for hollow-cathode lamps enabled the use of a low time constant and provided a fine control of the hollow-cathode lamp current. This fine control was necessary as it has been found that the best sensitivities could be achieved at the lowest usable lamp currents. The light beam was focused to a minimum diameter of 7 mm as it passed through the middle (horizontal axis) of the atomizer. The atomizer, the hollow cathode lamps, the two bi-convex lenses and the monochromator were all mounted on the same optical rail. The rail, the mounts and the lenses were cannibalized from an atomic absorption spectrophotometer (Varian Techtron, model AA5). The monochromator used was from a Techtron atomic absorption spectrophotometer, model AA4. The photomultiplier was a Hamamatsu R1527, powered by a Kepco ABC 1500 volt regulated DC power supply. The signal from the photomultiplier tube was passed to a dual-channel lock-in amplifier (Stanford Research, model SR530) having a variable time constant down to 1 ms. The output from the lock-in amplifier was passed through a log converter and the absorbance data were collected on one channel of the digital oscilloscope.

Atomic emission measurements. For the atomic emission measurements the output from

the photomultiplier tube was sent direct to one channel of the digital oscilloscope, where it was amplified and recorded.

Procedure

Steady-state atomization. For the evaluation of the effects of argon flow rate, both emission and absorption measurements were made. The atomic emission of copper was measured by sputtering blocks of solid, 99% pure copper. Emission interferences from impurities were not expected to affect the emission signal of copper. The atomic absorption of copper was measured by sputtering blocks of the National Bureau of Standards Standard Reference Material 1263a Chromium-Vanadium Steel (modified) that contained 0.09₈% copper by weight. Both the atomic emission and the atomic absorption of copper were measured at the copper wavelength of 324.8 nm. For the measurement of the atomic absorption of copper a hollow-cathode lamp current of 4 mA and a spectral bandpass of 0.30 nm were used.

The effects of the argon gas flow rate on the analytical signal were studied at either a constant power (300 W) or a constant voltage (1000 V) and a constant argon gas pressure of 10 Torr.

For the analytical studies, the hollow-cathode lamps and the monochromator settings used are given in Table 7. The hollow-cathode lamp power supply was modulated at 1 kHz, and a time constant of 1 s was used with the lock-in amplifier. To determine the characteristic concentration, the conditions for all elements were the following: power = 900 W, argon flow rate = 1.0 SLPM, argon pressure = 14 Torr. The above are the conditions that gave the highest absorbance but not the optimum signal-to-noise ratio; these conditions are given in Table 8. These conditions were used

Table 7. Hollow-cathode lamps and monochromator settings for the steady-state mode of atomization.

Element	Wavelength / nm	Hollow-Cathode Lamp		Spectral Bandpass / nm
		Manufacturer	Current / mA	
Co	240.7	Westinghouse	10	0.16
Cu	324.8	Varian	5	0.33
Mn	279.5	Westinghouse	5	0.16
Mo	313.3	Westinghouse	8	0.16
Ni	232.2	Westinghouse	10	0.08
V	318.4	Perkin-Elmer	5	0.16

Table 8. Experimental parameters for the determination of the limits of detection using the steady-state mode of atomization.

Element	Argon Pressure / Torr	Ar Flow Rate / SLPM	Atomizer Power / W
Co	15	0.9	420
Cu	12	0.8	370
Mn	13	1.0	350
Mo	14	0.9	350
Ni	15	0.7	500
V	15	1.0	500

to determine the limits of detection. The samples used for the analytical determinations were NBS Standard Reference Materials steel samples. For cobalt, copper, manganese, molybdenum, and nickel the steel sample used was NBS SRM 1265a, Electrolytic Iron. For vanadium the steel sample used was NBS SRM 1264a, High-Carbon Steel (modified).

For all the measurements the following procedure was used. The cathode was clamped to the cathode plate of the atomizer and the gas solenoid on the vacuum line was opened, evacuating the cell to approximately 300 mTorr. When this pressure was reached the gas solenoid on the argon inlet line was opened and the fine-regulating needle valve was adjusted to give the desired argon gas flow rate. When the desired flow rate was reached the valves on the vacuum line were adjusted to give the desired pressure. The oscilloscope and the function generator that controlled the power supply were then triggered simultaneously and plots of the signal intensity versus time were obtained together with the corresponding voltages.

Pulsed Atomization. The hollow-cathode lamps and the monochromator settings used are given in Table 9. The hollow-cathode lamp power supply was modulated at 1 kHz, and a time constant of 1 ms was used with the lock-in amplifier.

All the metals were taken as the nitrates in aqueous solution except gold which was taken as the chloride in aqua regia solution, diluted with ultrapure water. The 1000 $\mu\text{g mL}^{-1}$ stock solutions were prepared as outlined in Chapter 1. Test solutions were made by serial dilution of the stock solutions using ultrapure water. The ultrapure water was obtained direct from a Milli-Q2 water purification system.

The cathodes used for all measurements were 99% pure copper. A 1 μL volume

Table 9. Hollow-cathode lamps and monochromator settings for the pulsed mode of atomization

Element	Wavelength / nm	Hollow-cathode lamp		Spectral bandpass / nm
		Manufacturer	Current / mA	
Ag	328.1	Westinghouse	3.0	0.08
Au	242.8	Westinghouse	4.0	0.20
Co	240.7	Varian	11.0	0.08
Fe	248.3	Westinghouse	5.0	0.30
Mg	285.2	Westinghouse	0.5	0.60
Ni	232.0	Westinghouse	8.0	0.20

of the aqueous samples was pipetted into a cavity that had been sputtered into the cathode surface. The removable cathode was then clamped onto the cathode plate of the atomizer. The atomizer was evacuated to approximately 300 mTorr, the needle valve on the gas inlet was adjusted to give the desired argon flow rate and the valves on the vacuum line were adjusted to give the desired pressure. The discharge was initiated (at the pre-selected power) and the data collection was initiated. The absorbance and discharge voltage were simultaneously recorded as a function of time using a Nicolet, model 201, dual-channel digital oscilloscope. The discharge parameters and the analyte masses that were optimized to determine the characteristic mass and limit of detection for each element are given in Table 10.

RESULTS AND DISCUSSION

Steady-state measurements. A similar study of the effects of the argon gas flow-rate upon the emission signal of copper was made by Banks and Blades [53], who reported that although the gas jets enhanced the sputtering yield they decreased the emission signal. This is in contrast with the results obtained by Kim and Piepmeier [43], who found a substantial increase in the magnitude of atomic absorption signals by using a single-jet glow discharge device. Banks and Blades [53] initially concluded that the decrease in the atomic emission signal with increasing argon gas flow rate was due to either a physical disruption of the glow discharge or a cooling of the negative glow, but they were unable to prove this conclusively. In a subsequent examination, Banks and Blades [55] stated that the jets act to entrain sputtered atoms along the optical axis and that the entraining by the jets increases the absorption path length. The authors concluded that these factors would contribute to self-absorption.

Table 10. Experimental parameters for the determination of the characteristic mass and the limits of detection of the pulsed mode of atomization.

Element	Analyte mass / pg	Instrumental settings of			Measured	
		Flow rate / SLPM	Pressure / Torr	Power / W	Voltage / V	Current / mA
Ag	1000	0.50	8.0	308	925	333
Au	2000	0.50	5.0	309	1380	224
Co	1000	0.70	8.0	221	705	313
Fe	500	0.70	10.0	496	945	525
Mg	10	0.50	5.0	309	1380	224
Ni	1000	0.70	8.0	271	1215	470

The study of Banks and Blades [53] was carried out using a constant pressure and a constant power; the latter was rationalized because both the sample loss (*i.e.*, sputtering) rates and the emission intensities increased with an increase in the discharge power at a given flow rate and pressure. However, this justification is an oversimplification since both the rate of sputtering and the emission intensity have been shown to be dependent on other parameters within the glow discharge in addition to the discharge power. Indeed, the increase in the rate of sputtering with an increase in discharge power has been shown to be linear by Fang and Marcus [52] in a parametric evaluation of the sputtering of oxygen-free, hard copper. However, this same paper [52] also reported an increase in the rate of sputtering with an increase in the discharge voltage. In another case, the excitation temperature (7000 ± 700 K) was calculated by Brackett and Vickers by the two-line method of measuring temperature [44]. The two-line method is a measure of the relative population of the electronic energy levels involved in the measurement. This relative population of the excited state was shown to be dependent on the discharge current. The curve of excitation temperature vs. discharge current actually showed a maximum, the decrease started with the onset of self-absorption. It can be seen that simply maintaining a constant power is not sufficient to avoid these factors, and may lead to unjustifiable conclusions.

The apparatus used by Banks and Blades [53] measured the emission intensity at right angles to the cathode surface and therefore it was impossible for them to confirm their conclusions with absorption measurements. The new laboratory-constructed cathodic sputtering apparatus allowed both absorption and emission measurements to be made in order to separate excitation processes from sputtering and transport processes.

The change in the normalized emission intensity and the normalized absorbance of copper with an increase in argon gas flow rate at a constant discharge power (and constant pressure) are shown in Fig. 9. The normalization factor for both the emission and the absorbance measurements was calculated by considering the largest signal measured for a given set of experiments as equal to 1.00. The emission curve shows an initial small increase, followed by a steady decline in the emission intensity with increasing flow rate. This curve is very similar in form with the upper curve in Fig. 7 of Banks and Blades, although the flow rates are higher and the discharge power is greater in Fig. 9 in this work. The normalized absorbance signal shows an initial increase with increasing argon gas flow rate up to a flow rate of approximately 0.5 SLPM, after which the curve levels off, but does not decrease as was seen for the atomic emission signal of copper. At flow rates larger than 1.0 SLPM, a decrease in the atomic absorption signals was observed (this is not shown in Fig. 9). This decrease can be attributed to a decreased residence time for atoms within the analysis volume. From the absorbance measurements it is reasonable to conclude that the transport efficiency of atoms is at a maximum at a flow rate of 0.5 SLPM for a pressure of 10 Torr. The optimum flow rate is pressure dependent and must be determined at a given pressure to achieve maximum sensitivity. This means that it is necessary to have the capability to control the argon gas flow rate independently of the argon gas pressure. Since the absorption signal is based on the number of ground-state neutral atoms (present in the glow discharge) which make up the majority of the sputtered species, it is more reasonable to base any conclusions about the transport and sputtering processes on the absorption signal. To maintain a constant power, while the argon gas flow rate is

Figure 9. Change in the normalized emission intensity (●) and the normalized absorbance signal (■) of copper with variation in argon gas flow rate at constant power and constant pressure.

Argon pressure = 10 Torr, power = 300 W.

increased at a constant pressure, the discharge voltage must decrease. The decrease in discharge voltage, for a constant power, with the increasing argon gas flow rate is shown in Fig. 10. It is predicted that the decrease in the number of excited-state atoms in Fig. 9 is partially due to the decrease in the discharge voltage shown in Fig. 10. To confirm this prediction the above experiments were repeated using a constant voltage, as reported below.

Figure 11 shows the variation in the normalized emission signal and the normalized absorbance signal of copper with the argon gas flow rate at a constant voltage. The change in the emission signal is essentially the same as the absorbance curve in Fig. 9, with the maximum signal being reached at 0.5 SLPM as before. The response of the absorbance signal to a change in the argon flow rate has two linear segments. To keep the voltage constant as the flow rate is increased at a constant pressure, it is necessary for the discharge power to increase. Figure 12 shows the increase in the discharge power, at a constant voltage, with increasing argon gas flow rate. Since the power increases linearly, and the rate of sputtering increases linearly with power, it seems reasonable to conclude that in Fig. 11 the initial, steeper segment of the absorbance curve is due to the combined effect of an increase in the atom transport (transport efficiency) with increasing gas flow rate and an increase in the rate of sputtering (sputtering efficiency) with increasing power; the final, gentler increase in the absorbance curve in Fig. 11 would then be due to an increase in the rate of sputtering (sputtering efficiency) with increasing power only. The fact that the intersection of the two linear segments of the absorbance signal occurs around the previously determined optimum flow rate (defined as the flow rate giving the highest transport efficiency) of 0.5

Figure 10. Dependence of discharge voltage on the argon gas flow rate at constant power and constant pressure. Argon gas pressure = 10 Torr, power = 300 W

Figure 11. Change in the normalized emission intensity (●) and the normalized absorbance signal (■) of copper with variation in argon gas flow rate at constant voltage and constant pressure.

Argon gas pressure = 10 Torr, voltage = 1000 V

Figure 12. Dependence of power on the argon gas flow rate at constant voltage and constant pressure. Argon gas pressure = 10 Torr, voltage = 1000 V

SLPM supports this interpretation.

It can be seen that regardless of whether a constant voltage (Fig. 11) or a constant power (Fig. 9) is maintained the change in the excited state population is different from the change in the ground state population with variation in the argon flow rate. This experimental observation has been interpreted in terms of a mechanism of excitation.

Electron impact excitation, the dominant mechanism for excitation in the glow discharge [26], has been postulated to account for the experimental observation: the variation in the excited and ground state populations. Electron impact excitation can be represented as follows:

where M represents the ground state neutral atom, M* the excited state atom, e_1^- is the incident electron that undergoes an inelastic collision with M, and e_2^- is the deflected electron that has lost an amount of energy equal to the excitation energy of M. The amount of energy that the electrons acquire is dependent on the discharge voltage and the total amount of excitation that the electrons are capable of is dependent on their energy. If the extent to which the above reaction proceeds is limited by the number of electrons available for excitation [26], the excited state population within the atomizer will depend on the discharge voltage.

The change in the excited state population (the emission signal) within the analysis volume at a constant voltage is shown in Fig. 11. If the excited state population within the atomizer remains constant when a constant voltage is used, then the excited state population within the analysis volume as a function of flow rate of argon gas will represent the transport efficiency. Therefore, the change in the excited state population

at a constant voltage (Fig. 11) should have the same shape as the curve of the ground state population (absorption signal) within the analysis volume at a constant power (Fig. 9). Since these curves do have the same shape, it is reasonable to conclude that the excited state population is determined by the discharge voltage, and the mechanism of excitation is by electron impact, as shown in the above equation. This mechanism is also consistent with the experimental observation of the excited state population vs. flow rate at a constant power (Fig. 9). The excited state population within the atomizer should decrease, with the decreasing voltage shown in Fig. 10, at the same time as the efficiency with which the atoms are transported into the analysis volume increases with the increasing flow rate of argon gas. At low flow rates, the increasing transport efficiency is the predominant factor and produces a net increase in the excited state population within the analysis volume. As the flow rate increases at a constant power (and constant pressure) resulting in the transport efficiency reaching a maximum, the decrease in the excited state population within the atomizer with decreasing voltage becomes the predominant factor, producing a net decrease in the excited state population within the analysis volume.

Although the postulated mechanism of electron impact excitation can be used to explain the observed behaviour of the emission signal, the role of self-absorption in decreasing the emission intensity should not be overlooked. With the design of the Atomsources, in which the vacuum ports serve to pull the atoms along the optical path in order to increase the sensitivity of atomic absorption measurements, self-absorption is to be expected. In fact, high resolution Fourier Transform investigations of emission line profiles within the Atomsources have shown that emission lines are self-reversed, even

at very low flow rates [56]. Although self-absorption is a factor that can lead to a decrease in the emission intensity it cannot be used to explain why the emission intensity decreases while the ground-state population in the light path remains constant.

The results of the analytical studies are given in Table 11. The concentrations given are the certified values provided by the National Bureau of Standards. The limits of detection and the characteristic concentrations are compared with the results obtained using an Atomsource atomizer and the Perkin-Elmer 5000 spectrophotometer. It can be seen that in most cases the values obtained for the new atomizer are an improvement over those obtained for the Atomsource.

Pulsed atomization. For the parametric studies, 10 ng of silver taken as the nitrate in aqueous solution was used in all cases. The hollow-cathode lamp and monochromator settings were as indicated in Table 9 except that the hollow-cathode lamp current was 6 mA and the hollow-cathode lamp was modulated at 3.4 kHz instead of 1 kHz.

Figure 13 shows the variation in the peak-height and the peak-area absorbance with power. Figure 14 shows the variation in the rate constants k_1 and k_2 with power. For these experiments the argon flow rate and pressure were held constant at 0.6 SLPM and 8 Torr, respectively. It can be seen that the peak-height and the peak-area absorbance increase with increasing power, as has been reported previously for the determination of cobalt in solution residues. With both argon flow rate and pressure held constant, any changes in k_1 can only result from changes in the rate of sputtering. Therefore, the rate constant for atom supply to the analysis volume, k_1 , should increase with power. From the results presented in Fig. 14, it can be seen that k_1 is the larger of the two rate constants. This confirms what was already expected, the larger rate

Table 11. Characteristic concentrations and limits of detection for the steady-state mode of atomization.

Element	Concentration in SRM % by weight	Characteristic Concentration ¹		Limits of Detection ²	
		Atomsource / ppm	This work / ppm	Atomsource / ppm	This work / ppm
Co	0.007 ₀ *	13.6	7.0	N.A.	12
Cu	0.0058*	6.3	5.4	14	9.2
Mn	0.0057*	30	9.0	23	14
Mo	0.0050*	2.2	5.9	21	12
Ni	0.041*	14.2	8.4	32	7.7
V	0.10 ₆ †	84	44	26	91

1 - Concentration required to give 1% absorption (0.0044 absorbance)

2 - Concentration giving a signal of 3σ /slope of the analytical calibration curve

* - National Bureau of Standards - SRM 1265a - Electrolytic Iron

† - National Bureau of Standards - SRM 1264a - High Carbon Steel

N.A. - Not Available

Figure 13. Peak height absorbance (●) and peak area absorbance (■) vs. applied power for 10 ng Ag (taken as the nitrate) at constant argon flow rate and pressure. Argon flow rate = 0.6 SLPM, pressure = 8 Torr.

Figure 14. Rate constants k_1 (●) and k_2 (■) vs. applied power for 10 ng Ag (taken as the nitrate) at constant argon flow rate and pressure.

Argon flow rate = 0.6 SLPM, pressure = 8 Torr.

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constant is the rate constant for atom supply to the analysis volume. This is the condition that is required to obtain the maximum sensitivity. The rate constant for atom removal, k_2 , should not show any dependence on power since variations in the power should not affect the rate of removal of analyte atoms from the analysis volume at constant argon flow rate and pressure. This behaviour is shown by the smaller rate constant in Fig. 14. For all further discussions, the smaller rate constant will be referred to as k_2 , the rate constant for atom removal, and the larger rate constant will be referred to as k_1 , the rate constant for atom supply.

It is also important to note that the independent control of argon flow rate and pressure of the new atomizer has allowed use of higher powers than could be obtained using the same power supply with the Atomsources. At higher argon flow rates and pressures, stable glow discharges have been obtained using a power of 1000 W, which is the limit of the power supply used; this high power cannot be obtained without independent control of argon flow rate and pressure.

Figure 15 shows the variation in the peak-height and the peak-area absorbance with the argon flow rate. Figure 16 shows the variation in the rate constants k_1 and k_2 with the argon flow rate. For these experiments the pressure and power were held constant at 8 Torr and 200 W, respectively. Both the rate constants increase with increasing argon flow rate. The rate constant for silver atom supply to the analysis volume, k_1 , increases with increasing argon flow rate because the sputtered silver atoms are efficiently entrained in the flowing argon gas, and an increase in the argon flow rate results in an increase in the rate at which the silver atoms that have been sputtered are supplied to the analysis volume. The rate constant for atom removal from the analysis

Figure 15. Peak height absorbance (●) and peak area absorbance (■) vs. argon flow rate for 10 ng Ag (taken as the nitrate) at constant pressure and power.

Pressure = 8 Torr, power = 200 W.

Figure 16. Rate constants k_1 (●) and k_2 (■) vs. argon flow rate for 10 ng Ag (taken as the nitrate) at constant pressure and power.

Pressure = 8 Torr, power = 200 W.

volume, k_2 , increases rapidly with increasing argon flow rate, starting at or about 0.4 standard litres per minute (SLPM), which accounts for the maxima in the peak-height and the peak-area absorbance at 0.4 SLPM as shown in Fig. 15. The increase in k_2 results from the increased convectional loss of analyte with increasing argon flow rate. Figures 15 and 16 thus show the effect of convection on the supply of silver atoms to and their removal from the analysis volume of the atomizer, and confirm that the argon flow rate is an important experimental parameter that must be controlled if maximum analyte transport efficiency and therefore, maximum sensitivity (peak-height or peak-area absorbance) is to be obtained.

Figure 17 shows the variation in the peak-height and the peak-area absorbance with pressure. Figure 18 shows the variation in the rate constants k_1 and k_2 with pressure. For these experiments, the argon flow rate and the power were held constant at 0.6 SLPM and 200 W, respectively. It can be seen that the rate constant for atom supply to the analysis volume, k_1 , increases with pressure. This can only be due to an increase in the sputtering rate since whatever is sputtered from the cathode surface is swept in to the analysis volume at a constant argon flow rate of 0.6 SLPM. That the sputtering rate increases with increasing pressure was observed earlier with the Atomsources, but it could not be determined if this was due to the increasing pressure, or increasing argon flow rate, or a combination of both, because the Atomsources does not allow for independent control of argon flow rate and pressure. With independent control of argon flow rate and pressure, it has been possible to examine the effect of argon flow rate and pressure separately and to confirm that increasing pressure results in an increased sputtering rate, at least for Ag, for the range of experimental conditions

Figure 17. Peak height absorbance (●) and peak area absorbance (■) vs. argon pressure for 10 ng Ag (taken as the nitrate) at constant argon flow rate and power. Argon flow rate = 0.6 SLPM, power = 200 W.

Figure 18. Rate constants k_1 (●) and k_2 (■) vs. argon pressure for 10 ng Ag (taken as the nitrate) at constant argon flow rate and power.

Argon flow rate = 0.6 SLPM, power = 200 W.

studied. The rate constant for atom removal, k_2 , is approximately constant at lower pressures and increases at higher pressures. Changes in the rate of removal of atoms from the analysis volume due to pressure reflect the relative importance of the diffusive and the convective mechanism for atom removal. Diffusion is more important at lower pressures and the rate of diffusion decreases with increasing pressure. Convection is more important at higher pressures and the rate of convection increases at higher pressures. As the increasing rate of atom removal due to convection more than offsets the decreasing rate of atom removal due to diffusion with increasing pressure, k_2 starts to increase (leading to a decreasing absorbance), resulting in the maxima in Fig. 17.

The values of the rate constants k_1 and k_2 for 10 ng silver at the optimum experimental conditions examined (8 Torr, 0.6 SLPM, 200 W) are $k_1 = (650 \pm 40) \text{ s}^{-1}$, $k_2 = (4.6 \pm 0.6) \text{ s}^{-1}$, with $k_1/k_2 = 140$. This compares with the previous values for silver of $k_1 = 100 \text{ s}^{-1}$, $k_2 = 52 \text{ s}^{-1}$, with $k_1/k_2 = 1.9$, obtained with the Atomsource. The new atomizer thus enhances the k_1/k_2 ratio by a factor of 74 compared with the ratio obtained with the Atomsource. Using Eqn. 7, and the above values for the rate constants, the enhancement in the k_1/k_2 ratio should result in twice the peak-height sensitivity. The observed enhancement in peak-height sensitivity is 3 times. The difference between the predicted and the observed enhancement in the peak-height sensitivity is due to an increase in the transport efficiency with an increase in the argon flow rate, which increases the value of A_0 . The ability to optimize the argon flow rate allows maximization of the transport efficiency. Independent control of argon flow rate and pressure has made it possible to decrease the rate constant for silver atom removal, k_2 , by an order of magnitude (which increases the silver atom residence time by an order

of magnitude), while increasing k_1 by a factor of 6.5. With $k_1 \gg k_2$, the maximum peak-height sensitivity is obtained. With the Atomsource, k_1 could be increased to the point where $k_1 > k_2$. That was as far as it was possible to go without independent control of argon flow rate and pressure required to decrease k_2 , and make $k_1 \gg k_2$. The new atomizer with independent control of argon flow rate and pressure allows control of k_2 and k_1 to the point where $k_1 \gg k_2$. From Eqn. 6 it can be seen that a large decrease in k_2 should result in a large increase in the peak-area sensitivity, as was observed for the new atomizer compared with the Atomsource. From Eqn. 6, the fact that the rate constant k_2 decreases by an order of magnitude would lead one to expect an increase in the peak-area sensitivity by an order of magnitude. This is not the case as the argon flow rate affects both the value of A_0 and k_2 . Since the transport efficiency is increased and the atom residence time is decreased by higher argon flow rates, both A_0 and k_2 increase with increasing argon flow rate. Therefore, the maximum peak-area sensitivity requires optimization of the argon flow rate to achieve the best compromise between these conflicting factors.

Table 12 presents the peak-height sensitivity of silver, gold, cobalt, iron, magnesium and nickel for the new atomizer compared with the Atomsource. Modest increases in the peak-height characteristic mass are observed for all the elements except gold, for which the peak-height characteristic mass is about the same for the two atomizers. More substantial increases in the peak-height limits of detection are the combined result of the improved peak-height characteristic mass and better electronics. Table 13 presents the peak-area sensitivity of the new atomizer compared with that of the Atomsource. As observed for the peak height, modest improvements in the characteristic

Table 12. Peak-height characteristic mass and limits of detection for the pulsed mode of atomization.

Element	Characteristic mass*		Limits of Detection†	
	This work / pg	Atomsource / pg	This work / pg	Atomsource / pg
Ag	15	46	63	280
Au	53	47	72	550
Co	14	38	72	260
Fe	6.6	30	45	140
Mg	0.079	0.11	0.86	6.5
Ni	20	100	220	410

*Mass required to give an absorbance signal of 0.0044 s (1% absorption).

†Mass giving a signal = 3σ /slope of the analytical calibration curve.

Table 13. Peak-area characteristic mass and limits of detection for the pulsed mode of atomization.

Element	Characteristic mass*		Limit of detection†	
	This work / pg	Atomsource / pg	This work / pg	Atomsource / pg
Ag	710	1900	34	240
Au	1500	1400	13	1300
Co	1100	310	19	7500
Fe	510	3500	12	1500
Mg	21	140	0.21	8.8
Ni	1900	4700	8.0	1900

*Mass required to give an integrated absorbance of 0.0044 s.

†Mass giving a signal = 3σ /slope of the analytical calibration curve.

mass are found for most elements, whereas the peak-area limits of detection have improved by 1-2 orders of magnitude for all the elements.

CONCLUSIONS

The steady-state absorbance measurements have shown that the transport efficiency increases with increasing argon gas flow rates up to the point where the maximum efficiency is reached at 0.5 SLPM. This is in addition to the increase in the rate of sputtering that has been reported by Banks and Blades [53]. This was not obvious from the emission measurements when a constant power was used because of the conflicting effects of increasing transport efficiency and decreasing excited state population with increasing argon gas flow rates. The steady-state emission measurements have shown that the excited state population within the atomizer depends on the discharge voltage. This is consistent with an electron impact excitation mechanism. The emission signal is not affected by changes in the sputtering efficiency since the excited state population is limited by the population of electrons capable of excitation, not by the number of ground state neutral atoms that are present.

It can be seen that for a given pressure there is an optimum flow rate that must be achieved to obtain the maximum sensitivity at a given gas pressure. The optimum flow rate is what gives a maximum transport efficiency. Therefore, it is necessary for the argon gas flow rate to be a controllable experimental parameter. The reduction in sensitivity at lower flow rates (and constant pressure) is due to lower transport efficiency caused by the deposition of material on the walls of the atomizer and the cathode surface before it reaches the analysis volume. At the optimum flow rate the amount of such deposition is minimal. At higher flow rates (and constant pressure) the decrease in the

sensitivity is due to a decreased residence time for atoms within the analysis volume.

The optimization of the experimental conditions for the atomization of solution residues using the new atomizer has allowed the use of lower hollow-cathode lamp currents, lower argon flow rates (for a given pressure) and higher powers than obtainable with the Atomsource. The use of lower hollow-cathode lamp current and higher discharge power has resulted in increased peak-height sensitivity. The increase in peak-height sensitivity is also accompanied by an increase in the peak-area sensitivity as expected, although this is minor compared to the increase in the peak-area limit of detection resulting from the optimization of the argon flow rate. The overall effect observed for the new atomizer is a slight increase in the peak-height sensitivity due to the lower hollow-cathode lamp current that can be used (because of the better lock-in amplifier used for the new atomizer compared with that used for the Atomsource) and the higher discharge power that is attainable (because of the optimization of the argon flow rate), whereas there is a large improvement in the peak-area limit of detection mainly because of the optimization of the argon flow rate. It can be seen that the argon flow rate is an important experimental parameter that must be controlled to achieve maximum sensitivity, especially for peak-area absorbance measurements. Since the residence time of the analyte atoms in the atomizer is inversely proportional to the argon flow rate, it stands to reason that the argon flow rate is an important experimental parameter that needs to be optimized, separately from and independently of other experimental parameters, such as the argon pressure and the discharge power.

It has been shown that independent control of argon flow rate and pressure is crucial for maximizing the sensitivity and for understanding the atomization and transport

efficiency of silver in the cathodic sputtering atomizer designed for atomic absorption spectrometry. Pressure and power have been found to affect the sputtering rate (atomization efficiency), whereas the argon flow rate has a significant effect only on the rate of supply of analyte atoms to the analysis volume (transport efficiency), but not on the sputtering rate. Both argon flow rate and pressure affect the rate of atom removal from the analysis volume.

CHAPTER 4

THE SPATIAL AND TEMPORAL DISTRIBUTION OF ALUMINIUM SPECIES IN ELECTROTHERMAL ATOMIZATION FOR ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

The investigation of the distribution of analyte atoms in atomizers for atomic absorption spectrometry (AAS) is important for two reasons. First, the measurement of the distributions of species in a given atomizer provides a wealth of information for the understanding of fundamental processes that are occurring within the atomizer. Secondly, it has been shown theoretically that the absorbance signal is dependent not only on the number of absorbing species in the analysis volume but also on the spatial distribution of these species [57]. In this research, fundamental investigations of atomization in electrothermal atomization AAS have been concerned with answering the following three questions: What are the species that are present? How are these species distributed at any moment in time? What is the time-dependent behaviour of these distributions? An imaging spectrometer has been constructed to allow these three questions to be answered.

Previous detection systems that had been designed to measure the distribution of species by atomic absorption spectrometry have suffered from several shortcomings that will be discussed later. In this work, a detection system that has been designed to provide both quantitative and qualitative images of the two-dimensional distribution of the absorbing species within the analysis volume is presented.

The electrothermal atomizer that is studied in this chapter of the thesis is a Perkin-Elmer graphite furnace. The transient signal that is produced in electrothermal atomization AAS requires that the detection system provides temporal resolution. Although the exact mechanism of atomization is still uncertain, it is known that in a pyrolytic graphite coated furnace operated in the gas-stop mode, analyte atoms are produced thermally within the analysis volume and are subsequently lost from the analysis volume either by diffusion and/or by reaction with the heated graphite surface or with other species in the atomizer to produce involatile, undissociable species.

Earlier studies of concentration gradients in flame AAS involved making point-by-point measurements at several locations within the flame [58, 59]. Although this approach can provide adequate results for flame atomizers, it cannot be used for electrothermal atomizers. The reason for this is that atomization events in electrothermal atomizers are not always reproducible. Even for steady-state-temperature atomizers (flame), point-by-point mapping may not always provide satisfactory results. Point-by-point mapping may have poor reproducibility because for good reproducibility the system under investigation must remain stable for the duration of the mapping. The use of an imaging detector solves the problem of poor reproducibility.

Various approaches have been made to measure the distribution of species during atomization in electrothermal atomization AAS. Salmon and Holcombe [60] have devised a technique called the Spatial Isolation Wheel (SIW) technique that has allowed them to obtain temporally- and spatially-resolved absorbances for nine distinct zones within the graphite furnace. With the SIW technique these workers have shown that the concentration gradients along the vertical diameter of the graphite tube can be substantial

[60-62]. The SIW technique has been used for further investigations of atomization in electrothermal atomization AAS [62], but it is limited by the fact that it does not provide information about the entire cross-section of the atomizer. The resonance schlieren apparatus constructed by Stafford and Holcombe [63] provides the same one-dimensional resolution as the SIW technique, but has more than nine zones. Two-dimensional resolution of sodium atom distributions within the graphite furnace has been obtained by Huie and Curran [64] who have used a laser-based, silicon-vidicon imaging system. However, this system only allows for a single frame to be taken from each atomization event. Therefore, these two-dimensional measurements are subject to the uncertainty caused by the run-to-run variations in features of the atomization process. The recent development of the Shadow Spectral Filming (SSF) technique by Gilmudinov *et al.* [18] allows the recording of many images of the atomizer cross-section during a single atomization event. Also, the SSF system is designed to be used with standard, commercially-available hollow-cathode lamps and electrodeless discharge lamps. Therefore, it can be used for more elements than the imaging techniques that are laser-based.

The work presented in this thesis represents a significant step in the evolution of the SSF technique. In this work, the film camera that is employed in the SSF technique has been replaced by a Charge-Coupled Device (CCD) camera system. The CCD has been chosen because it is far superior to films for quantitative scientific imaging. Some of the main advantages of the CCD over film as an imaging device are; 1) linear response, 2) wide dynamic range, 3) low noise, 4) high sensitivity, and 5) wide spectral response. Also, the CCD provides digital results that facilitate the computer handling

of the large amount of data that is collected.

A description of the operation of the CCD and a list of the advantages of CCDs as imaging devices has been given by Janesick and Blouke [65]. CCDs belong to a class of devices known as charge transfer devices. Thorough reviews of the theory and applications of charge transfer devices are given in two two-part reviews [66-69].

The CCD has already been used as a detector for imaging in atomic emission spectrometry. Mork and Scheeline [70] have applied it to the spark discharge, whereas Monnig *et al.* [71] have used the CCD to investigate atomic and molecular emission signals from diffusion flames, an inductively coupled plasma (ICP), and a direct current plasma (DCP). However, the CCD devices employed by these workers [70, 71] employed relatively slow analog-to-digital convertors and, therefore, would not be able to provide the temporal resolution necessary to image events in graphite furnace AAS. In this work, the CCD camera system employs a 500 kHz analog-to-digital convertor which is sufficient to provide the time resolution that is necessary. Also, because there is a high probability that spectral interferences will occur in emission measurements, the imaging systems employed by the above workers [70, 71] require the use of a monochromator. The need for a monochromator complicates the experimental apparatus. From the previous SSF studies [18], it was concluded that, because the high resolution of atomic absorption spectrometry is provided by the extremely narrow lines given by hollow-cathode lamps, a high-resolution monochromator was not required. For this work the monochromator of the SSF set-up [18] was replaced by a narrow-bandpass interference filter covering the appropriate wavelength range.

The imaging spectrometer used in the investigations of Monnig *et al.* [71] was

constructed to allow them to calculate a tomographic reconstruction of the emission source. In an earlier paper by this same group [72], the theory of computed tomography (CT) was presented. The authors stated [71] that the widespread use of CT has been discouraged by the relative difficulty of acquiring and processing the necessary data. However, recent advances now make CT methods of investigation practical for routine studies. In particular, it is the development of the CCD that has simplified the acquisition of image data for computational purposes.

In this study, aluminium was chosen as the element to demonstrate the possibilities of the CCD-imaging system, the reason being that it has been shown previously [18, 62] that the distribution of aluminium in electrothermal atomizers is highly non-uniform, which will present a challenge to the capabilities of the CCD-imaging system for providing fine spatial resolution. Also, the atomization mechanism of aluminium in electrothermal atomization is still unresolved, and it is hoped that this investigation will shed further light on the processes that are occurring.

Spectra taken during the atomization of aluminium have shown that a strong molecular absorption band exists between 240 and 260 nm. The 253.7 nm resonance line of mercury is coincident with this aluminium molecular absorption band. Therefore, a mercury electrodeless-discharge lamp was used for imaging the distribution of aluminium-containing molecules in the analysis volume.

The distribution of both aluminium atoms and aluminium-containing molecules in the analysis volume was investigated to give more information about the processes that are occurring.

EXPERIMENTAL

Digital Imaging System. Figure 19 shows a schematic diagram of the digital imaging system. The principal component of the digital imaging system is the CCD detector (h). The CCD camera used in this work is a Photometrics Series 200 CCD Camera System (Photometrics Ltd., Tucson, Arizona.). This camera system consists of a CH250/A passive air-cooled camera that houses a Thompson Th7883 CCD chip. The working surface of the CCD is coated with a Metachrome™ II coating to enable imaging in the UV region. The output of this CCD is digitized at a rate of 500 kHz to give 12-bit image information. These images can then be displayed using the Image200™ Image Acquisition Software (Version 2.0.0).

The light striking the working surface of the CCD first passes through a narrow-bandpass interference filter (g) (Andover Corporation, Lawrence, Massachusetts.). The filter is used to isolate the analysis lines and to reduce the amount of background emission. For the atomic absorption experiments, the filter isolates the two aluminium resonance lines at 394.4 and 396.1 nm. For the molecular absorption experiments, the filter isolates the mercury resonance line at 253.7 nm. The transmission profile of the longer-wavelength filter (~ 400 nm) has a central maximum at 395 nm and a full width at half maximum (FWHM) of 10 nm. The absence of any spectral lines from the aluminium hollow-cathode lamp within the bandpass of the filter, other than the above-mentioned two resonance lines of aluminium, was verified. The transmission profile of the shorter-wavelength filter (~ 250 nm) has a central maximum at 254 nm and a FWHM of 10 nm. The absence of any spectral lines from the mercury electrodeless-discharge lamp within the bandpass of the filter, other than the above-mentioned resonance line of

Figure 19. A schematic diagram of the imaging apparatus. The apparatus is made up of the following components: (a) - primary source, (b) - collimating lens, (c) - atomizer, (d) - chopper, (e) - focussing lens, (f) - aperture, (g) - narrow-bandpass interference filter, (h) - CCD chip, (i) - primary-source power supply, (j) - atomizer power supply and controller, (k) variable-frequency chopper power supply and controller, (l) - personal computer, and (m) CCD power supply and controller.

mercury, was verified. Therefore, spectral interferences are not expected and these filters have been used in the following imaging experiments. The filters are mounted on a precision post rotator (Melles Griot, Irvine, California.) in order to rotate the filter to obtain the maximum transmission. A flexible bellows (Ealing Electro-Optics Inc., Holliston, Massachusetts.) is used to couple the filter to the CCD and keeps stray light from interfering with the image.

An image of the interior of the atomizer (c) is focused onto the CCD by a bi-convex UV-grade synthetic fused silica lens (e) of 150 mm focal length. An iris diaphragm (f) is placed between the atomizer and the lens to improve the depth of field and reduce the amount of background radiation that strikes the CCD. A plano-convex UV-grade synthetic fused silica lens (b) of 125 mm focal length is used to collimate the emission from the primary source (a). For the atomic absorption measurements an aluminium hollow-cathode lamp (Perkin-Elmer Corporation, Norwalk, Connecticut.) is used. For the molecular absorption measurements a mercury electrodeless-discharge lamp (Perkin-Elmer Corporation, Norwalk, Connecticut.) is used. The power supply for the hollow-cathode lamp (i) was scavenged from a Varian Techtron AA5 atomic absorption spectrophotometer (Techtron Pty. Ltd., Melbourne, Australia). The power supply for the electrodeless-discharge lamp was manufactured by Perkin-Elmer.

Time resolution is achieved by operating the CCD camera in the frame transfer mode. In this mode of operation only one half of the CCD's working surface is illuminated. The image is formed on the illuminated half of the CCD and then the image is quickly transferred to the dark half of the CCD from which it is read out and digitized.

To avoid any blurring during the transfer of the image, the light from the hollow-cathode

lamp is chopped. A variable-frequency chopper (d,k) (Model SR540, Stanford Research Systems Inc., Sunnyvale, California.) that has a frequency output is used for this purpose. The timing of the frame transfer is controlled by the frequency output of the chopper so that the transfer takes place when the entire CCD is darkened by the material segment of the chopper. The frequency output of the chopper is connected to the Photometrics AT200 controller which is a 16-bit computer interface board. The computer interface board controls the operation of the camera and receives the digital image information from the CCD. This board resides in a Raven 386/16 AT-computer (16 MHz 80386SX main processor with 80387 math co-processor). The speed of the imaging system for recording events in dynamic atomizers is a compromise between two conflicting requirements: the spatial resolution and the temporal resolution. For all the experiments, images of the furnace interior were obtained at a rate of 20 Hz with a spatial resolution of $\sim 1 \times 10^{-2}$ mm². The spatial resolution that can be used for static (time-invariant) atomizers is much better than the spatial resolution that can be used with dynamic (time-variant) atomizers because the former do not have the added necessity that the detector provides temporal resolution.

Graphite Furnace. The electrothermal atomizer used in the imaging experiments is a Perkin-Elmer HGA-500 graphite furnace. Tables 14 and 15 show the temperature programs for the atomic absorption measurements with atomization from the graphite tube wall and from the graphite platform, respectively. Table 16 shows the temperature programs for the molecular absorption measurements with vaporization from both the graphite tube wall and the graphite platform. Perkin-Elmer pyrolytic graphite coated graphite tubes (Part No. 091504) and laboratory-fabricated platforms made of pyrolytic

Table 14. Experimental conditions for the atomization of aluminium from the graphite tube wall.

Step	Temperature / °C	Time / s		Internal Ar gas flow / mL min ⁻¹
		Ramp	Hold	
Dry	120	10	30	300
Ash	1200	10	20	300
Atomize	2150	0	6	0
Clean	2650	1	5	300

Table 15. Experimental conditions for the atomization of aluminium from the graphite platform.

Step	Temperature / °C	Time / s		Internal Ar gas flow / mL min ⁻¹
		Ramp	Hold	
Dry	140	10	30	300
Ash	1200	10	20	300
Atomize	2250	0	6	0
Clean	2650	1	5	300

Table 16. Experimental conditions for the vaporization of aluminium-containing molecules from both the graphite tube wall and the graphite platform.

Step	Temperature / °C	Time / s		Internal Ar gas flow / mL min ⁻¹
		Ramp	Hold	
Dry ¹	120	10	30	300
Dry ²	140	10	30	300
Ash	1200	10	20	300
Atomize	2200	0	6	0
Clean	2650	1	5	300

1. Drying conditions for graphite tube wall vaporization.
2. Drying conditions for graphite platform vaporization.

graphite coated graphite were used. The platforms were fabricated to have the same shape as the "I"-shaped Perkin-Elmer platforms.

The 1000 mg/L aluminium standard solution was prepared by dissolving Spex aluminium powder in 1:1 (v/v) HCl:H₂O with heating and the solution was diluted with ultrapure water. The HCl was of Ultrex brand (Baker Chemical Co.). The ultrapure water (18.3 M Ω -cm resistivity) was obtained direct from a Milli-Q2 water purification system (Millipore Corp.). All test solutions were freshly prepared daily and the samples were injected into the furnace using a Perkin-Elmer AS-40 Autosampler.

A Perkin-Elmer Zeeman 5000 atomic absorption spectrophotometer was used for making the conventional graphite furnace AAS measurements. The temperature programs used for these measurements were the same as the temperature programs used for the atomic absorption imaging experiments and they are given in Tables 14 and 15. Also, the same graphite furnaces and graphite platforms that were used in the imaging experiments were used to make the conventional AAS measurements. The aluminium hollow-cathode lamp was operated at 10 mA current and the aluminium 396.1 nm resonance line was used for the graphite furnace AAS measurements. A spectral bandpass of 0.7 nm was used. The same stock solution that was used in the imaging experiments was used in the conventional AAS measurements and all test solutions were prepared the same day that the measurements were made. The test solutions were injected into the furnace using the AS-40 Autosampler. The temperature measurements were made using an Ircon 1100 Series (Ircon, Inc. Niles, Illinois) automatic optical pyrometer that was focused either on the bottom of the graphite tube or on the graphite platform, directly under sample injection port. The output of the pyrometer was

collected and stored on a Nicolet Series 4094 digital oscilloscope (Nicolet Instrument Corp.) and was printed out as a temperature vs. time plot (temperature profile).

RESULTS AND DISCUSSION

CCD-Imaging System. To obtain absorbance values from the CCD-imaging system it is necessary to obtain four images. These images correspond to: 1) the image of the atomizer interior when the atomizer is being operated and the primary light source is on (SIGNAL), 2) the image of the atomizer interior when the atomizer is not being operated and the primary light source is on (REFERENCE), 3) the image of the atomizer interior when the atomizer is being operated and the primary light source is off (BACKGROUND EMISSION), and 4) the image of the atomizer interior when the atomizer is not being operated and the primary light source is off (DARK CURRENT). The absorbance is calculated as follows:

$$A = - \log \left(\frac{\text{SIGNAL} - \text{BACKGROUND EMISSION}}{\text{REFERENCE} - \text{DARK CURRENT}} \right) \quad (9)$$

It would be more correct to take the REFERENCE signal for an empty furnace that was heated and then subtract the BACKGROUND EMISSION image from both the SIGNAL image and the REFERENCE image. However, this procedure requires an additional firing of the furnace which decreases the life of the graphite tube. There is no difference in the results that are obtained using either of these two methods, therefore the method that does not require the additional firing of the furnace was used.

The CCD-imaging system has been calibrated vs. neutral density filters at two different temperatures; 20 °C and 2250 °C. Both of the calibration curves were linear to ~2 absorbance with a slope of 1.00 and both had an intercept of 0.00. This trivial

calibration curve means that it is possible to obtain absorbance values direct from the measured distributions with a minimal amount of data manipulation. Also, the temperature of the atomizer had no effect on the absorbance values that were measured. All the following images of the atomizer interiors are grey-scale representations of the atom densities; the darkest regions represent the highest concentration of atoms, and the lightest regions represent the lowest concentration of atoms.

Distribution of Aluminium Atoms

Atomization from the Graphite Tube Wall. For the atomization from the graphite tube wall, 5 μL of a 1 $\mu\text{g/mL}$ solution of aluminium was injected into the furnace; this amounted to 5 ng of aluminium. Figure 20a shows the atomic absorbance profile recorded using a conventional atomic absorption spectrophotometer for atomization of aluminium from the graphite tube wall with its associated temperature profile. The absorbance profile shows the characteristic feature of the atomization of aluminium, namely a very sharply rising absorbance signal. Figures 20b and 20c show the distributions of aluminium atoms along the vertical diameter of the graphite tube prior to and after the maximum of the absorbance profile. These distributions were obtained by reading out the appropriate portion of the total image recorded by the CCD-imaging system. The absorbance along the vertical diameter of the graphite tube is only a portion of the complete image that is obtained, but it is useful for comparing the results obtained with results that have been obtained previously. As McNally and Holcombe [62] showed using the SIW technique, there are considerable gradients in the atom density distribution for the atomization of aluminium from the graphite tube wall, with the region of lowest concentration being found away from the graphite tube wall, and the region of highest

Figure 20. (a) Conventional recording of the atomization of aluminium from the tube wall and the associated temperature profile. (b) & (c) Distributions of aluminium atoms along the vertical diameter of the graphite tube during atomization from the tube wall. Figure (b) is for distributions prior to the absorbance maximum; Fig. (c) is for distributions after the absorbance maximum.

concentration being found at the graphite tube bottom. As these authors suggested, a likely reason for this distribution is a reaction of Al(g) with $\text{O}_2(\text{g})$, and the oxides that are formed are then reduced at the graphite surface. McNally and Holcombe [62] suggest that the source of the oxygen is the decomposition of the nitric acid matrix used by them. Also, these workers suggest that the reason the region of highest concentration is at the graphite tube bottom is because the sample is initially located there.

The images in Fig. 21 show the complete dynamics of atom formation and dissipation. The distributions were recorded at the times indicated by the filled-in circles on the conventionally-recorded atomic absorbance profile (Fig. 20a). From these images the influence of the sample injection port in the upper left-hand corner of each image is obvious. It can be seen that the region of lowest aluminium concentration is always close to the sample injection port. This suggests that ingress of oxygen through the sample injection port is more important than other sources of oxygen. In the first frame after the onset of atomization [Fig. 21 (ii)], it can be seen that the region of highest concentration is at the graphite tube bottom where the sample was initially located. However, at later times [Fig. 21 (iii) and later], the aluminium atoms redistribute themselves to be far from the source of oxygen (the sample injection port) and this leads to the maximum concentration of atoms being located against the graphite tube wall that is furthest from the sample injection port. The fact that the number density of aluminium atoms is considerably higher in the region that is quite close to the graphite walls indicates the presence of extremely strong gas-phase reactions. The reactions that lead to the formation of aluminium molecular species (that do not absorb at the aluminium atomic resonance lines of 394.4 and 396.1 nm) within the analysis volume occur faster

Figure 21. Sequence of images for atomization of aluminium from the tube wall.

than the diffusion of the aluminium atoms away from the graphite surface, even at elevated temperatures.

Although the images are qualitatively the same as the SSF images that have been obtained previously [18], quantitative information can now be taken direct from the images, both rapidly and reliably. The features of the atomization process are shown quantitatively in the absorbance contour maps shown in Fig. 22. The absorbance contour maps correspond to the images in Fig. 21 having the same Roman numeral identification. The data for these absorbance contour maps have not been smoothed. It can be seen that the absorbance near the graphite tube wall is up to 75% higher than the absorbance near the sample injection port [Fig. 22 (ii)].

Atomization from the Graphite Platform. For the atomization from the graphite platform, 15 μL of a 1 $\mu\text{g/mL}$ solution of aluminium was injected into the furnace; this amounted to 15 ng of aluminium.

Figure 23a shows the atomic absorbance profile recorded by the conventional atomic absorption spectrophotometer for the atomization of aluminium from the graphite platform along with the associated temperature profiles. Of the two temperature curves shown the lower curve was recorded by focusing the optical pyrometer onto the graphite platform surface through the sample injection port; the upper curve was recorded by focusing the optical pyrometer on the graphite tube wall through the sample injection port when the graphite platform had been removed from the furnace. The same heating program was used for both curves. Since a heated graphite platform inside a heated graphite tube is not a blackbody, optical pyrometry based on blackbody radiation cannot give the correct temperature of the heated graphite platform. Therefore, neither of these

(ii)

(iii)

(iv)

(vi)

Figure 22. Contour maps for atomization of aluminium from the tube wall.

Figure 23. (a) Conventional recording of the atomization of aluminium from the platform and the associated temperature profile. (b) & (c) Distributions of aluminium atoms along the vertical diameter of the graphite tube during atomization from the platform. Figure (b) is for distributions prior to the absorbance maximum; Fig. (c) is for distributions after the absorbance maximum.

two temperature curves should be considered as representative of the actual temperature of the graphite platform and they are only meant to serve as an indication of how the graphite platform is heated. The actual temperature of the graphite platform is less than the temperatures indicated by either of the two temperature profiles.. The atomic absorbance profile recorded for the atomization of aluminium from the graphite platform shows a considerably greater amount of tailing than that recorded for atomization from the graphite tube wall.

Figures 23b and 23c present the distributions of aluminium atoms along the vertical diameter of the graphite tube prior to and after the absorbance maximum, respectively. Once again, these distributions were obtained by reading out the appropriate portion of the complete image obtained by the CCD imaging system. The dotted lines connect the absorbances that were measured both above and below the graphite platform at the same instant of time. In Fig. 23b, there are two noteworthy features. The first feature is the aluminium atom density that can be seen immediately under the graphite platform. The distributions presented in this figure show that the initial atomization occurs underneath the graphite platform. The second feature can be seen in the distribution recorded just before the absorbance maximum. In this distribution there are far less atoms under the graphite platform than above it even though the graphite platforms used in this work are the type that only contact the graphite tube surface at four corners. For the distributions recorded after the absorbance maximum the opposite is true. For these distributions there is a far greater concentration of atoms below the graphite platform.

The images recorded for atomization from the graphite platform are given in Fig.

24. The distributions were recorded at the times indicated by the filled-in circles on the conventionally-recorded atomic absorbance profile (Fig. 23a). During the initial instant of atomization [Fig. 24 (ii)], it can be seen that atomization is starting mainly from the graphite tube wall that is farthest from the sample injection port. There is also a smaller amount of atomization occurring from the graphite platform surface. However, since the atomization that is occurring from the graphite tube wall does not appear along the vertical diameter of the graphite tube, it is not recorded in Fig. 23b. The fact that the sample is initially deposited on the graphite platform and the atomization starts from the graphite tube wall indicates that the atomization does not occur directly from the sample. It appears that aluminium is vaporized as both gaseous atoms and molecules. The molecules that are vaporized are reduced to gaseous atoms when they come in contact with the heated graphite walls.

As is the case for the atomization from the graphite tube wall, it can be seen that the sample injection port plays an important role in determining the distribution of aluminium atoms. Once again, there is a pronounced decrease in the concentration of aluminium atoms near the sample injection port, which is in the upper left-hand corner of the images, and again this is most likely due to ingress of oxygen through the sample injection port which results in oxidation of the gaseous aluminium atoms. For later frames [Fig 24 (v), (vi), (vii) and (viii)] it can be seen that there is a redistribution of the aluminium atoms. The maximum concentration of aluminium atoms changes its location and occurs underneath the graphite platform. A probable reason for this is that the region underneath the graphite platform has the most reducing environment within the graphite furnace. Therefore, the aluminium oxides are most easily reduced to release

Figure 24. Sequence of images for the atomization of aluminium from the graphite platform.

gaseous aluminium atoms and the oxidizing effect of oxygen is minimized.

All of the above-mentioned features can be seen quantitatively in the absorbance contour maps in Fig. 25. The absorbance contour maps correspond to the images in Fig. 24 that have the same Roman numeral identification. Figure 25 (ii) clearly shows the simultaneous onset of atomization occurring from both the graphite tube walls and the graphite platform. This simultaneous onset of atomization from both the graphite tube wall and the graphite platform is a feature that had not been identified in the earlier SSF results [18]. This can be attributed to the lower sensitivity of the film recording compared to the CCD results. Figure 25 (ii) shows absorbance contours of 0.1; the minimum absorbance that could be recorded on the film was 0.2 [18]. Figures 25 (v) and 25 (vii) clearly show that the region of highest aluminium atom concentration is located under the graphite platform. In fact, all the features of the atomization process become more clear in the absorbance contour maps. The absorbance contour maps of atomization from both the graphite tube wall (Fig. 22) and the graphite platform (Fig. 25) show the same basic features, namely, a pronounced decrease in the aluminium atom number density near the sample injection port and a maximum aluminium atom number density near the graphite surfaces that are far away from the sample injection port.

Distribution of Aluminium-Containing Molecules. For the measurement of the distributions of aluminium-containing molecules, 20 μL of a 50 $\mu\text{g/mL}$ solution of aluminium was injected into the furnace; this amounted to 1 μg of aluminium. This amount of aluminium was used for imaging the distribution of aluminium-containing molecules vaporized from both the graphite tube wall and the graphite platform.

(ii)

(iii)

(v)

(vii)

Figure 25. Contour maps for atomization of aluminium from the graphite platform.

Vaporization from the Graphite Tube Wall. The images recorded for the vaporization of aluminium-containing molecules from the graphite tube wall are shown in Fig. 26. Figure 26(ii) shows that vaporization begins from the location where the sample was initially deposited. The gaseous, aluminium-containing molecules then begin to fill the analysis volume but the distribution of the molecules is not uniform at any time. There is always a much lower concentration of aluminium-containing molecules close to the surface of the graphite tube wall. In fact, even though the initial supply of aluminium-containing molecules comes from the graphite tube wall [Fig. 26(ii)], the region of maximum concentration moves to the centre of the atomizer [Figs. 26(iv) to 26(vi)]. This shifting of the location of maximum number density suggests the occurrence of a strong heterogeneous reaction between the hot graphite surface and the gaseous, aluminium-containing molecules. At even later times [Figs. 26(vii) and 26(viii)], strange features begin to appear in the distribution of aluminium-containing molecules. The "donut" structure in the measured distributions has been recorded previously by Gilmudinov *et al.* [19]. However, the images recorded using the film-based SSF technique [19] were not as well resolved as the images presented here. Whereas previous recording of the "donut" structure was blurry and indistinct [19], the "donut" structure recorded by the CCD detection system is well focused and distinct.

The absorbance contours for the vaporization of aluminium-containing molecules from the graphite tube wall are shown in Fig. 27. The absorbance contour maps correspond to the images in Fig. 26 that have the same Roman numeral identification. Once again, the features of the vaporization process that have been described above are more obvious in the absorbance contour maps. The supply of aluminium-containing

Figure 26. Sequence of images for the vaporization of aluminium-containing molecules from the graphite tube wall.

(ii)

(iii)

(v)

(vi)

Figure 27. Contour maps for vaporization of aluminium-containing molecules from the graphite tube wall.

molecules from the initial sample location [Fig 27(ii)], the filling of the analysis volume [Fig. 27(iii)], and the redistribution of the location of maximum absorbance [Figs. 27(v) and 27(vi)] can all be seen more clearly in the absorbance contour maps.

Vaporization from the Graphite Platform. The images recorded for the vaporization of aluminium-containing molecules from the graphite platform are shown in Fig. 28. For all frames it can be seen that the region of highest absorbance is always confined to the area immediately above the graphite platform. As is the case for the vaporization from the graphite tube wall, the images show that the region of minimum number density is adjacent to the graphite tube walls. In contrast to the situation that exists for the distribution of aluminium atoms in the case of atomization from the graphite platform, it can be seen in Fig. 28 that the number density of aluminium-containing molecules under the graphite platform is always lower than that above the graphite platform. Once again, all of these features have been presented quantitatively as absorbance contour maps in Fig. 29. From the values presented in the contour maps it can be seen that the absorbance above the graphite platform is as much as 5.5 times that below the graphite platform [Fig. 29(vi)]. These features, along with the high number density of aluminium atoms under the graphite platform at later times, indicate that the conditions in the region under the graphite platform are not favourable for the existence of the aluminium-containing molecules.

Mechanism of Atomization. The features of the distributions of both aluminium atoms and aluminium-containing molecules are consistent with the mechanism of atomization proposed by Gilmudtinov *et al.* [19]. The first event in this mechanism is the initial

Figure 28. Sequence of images for the vaporization of aluminium-containing molecules from the graphite platform.

(iii)

(vi)

(vii)

(viii)

Figure 29. Contour maps for vaporization of aluminium-containing molecules from the graphite platform.

thermal dissociation of aluminium oxide to form both gaseous aluminium atoms and gaseous sub-oxides of aluminium.

Evidence that supports the above formation of $Al(g)$ and $Al_xO(g)$ (where $x = 1, 2$) from $Al_2O_3(s)$ can be taken from Fig. 24(ii) which shows the initial formation of $Al(g)$ from both the platform and the graphite tube wall. The only way that atomization can start from the graphite tube wall when the sample has been deposited on the graphite platform is if the aluminium has been transported to the graphite tube walls in the form of gaseous molecules. The fact that the atomization of aluminium starts simultaneously from both the graphite tube wall and the graphite platform supports the proposal that a fraction of the aluminium oxide is dissociated directly from the initial sample location to yield gaseous aluminium atoms. Although this step of the overall mechanism has been proposed previously [19], there was never any evidence to support the simultaneous formation of gaseous aluminium atoms and gaseous aluminium-containing molecules. The more sensitive CCD imaging system has provided the necessary evidence for supporting this step of the overall mechanism.

The next event in the atomization mechanism for aluminium is the oxidation of the gaseous aluminium atoms to form gaseous sub-oxides.

The source of oxygen molecules for this event in the mechanism is the ingress of oxygen molecules through the sample injection port. Calculations that will be presented in the next chapter show that the ingress of oxygen through the sample injection port can be

considerable. The influence that this oxidation step has on the distribution of aluminium atoms in the gas phase is clearly seen in the decrease in the number density of Al(g) near the sample injection port.

The final event in the mechanism of the atomization of aluminium that is consistent with the experimental evidence provided by the CCD imaging is the heterogeneous reduction of the gaseous sub-oxides of aluminium at the heated graphite surface.

This step in the mechanism is supported by both the localization of the maximum number density of aluminium atoms close to the graphite surface and the fact that the minimum number density of aluminium-containing molecules is at the hot graphite tube walls. This localization of the maximum number density of aluminium atoms close to the graphite surface goes to the extreme for atomization from the graphite platform. The redistribution of the aluminium atoms leading to their concentration under the graphite platform shows that this step [reduction by C(s)] in the mechanism has a very strong effect on the distributions of aluminium atoms that are measured. It can be seen in this final reaction of the overall mechanism that the identity of the aluminium-containing molecules has been assigned to aluminium sub-oxides. The high concentration of aluminium atoms and the low concentration of aluminium-containing molecules under the graphite platform at later times indicates that the environment under the graphite platform becomes highly reducing at elevated temperatures.

CONCLUSIONS

The CCD-SSF imaging system is a valuable tool for fundamental investigations

of processes occurring in atomizers for analytical atomic spectrometry. The major improvements of the new CCD-SSF apparatus over the previous SSF apparatus are the possibility to obtain quantitative results and the simplified optical set-up.

The concentration gradients of both aluminium and aluminium-containing molecules (aluminium sub-oxides) in the electrothermal atomizer that were measured for atomization/vaporization from both the graphite tube wall and the graphite platform can be interpreted in terms of a three-step mechanism of atomization. All of the features of the measured distributions of aluminium atoms in the electrothermal atomizer are consistent with an atomization mechanism that consists of the following sequence of three reactions: 1) thermal dissociation of solid aluminium oxide that yields both gaseous aluminium atoms and gaseous aluminium sub-oxides; 2) homogeneous oxidation of aluminium atoms by gaseous oxygen molecules that yields gaseous aluminium sub-oxides; 3) heterogeneous reduction of gaseous aluminium sub-oxides at the graphite surface yielding gaseous aluminium atoms. The measured distributions of aluminium sub-oxides are also consistent with the above mechanism of atomization. However, there are additional features in the measured distributions of aluminium sub-oxides that cannot be explained (*e.g.*, the "donut" structure). These unexplained features will require further investigation.

CHAPTER 5

THREE-DIMENSIONAL DISTRIBUTIONS OF OXYGEN IN GRAPHITE AND METAL TUBE ATOMIZERS FOR ANALYTICAL ATOMIC SPECTROMETRY

INTRODUCTION

The distribution of atomic and molecular species over the cross-section of tube atomizers in electrothermal atomic absorption spectrometry (AAS) was for a long time considered to be uniform because of the relatively fast diffusional processes that take place at elevated temperatures [5]. However, later investigations by Holcombe and co-workers [61, 73, 74] showed that in many cases the analyte distributions across the tube diameter (as viewed by the slit of the monochromator) are non-uniform. Further studies by Huie and Curran [64, 75] and by Gilmutdinov and co-workers [18, 19] showed that the main atomization event may be limited to a region very close to the atomizer walls and that the degree of non-uniformity is generally much higher when using platform atomization. There is also direct experimental evidence of pronounced non-uniformities in analyte distributions along the tube length [76, 77]. Strong non-uniformities are also characteristic of molecular distributions in both the atomizer cross-section and along the tube length [19]. From these experimental results it can be concluded that both molecular and atomic distributions within tube atomizers are generally highly non-uniform and that uniform distributions are an exception rather than a rule.

There are two reasons why investigations of these non-uniformities are necessary. Firstly, the non-uniformities are a direct consequence of strong homogeneous and heterogeneous analyte reactions and therefore an understanding of the non-uniformities

will lead to an understanding of the fundamental processes in electrothermal atomization. Secondly, as was recently shown by Gilmudtinov *et al.* [57], the absorbance signal that is measured is directly influenced by the spatial non-uniformities of analyte distributions.

The non-uniform distributions mentioned above are complex experimental results which should be described theoretically. Extensive theoretical models that enable the description of the longitudinal non-uniformities of analyte distributions in tube atomizers have been constructed previously [20-22]. However, all of these previous models neglected heterogeneous processes at the atomizer walls. It has been shown that these heterogeneous processes may be crucial to the atomization process [18, 19, 61, 64, 73-75]. A powerful approach for theoretical descriptions of spatially resolved analyte distributions in electrothermal atomization AAS has been developed by Holcombe *et al.* [23-25]. This is the approach of Monte Carlo simulations, which is based on the use of a large number of random selections that are treated in a statistical fashion. However, because of the huge amount of computation necessary for this approach, it only becomes practical when a super-computer is available for use.

This chapter of the thesis represents the development of a different approach for obtaining a fundamental description of the dynamics of spatially-resolved processes. The approach is based on a direct solution of the three-dimensional mass-transfer equations taking into account the boundary conditions that exist at the tube walls and tube ends and the sample dosing hole. The computations necessary for this approach can be easily handled by a personal computer and rarely take longer than a few minutes.

In this chapter the three-dimensional distributions of oxygen in a dry, unloaded furnace are described. This situation is the common background for all atomization

events. The computer model that will be described below represents the first step in this attempt to describe the distribution of atomic and molecular species in tube-type electrothermal atomizers.

The importance of oxygen in electrothermal atomization AAS has been stressed by many workers [78-92]. Oxygen at elevated temperatures is extremely reactive and has been shown to have a strong effect on: 1) the kinetics of atomization of analyte oxides [78-80], 2) the sensitivity of determination of a number of elements [81, 82], 3) physico-chemical interferences [83] and 4) the nature of the atomization surface which, because of a change in the surface activity, may lead to temporal shifting of the absorption pulse [83-85]. It can be seen that oxygen has a significant effect on almost all aspects of the atomization process.

Previous studies have shown that there are four potential sources of gaseous oxygen in electrothermal atomization AAS. These sources are: 1) impurities in the argon sheath gas [80], 2) ingress through the sample dosing hole [86, 87], 3) decomposition of the sample matrix [79, 88-91], and 4) other possible sources, such as diffusion through the atomizer walls and ingress through cracks or pores at the contact point between the tube and the graphite support ring [92].

Extensive investigations made by Sturgeon and Falk [87, 90] have shown that for Perkin-Elmer HGA-type pyrolytic graphite coated graphite furnaces, the major source of free oxygen in a dry and unloaded furnace is the ingress of oxygen through the sample dosing hole [87] and in loaded furnaces the major source of oxygen arises from the decomposition of analyte oxide [90].

Information about oxygen in metal tubes is limited. It is, however, of some

importance because of attempts to use metal tubes in analytical practice [93, 94]. The use of metal tubes is also important in the investigation of atomization mechanisms (where the results are compared with results obtained using graphite furnaces). Sturgeon *et al.* [95] have given direct experimental evidence that the value of the partial pressure of oxygen, p_{O_2} , in a tantalum-lined graphite tube is orders of magnitude lower than the value of p_{O_2} in a graphite tube at a given temperature. These results indicate that the behaviour of oxygen in a metal tube is significantly different from its behaviour in a graphite tube. Therefore, metal tubes merit individual consideration.

Although all workers agree on the importance of oxygen in electrothermal atomization AAS, there is no consensus on the p_{O_2} within the atomizer. In fact, existing estimates of p_{O_2} in graphite tube atomizers differ by as much as 12 orders of magnitude at a temperature of 2500 K [8].

All previous attempts to estimate p_{O_2} in electrothermal atomization AAS have been limited by two factors. The first limitation is because of the fact that all considerations have been based on thermodynamically-constructed models. This approach is limited by the necessity of establishing thermodynamic equilibrium. As has been clearly shown by Sturgeon and co-workers [87, 90, 92] the graphite furnace is not a closed system and thermodynamic equilibrium is not established until high temperatures are reached. Therefore, a more appropriate description of oxygen in electrothermal atomization AAS can be provided by a kinetically-constructed model. The second

limitation for all previous considerations is that the results obtained are spatially integrated. These results provide no information about the distribution of oxygen in electrothermal atomization AAS. As stressed above, the distributions of species in tube atomizers may be strongly non-uniform. Therefore, a more complete description of oxygen in electrothermal atomization AAS would provide information on the distribution of oxygen within the atomizer.

The main objective of this chapter of the thesis is to provide three-dimensional oxygen distributions for both graphite and metal-tube atomizers obtained from a model that is based on a kinetic description of electrothermal atomization AAS.

THEORY

Construction of the Kinetic Model. The following basic assumptions were taken for the construction of the kinetic model. 1) Stationary conditions exist, *i.e.*, the furnace has been heated to its final temperature. 2) The furnace is used under the gas-stop mode of operation. 3) The only oxygen reaction within the atomizer is the heterogeneous reaction of molecular oxygen with the tube walls. This assumption means that there are no gas-phase reactions that will lead to a change in the oxygen concentration within the furnace. 4) There are only longitudinal temperature gradients within the furnace, *i.e.*, a given furnace cross-section is isothermal. 5) A dry, unloaded tube is used. Therefore, there will be only two significant sources for oxygen ingress into the furnace volume. These two sources are ingress through the dosing hole, and impurities in the argon sheath gas. The construction of a model based on the assumptions made above will provide a general case. Further complications to the model can be incorporated as the need arises. It can

be seen that all assumptions made are reasonable for an electrothermal atomizer operated using standard operating conditions. The results obtained from the solution of this model will provide a general background for any atomization situation in electrothermal atomization AAS.

The notational convention used in the formulation of the model is shown in Fig. 30. The frame of reference for the three cylindrical coordinates, r , φ and z , is given. The model is used to calculate the three-dimensional distribution of oxygen in cylindrical coordinates. The choice of a cylindrical coordinate system is appropriate for the tube geometry of electrothermal atomizers. The geometry of tube atomizers can be completely described by 3 physical parameters. These three parameters, shown in Fig. 30, are: L , the half-length of the tube; R , the inside radius of the tube; and a , the radius of the sample dosing hole. Any location within the tube atomizer can be described by the three coordinates $\{r, \varphi, z\}$. Although all results presented in this chapter reflect the geometry of Perkin-Elmer HGA-type furnaces, the model has been constructed to be able to account for any tube geometry.

The most complete description of the concentration distribution, $n(r, \varphi, z)$, of any species within the atomizer is given by the following continuity equation [20]:

$$\frac{\partial n}{\partial t} + \text{div } \vec{\Phi} = \left(\frac{\delta n}{\delta t} \right)_v \quad (13)$$

which is a mathematical presentation of the law of mass conservation. The right-hand-side of Eqn. (13) expresses the rate of variation of the concentration of the species under consideration due to gas-phase reactions.

Figure 30. Tube atomizer geometry in longitudinal section (a) and cross-section (b).

With the basic assumptions that have been made, $\frac{\partial n}{\partial t} = 0$ (*i.e.*, stationary conditions) and $\left(\frac{\delta n}{\delta t}\right)_v = 0$ (*i.e.*, no gas-phase chemical reactions). For typical

electrothermal atomization conditions, the flux vector $\vec{\Phi}$ is completely determined by gas convection, concentration diffusion and, thermal diffusion [20]. Once again, with the basic assumptions that have been made there will be no gas convection (*i.e.*, gas-stop mode of atomization and stationary conditions). Also, under typical electrothermal atomization AAS operating conditions thermal diffusion of molecular oxygen can be neglected. Therefore, the molecular flux of oxygen within the electrothermal atomizer is determined by concentration diffusion alone and is given by the following equation:

$$\vec{\Phi} = -D \text{ grad } n \quad (14)$$

where D is the diffusion coefficient for molecular oxygen. Combining Eqns. 13 and 14 gives the general diffusion equation for the conditions that have been chosen:

$$\frac{\partial n}{\partial t} = \text{div} (D \text{ grad } n) = 0 \quad (15)$$

Since it has been assumed that there are only longitudinal temperature gradients and since the diffusion coefficient varies with temperature, it can be seen that $D(r, \varphi, z) = D(z)$. Therefore, with a cylindrical coordinate system Eqn. 15 can be rewritten as:

$$\frac{\partial}{\partial z} \left[D(z) \frac{\partial n}{\partial z} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[r D(z) \frac{\partial n}{\partial r} \right] + \frac{1}{r^2} \frac{\partial^2 n}{\partial \varphi^2} D(z) = 0 \quad (16)$$

The final step in formulating the mathematical model is the establishment of the boundary conditions that exist. There are four boundary conditions for this particular problem. The first boundary condition is the following:

$$\frac{\partial n}{\partial z} \Big|_{z=0} = 0, \text{ for any } r, \varphi \quad (17)$$

This condition takes into account the fact that there is a longitudinal symmetry to the distribution of species in the atomizer [*i.e.*, $n(r, \varphi, z) = n(r, \varphi, -z)$].

The second boundary condition accounts for the fact that there is also a transverse symmetry to the distributions [*i.e.*, $n(r, \varphi, z) = n(r, -\varphi, z)$]. This boundary condition is given by the following equation:

$$\frac{\partial n}{\partial \varphi} \Big|_{\varphi=0} = \frac{\partial n}{\partial \varphi} \Big|_{\varphi=\pi} = 0, \text{ for any } z, r \quad (18)$$

The third boundary condition is the following:

$$n(r, \varphi, z = L) = n_{\text{end}}, \text{ for any } r, \varphi \quad (19)$$

This boundary condition accounts for the fact that oxygen impurities in the purge gas will lead to an ingress of oxygen into the furnace from the ends of the tube. The concentration of the oxygen impurity in the purge gas is given by n_{end} .

The final boundary condition accounts for: the ingress of oxygen through the dosing hole at a rate of J (molecules s^{-1}) and the disappearance of the oxygen molecules as a result of the heterogeneous reaction with the tube walls. These two factors are represented as follows:

$$-D(z) \frac{\partial n}{\partial r} \Big|_{r=R} = \begin{cases} -\frac{J}{\pi a^2}, & \text{at the dosing hole} \\ k(z) n \Big|_{r=R}, & \text{at the wall} \end{cases} \quad (20)$$

At the dosing hole the diffusion of oxygen away from the dosing hole is equal to the flux of oxygen into the furnace, J , over the entire surface area of the dosing hole, πa^2 , where a is the radius of the dosing hole. The negative sign in front of the flux term, $-J/\pi a^2$, indicates that the ingress of oxygen occurs in the opposite direction to the increasing radial coordinate, r (see Fig. 30). At the tube wall the diffusion of oxygen to the wall is equal to the first-order rate of the heterogeneous reaction. The temperature-dependent rate constant for this reaction is $k[T(z)]$.

In order to make the numerical analysis more general it is useful to express the equations in a normalized form. Equation 16 can be rewritten as:

$$\frac{1}{D(z')} \left(\frac{R}{L} \right)^2 \frac{\partial}{\partial z'} \left[D(z') \frac{\partial n^*}{\partial z'} \right] + \frac{1}{r'} \frac{\partial}{\partial r'} \left(r' \frac{\partial n^*}{\partial r'} \right) + \frac{1}{r'^2} \frac{\partial^2 n^*}{\partial \varphi^2} = 0 \quad (21)$$

where the normalized coordinates are defined as follows:

$$\left\{ \begin{array}{l} z' \equiv \frac{z}{L}, \text{ dimensionless axial coordinate, } z' \in [0,1] \\ r' \equiv \frac{r}{R}, \text{ dimensionless radial coordinate, } r' \in [0,1] \\ \varphi, \text{ angle coordinate, } \varphi \in [0,\pi] \\ n^* \equiv \frac{n}{n_{\max}}, \text{ normalized concentration, } n^* = n(r', \varphi, z') \\ n_{\max} = \frac{J}{\pi a^2} \frac{R}{D_0}, \text{ estimation of maximal concentration inside the tube} \end{array} \right.$$

The normalization factor for the concentration, $n_{\max}$, was chosen to make the rate of oxygen ingress equal to one. It can be seen that $n_{\max}$ is an estimation of the

concentration of oxygen near the dosing hole (D_0 is the value of the diffusion coefficient near the dosing hole).

Under these conditions of normalization, the boundary conditions take the following form:

$$\left\{ \begin{array}{l} \frac{\partial n^*}{\partial r'} \Big|_{z'=0} = 0 \\ n^*(r', z' = 1, \varphi) = \frac{n_{end}}{n_{max}} \\ \frac{\partial n^*}{\partial \varphi} \Big|_{\varphi=0} = \frac{\partial n^*}{\partial \varphi} \Big|_{\varphi=\pi} = 0 \\ \frac{\partial n^*}{\partial r'} \Big|_{r'=1} = \begin{cases} 1, & \text{at the dosing hole} \\ -\frac{k(z')}{D(z')} R n^* \Big|_{r'=1}, & \text{at the wall} \end{cases} \end{array} \right. \quad (21a)$$

In order to obtain a numerical solution for Eqn. 21 with the boundary conditions given above, the furnace was divided into many elementary volumes, $dV' = r' dr' d\varphi dz'$ (see Fig. 31). The concentration of oxygen, $n(r', \varphi, z')$, is assumed to be constant within a unit of elementary volume. The symmetry of the problem as reflected by Eqns. 17 and 18 allows for the calculation of the distributions for only one-quarter of the total furnace volume. Preliminary calculations showed that good accuracy could be obtained with the following computational network: the tube half-length, L , is divided into 14 sections; the tube radius, R , is divided into 10 sections; and the angle $\varphi \in (0, \pi)$ is divided into 39 sections. Therefore, one quarter of the furnace volume, 0.05 cm^3 , is divided into 5,460 units of elementary volume for the calculations that will be described later. The system of finite difference equations for the above network was solved using the method of summary approximations.

Figure 31. Tube atomizer geometry in normalized coordinates showing the network used for the numerical solution (because of the symmetry of the problem it is only necessary to consider one-quarter of the tube's volume).

Temperature Dependence for Gas-Phase Diffusion Coefficients. As can be seen from Eqns. 14 - 21, the diffusion coefficient is a crucial parameter that determines both the distribution and the concentration of oxygen inside tube atomizers. Marrero and Mason [96] have written an extensive review of gaseous diffusion coefficients. In this review the temperature dependence of the diffusion coefficient for oxygen in argon over a temperature range of 243 - 10 000 K has been given as:

$$D(T) = D_0 T^\alpha \quad (22)$$

with the error not exceeding 3%.

This same form of presentation is also valid for the diffusion coefficient of carbon monoxide in argon. The parameters D_0 and α for O_2 , and CO taken from Ref. [96] and the diffusion coefficients for these species calculated at both low and high temperatures ($T = 1500$ K and $T = 2500$ K) are given in Table 17.

The dependence of the diffusion coefficients on the longitudinal coordinate, $D(z)$, can be described using Eqn. 22 if the temperature distribution along the longitudinal coordinate, $T(z)$, is known. The temperature gradients that exist under typical operating conditions can be adequately described by the following equation [20]:

$$T(z) = T_0 \exp \left[-(\ln \Delta) \left(\frac{z}{L} \right)^2 \right] \quad (22a)$$

where T_0 is the temperature at the tube centre and Δ is the ratio of the temperature of the centre of the tube to the temperature at the ends of the tube, T_0/T_L (i.e., in an isothermal furnace, $\Delta = 1$). A larger value of Δ reflects a larger degree of non-isothermality. Therefore, the parameter Δ has been termed the degree of non-isothermality. While Eqn. 22a is only an approximation of the real temperature gradients

Table 17. Diffusion parameters and diffusion coefficients for oxygen and carbon monoxide in an argon atmosphere.

Species	$D_0 / 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	α	$D / \text{cm}^2 \text{ s}^{-1}$	
			1500 K	2500 K
O_2	9.77	1.736	3.19	7.74
CO	9.04	1.752	3.31	8.12

that exist it has been found that the final results obtained do not differ significantly when a more refined approximation is used.

Rate constants for oxidation processes

Oxygen - pyrolytic graphite. The $O_2(g) - C(s)$ interaction is one of the most researched systems in heterogeneous kinetics. The reaction scheme in its simplest form involves the reaction of gaseous oxygen with solid graphite to form two gaseous products, carbon monoxide and carbon dioxide, as follows:

where C_a is an active site on the graphite surface where reaction is possible. The simplicity of the above stoichiometric relationships is misleading and actually tends to obscure the complexity of the oxygen-graphite interaction. Marsh [97] has stated that reactions 23a and 23b require at least 10 intermediate steps to give a complete kinetic description of the processes that are occurring.

It is also well recognized that the reactivity of carbon may vary by as much as three orders of magnitude depending on the type of graphite that is used [98]. For studies in electrothermal atomization AAS the most important type of graphite is pyrolytic graphite coated. A comprehensive description of the interaction of pyrolytic graphite with oxygen at elevated temperatures (1000 - 2400 °C) and at partial pressures of oxygen up to 0.2 atm has been given [99-101]. The standard operating conditions for electrothermal atomization AAS are within this range of temperatures and the partial pressure of oxygen within the furnace is definitely lower than 0.2 atm. Although these studies [99-101] were carried out in independent laboratories, using different

experimental techniques, the results were all similar.

From these investigations [99-101] the rate of oxidation of pyrolytic graphite can be expressed as follows:

$$\begin{aligned} \text{rate of loss of carbon} &= \left(\frac{k_A p_{O_2}}{1 + k_z p_{O_2}} \right) x + k_B p_{O_2} (1 - x) \\ \text{where } x &= \left(1 + \frac{k_T}{k_B p_{O_2}} \right)^{-1} \end{aligned} \quad (24)$$

where the rate is given in units of moles of carbon $\text{cm}^{-2} \text{s}^{-1}$, p_{O_2} is the partial pressure of oxygen in atm. and k_A , k_B , k_T and k_z are rate constants that are used to describe the elementary reactions that are occurring. The temperature-dependent values of these four rate constants are given below:

$$\begin{aligned} k_A &= 20 \exp(-30,000/RT) \text{ (mole cm}^{-2} \text{s}^{-1} \text{atm}^{-1}) \\ k_B &= 4.46 \times 10^{-3} \exp(-15,200/RT) \text{ (mole cm}^{-2} \text{s}^{-1} \text{atm}^{-1}) \\ k_T &= 1.51 \times 10^5 \exp(-97,000/RT) \text{ (mole cm}^{-2} \text{s}^{-1}) \\ k_z &= 21.3 \exp(4,100/RT) \text{ (atm}^{-1}) \end{aligned}$$

As boundary condition 21a shows, the computer model has been designed to consider the wall reaction of oxygen as a first-order heterogeneous reaction which is expressed as follows:

$$\text{rate of loss of oxygen} = k(T) n_{O_2} \quad (25)$$

where k is the first-order rate constant in units of cm s^{-1} . Equation 24 shows that the oxidation of graphite is not first order with respect to oxygen over the entire range of temperatures (1000 - 2400 °C) and partial pressures of oxygen (up to 0.2 atm) considered by the previous workers [99-101]. In order to determine the region where Eqn. 24 can be adequately described by a first-order equation, Fig. 32, which is a plot

Figure 32. The rate constant for the oxygen - pyrolytic graphite reaction vs. temperature and partial pressure of oxygen.

of the rate constant, k , vs. temperature, T , vs. $\log(\text{pressure})$, $\log(p_{O_2})$, was constructed.

The rate constant shown is calculated by assuming: 1) first-order kinetics, 2) the ideal gas law in order to convert from pressure, p , to concentration, n , and 3) that carbon monoxide is the major product of the oxidation reaction, therefore the rate of oxidation of carbon atoms is twice the rate of loss of oxygen molecules. With these assumptions,

$k = \text{Eqn}(24)RT/2p_{O_2}$. The first-order approximation is valid where this function is

constant with respect to pressure. There are two regions where the first-order approximation is valid: one at high oxygen partial pressures and relatively low temperatures (Region I in Fig. 32) and the other at low oxygen partial pressures and high temperatures (Region III in Fig. 32). In the intermediate region II, the reactivity of pyrolytic graphite appears to be anomalous, there is a decrease in reactivity with an increase in temperature. According to Nagle and Strickland-Constable [99] these results can be attributed to the oxidation reaction occurring on two types of sites, reactive A sites and less-reactive B sites on the graphite surface. The B sites are produced from the A sites by a temperature-dependent annealing process that results in the decrease in reactivity at higher temperatures.

Since the operating conditions for electrothermal atomization AAS are in the low oxygen partial pressure - high temperature region (Region III in Fig. 32), Eqn. 24 can be simplified to reflect the situation that exists in this region. At low oxygen partial pressures and high temperatures the oxygen - pyrolytic graphite interaction is dominated by the elementary reaction step described by the rate constant k_B . Also, under these conditions, the major product formed is carbon monoxide and reaction 23a dominates.

Therefore, for the normal operating conditions of electrothermal atomization AAS, Eqn. 24 can be simplified to:

$$\text{rate of loss of oxygen} = 0.5 k_B p_{O_2} \quad (26)$$

Using the ideal gas law to convert from pressure, p , to concentration, n , and the value of k_B taken from Ref. [99] given above, the first-order rate constant, $k(T)$, in Eqn. 25 can be described adequately by the following Arrhenius-type expression:

$$k(T) = b T \exp\left(\frac{-c}{T}\right) \quad (27)$$

The values of the parameters b and c for pyrolytic graphite are given in Table 18.

Oxygen - Tantalum. The kinetics of the interaction of tantalum with oxygen is fairly complex and has been studied in great detail [102]. For typical operating temperatures of tantalum-lined graphite furnaces it has been established [102] that the major product of the oxidation reaction is TaO which is immediately volatilized from the surface of the atomizer. Under these conditions the rate of surface recession of tantalum metal under oxidization can be adequately expressed by the following relationship [102]:

$$\log(\text{rate of loss of tantalum}) \approx \log(p_{O_2}) + 8.9 - 12200/T \quad (28)$$

where the rate is given in units of $\mu\text{m h}^{-1}$ and p_{O_2} is the partial pressure of oxygen in Torr. This rate expression gives the net rate of removal of tantalum as TaO from the surface of the atomizer as a function of temperature and oxygen partial pressure and is directly proportional to the rate of oxygen consumption at the surface of the atomizer. Using: 1) the ideal gas law to convert pressure to concentration; 2) the stoichiometry of the over-all reaction; and 3) the density and relative atomic mass of tantalum, the first-order rate constant for the heterogeneous reaction of oxygen molecules with tantalum can

Table 18. Parameters for the first-order rate constant, $k(T) = bT \exp(-c/T)$, and values of the rate constants calculated at two different temperatures.

Furnace	$b/\text{cm s}^{-1}\text{K}^{-1}$	c/K	$k/\text{cm s}^{-1}$	
			1800 K	2300 K
C	1.83×10^{-1}	7.65×10^3	4.70	15.1
W	6.23×10^2 *	1.23×10^4	1210	6820
Ta	6.31×10^4	2.00×10^4	1700	24300

*The oxygen partial pressure is assumed to be $\sim 10^{-7}$ atm.

be expressed by Eqn. 27. The b and c parameters for the rate constant are given in Table 18.

Oxygen - Tungsten. The simplest expression for the rate of loss of tungsten due to oxidation at elevated temperatures is given in Ref. [103] as:

$$\text{rate of loss of tungsten} = 1.813 \times 10^{-3} \exp(-43900/RT) p_{O_2}^{0.82} \quad (29)$$

where the activation energy (43 900) is in calories and p_{O_2} , the partial pressure of oxygen, is in Torr. The dominant product of the oxidation reaction of tungsten at the standard operating temperatures of a tungsten-lined graphite furnace [103] is WO_2 which is immediately volatilized from the surface of the atomizer. Once again, using the ideal gas law to convert pressure to concentration, the rate constant for the consumption of molecular oxygen because of the oxidation of tungsten can be presented in the same form as Eqn. 27. In this case the b-parameter has the following value: $b = 1.13 \times 10^2 p_{O_2}^{-0.18}$ $\text{cm atm}^{-0.18} \text{ s}^{-1} \text{ K}^{-1}$. The c-parameter is given in Table 18. It can be seen from the value of b that this rate expression is not strictly first-order but can be used to approximate a first-order reaction for a change in oxygen partial pressures within a few orders of magnitude. Therefore, an approximate oxygen partial pressure is used initially to calculate the value of the b-parameter and this value is then used for calculations with the computer model. Taking an oxygen partial pressure of $p_{O_2} = 10^{-7} \text{ atm}$, $b = 6.3 \times 10^4 \text{ cm s}^{-1} \text{ K}^{-1}$.

The rate of oxidation of the different materials used in electrothermal atomization AAS that are considered in this thesis can be expressed with reasonable accuracy as first-

order rate equations with an Arrhenius-type rate constant (see Eqn. 27). The values of the two parameters that determine the rate constants for pyrolytic graphite, tantalum and tungsten are given in Table 18 together with illustrative values of the rate constants calculated at $T = 1800\text{ K}$ and $T = 2300\text{ K}$. This table shows surprisingly low values for the rate constant of oxidation of pyrolytic graphite, 4.7 cm s^{-1} and 15.1 cm s^{-1} for the temperatures of 1800 K and 2300 K , respectively. The rate constants for tantalum and tungsten are almost three orders of magnitude greater. The consequences of these values for both the concentration of free oxygen and its distribution within tube-type atomizers are analyzed below.

Flux of oxygen through the dosing hole. With the normalization conditions described above, the model has been designed to calculate the distribution of oxygen within a tube atomizer in terms of the flux of oxygen through the sample dosing hole. In order to make an estimation of this flux and, consequently, to get an estimation of the absolute value of the oxygen concentration, a simplified model of a Perkin-Elmer HGA-type furnace near the dosing hole (Fig. 33) has been created. Although the actual geometry of the region surrounding the sample dosing hole and the patterns of gas flow are fairly complex (with the oxygen having to diffuse through both the graphite cones and through the sample dosing hole in the furnace) the following model can give a reasonable estimate of the flux.

The path by which oxygen enters the furnace through the dosing hole [the dotted lines in Fig. 33(b)] can be divided into three separate regions: in region I there is diffusional transport of the molecules from the environmental atmosphere, where the molecules are at a concentration of $n_o\text{ [cm}^{-3}\text{]}$, to the sample dosing hole. In region II

Figure 33. Schematic diagram of a Perkin-Elmer HGA-type furnace in longitudinal section, (a), and its modelling for the calculation of molecular oxygen ingress through the sample dosing hole, (b). Region II represents the holes in both the furnace and in the cones which have been combined into a single hole for simplification of the model.

there is diffusion of the molecules inside the dosing hole against the external purge gas flow that has a linear velocity of v [cm s⁻¹]. The dosing hole has an effective length of l [cm] and a radius of a [cm]. It should be noted that, in reality, the external purge gas velocity is not constant along the entire length of the dosing hole: initially, as the horizontal flow changes to a vertical flow [see Fig. 33(a)] the vertical component will be zero. Subsequently, the vertical component of the external purge gas flow velocity will increase until the flow escapes from the dosing hole. Therefore, the parameters introduced above to describe the situation in the dosing hole should be considered effective values that do not necessarily coincide with the actual values. Finally, in region III the molecules diffuse into the furnace volume producing the flux of ingressing molecules of J [molecules s⁻¹]. It is assumed that in Region III the molecular cloud inside the furnace has a spherical symmetry and that all molecules are completely reacted at a distance of $r = R^*$ from the sample dosing hole [*i.e.*, $n(R^*) = 0$]. The effective radius, R^* , can be greater or less than the actual radius of the furnace depending on the reactivity of the furnace wall. This is a simplified interpretation of the furnace conditions but it will be shown later that the flux J is not very sensitive to the conditions within the furnace volume. It has also been assumed that the three regions have different temperatures $T_1 < T_2 < T_3$ and that the three regions are isothermal. Therefore, each region will have a separate diffusion coefficient (D_1 , D_2 , and D_3) associated with it.

The general solution of this model (particulars of the solution are given in the Appendix) yields the following expression for the ingress flux, J [molecules s⁻¹], through the dosing hole:

$$J = \frac{2\pi a n_0}{\frac{1}{D_1} + \frac{2l}{a} \frac{1}{D_2} \frac{1}{P} (e^P - 1) + \frac{1}{D_3} \left(1 - \frac{a}{R^*}\right) e^P} \quad (30)$$

where $P = (v/D_2)l$ is a protection parameter (a description of the physical meaning of this parameter will be given later). From the numerator of the Eqn. 30 it can be seen that the flux of oxygen into the furnace is directly proportional to the concentration of oxygen in the ambient atmosphere, n_0 (if the ambient atmosphere is air, $n_0 \approx 0.5 \times 10^{19} \text{ cm}^{-3}$). The denominator of the above equation consists of three terms, each of which contains one diffusion coefficient. Therefore, each term can be considered to be the resistance of each region to the diffusional flow of oxygen.

There are two extreme situations that are worth considering. In the first case the external gas flow rate near the dosing hole is taken to be very low and therefore the protection parameter, $P = (v/D_2)l \ll 1$. In this case $e^P \approx 1 + P$ and the general expression 30 can be reduced to:

$$J = \frac{2\pi a n_0}{\frac{1}{D_1} + \frac{2l}{a} \frac{1}{D_2} + \left(1 - \frac{a}{R^*}\right) \frac{1}{D_3}} \quad (31)$$

From this equation it can be seen that the total flux of oxygen into the atomizer is independent of the external gas flow (*i.e.*, no protection parameter) and is only determined by the concentration diffusion of oxygen through the three regions. Equation 31 allows for the estimation of the maximum value of the flux if the atomizer geometry and the temperature distributions are known for each region. As an example, the following values can be taken to get an estimation of the flux: $T_1 = 300 \text{ K}$, $T_2 = 1000 \text{ K}$, and $T_3 = 2500 \text{ K}$, which give the following values for the three diffusion

coefficients: $D_1 = 0.2 \text{ cm}^2\text{s}^{-1}$, $D_2 = 1.5 \text{ cm}^2\text{s}^{-1}$, and $D_3 = 7.9 \text{ cm}^2\text{s}^{-1}$ (see Eqn. 22). Taking the other parameters as: $a = 0.1 \text{ cm}$, $l = 0.5 \text{ cm}$ and $R^* = 1 \text{ cm}$, the value for the flux of oxygen into the furnace will be $J \approx 2 \times 10^{17} \text{ s}^{-1}$. This calculated value for J provides an estimation of the ingress of oxygen into a Perkin-Elmer HGA-type atomizer in the absence of protective external purge gas flow.

The other extreme case is more important from a practical point of view. In this case the protection parameter, $P = (v/D_2)l \gg 1$. Indeed, under normal operating conditions [104] it is usual to use an external gas flow rate of around 1 L min^{-1} . To convert this flow rate to a linear velocity near the dosing hole, as needed in Eqn. 30, the actual geometry of the atomizer should be taken into account. The Perkin-Elmer HGA-2200 system that was used for the experiments carried out by Sturgeon and Falk [87, 90], has two holes in one graphite cone (the sample dosing hole and the hole through which the temperature is monitored) and a slit between the two graphite cones. For this type of furnace, the total surface area through which the external gas flow can escape to the atmosphere is 0.7 cm^2 . Assuming that the external gas flow escapes uniformly over the entire cross-sectional area available, an estimate for the linear velocity near the dosing hole of $v \approx 25 \text{ cm s}^{-1}$ can be obtained. This means that under the normal operating conditions for a Perkin-Elmer HGA-type atomizer, the protection coefficient, $P \approx 6 - 10$. With these values the dominant term in the denominator of Eqn. 30 is the resistance to flux of region II and this general expression is reduced to:

$$J = \frac{\pi a^2 D_2 n_0}{l} \times \frac{P}{e^P - 1} \quad (32)$$

This equation provides an estimation of the value for the flux of oxygen into the atomizer

if a substantial external gas flow exists and, as a consequence, if the diffusion through regions I and III are not limiting factors. To provide the physical meaning for this equation the following analysis can be made: when $P = 0$, Eqn. 32 is reduced to

$$J = \frac{\pi a^2 D_2 n_0}{l} = J_{dif}. \text{ It can be seen that this is the solution for the diffusional ingress}$$

of oxygen in the simplest case of neglecting diffusion in Regions I and III and without the presence of a convective flow of gas in Region II. Obviously, this equation will provide an estimation for the largest possible ingress of oxygen into the atomizer. An estimation made using the same conditions as taken in situation 1) above yields $J_{dif} = 4.3 \times 10^{17} \text{ s}^{-1}$. This value is two times greater than the value calculated based on Eqn. 31 which accounts for diffusion in all three regions. The presence of the external gas flow will reduce the ingressing flux by a factor of $P/(e^P - 1) \approx Pe^{-P}$. Therefore, this factor will be called the protection coefficient. The parameter, P , which is the only term that is required to determine the coefficient, has been previously named the protection parameter. It is interesting to note that the relationship D_2/l in the protection parameter is an estimation of the velocity, v_D , of diffusional propagation of oxygen through the dosing hole. Therefore, rewriting the protection parameter as $P = v/v_D$ shows the clear physical meaning of this term: it shows how many times the diffusional velocity for the ingress of oxygen into the atomizer is exceeded by the velocity for convectional removal of the oxygen atoms.

Taking these results into account the resulting flux can be presented as the product of two components, diffusion and convection:

$$J \approx J_{af} P e^{-P} \quad (33)$$

Figure 34 shows the logarithmic dependence of the protection coefficient on the protection parameter, P . Using the previous estimation for the value of the protection parameter, $P \approx 6 - 10$, it can be seen from Fig. 34 that the use of an external gas flow rate of about 1 L min^{-1} , reduces the ingress of oxygen into the furnace by a factor of $(0.5 - 30) \times 10^2$. This means that, under normal operating conditions, the flux of oxygen into the graphite furnace is approximately $10^{14} - 10^{16} \text{ molecules s}^{-1}$.

An estimation of the value for the ingress of oxygen into graphite furnaces can also be obtained from previous experimental evidence [87]. Sturgeon and Falk [87] reported that at $T = 2100 \text{ K}$ the partial pressure of carbon monoxide is equal to $1.1 \times 10^{-3} \text{ atm}$ for a pyrolytic graphite coated graphite tube. According to these workers [87], under these conditions the oxygen is totally converted to carbon monoxide and the only source for oxygen molecules is by their ingress through the sample dosing hole. Assuming that each oxygen molecule produces two molecules of carbon monoxide (see Eqn. 23a) and that steady-state conditions exist, the following balance equation can be written:

$$2J_{O_2} = \frac{N_{CO}}{\tau} \quad (34)$$

where N_{CO} is the total number of carbon monoxide molecules present within the furnace and τ is their residence time within the furnace. Expressing N_{CO} in terms of concentration (*i.e.*, $N_{CO} = n_{CO} \pi r^2 L^*$) and assuming that the residence time is determined only by diffusion through the tube ends, so that $\tau = L^{*2}/8D_{CO}$, where L^* is the length within the furnace where carbon monoxide molecules exist and D_{CO} is their diffusion coefficient, the following expression can be obtained from Eqn. 34:

Figure 34. Protection coefficient vs. protection parameter.

$$J_{O_2} = n_{CO} \frac{4\pi r^2 D_{CO}}{L^*} \quad (35)$$

For $T = 2100$ K, $D_{CO} = 5.98 \text{ cm}^2\text{s}^{-1}$ (Eqn. 22 and Table 17). Taking L^* as equal to the entire length of the tube, the value of oxygen ingress necessary to sustain the carbon monoxide partial pressure reported by Sturgeon and Falk [87] can be calculated:

$J_{O_2} \approx 9.3 \times 10^{15} [\text{molecules s}^{-1}]$ which is within the limits of the above theoretical estimations.

A graphical representation of the oxygen concentration is shown in Fig. 35 for all three of the regions along the path from: 1) furnace bottom to 2) dosing hole to 3) the ambient atmosphere for two different situations. The distributions were obtained as a result of a general solution of the system of differential equations for the three regions (see the Appendix) for both a high (curve 1) and a low (curve 2) furnace temperature. The increase in the concentration of oxygen as the distance is increased from the bottom of the furnace and out into the ambient atmosphere is shown relative to the concentration of oxygen in the ambient atmosphere. The temperature of the gas phase in region II was taken to be related to the furnace temperature and therefore T_2 is taken to increase slightly with an increase in the temperature of the furnace. It can be seen in Fig. 35 that the value of T_2 is a crucial parameter: a 20% decrease in T_2 yields a decrease in the concentration of oxygen within the atomizer of more than one order of magnitude. This is because the temperature T_2 determines the value of the diffusion coefficient, D_2 , which strongly affects the protection parameter and therefore the flux, J , through the dosing hole. The two curves in Fig. 35 illustrate the following results: changes in the oxygen concentration in region I are negligible, that is $n_1(r) \approx \text{const} = n_o$, and a very large

Figure 35. Distribution of the normalized oxygen concentration along the line "furnace bottom - dosing hole - environment". Conditions for calculations: $T_1 = 300$, $T_2 = 1000$ (curve 1) and 800 K (curve 2); $T_3 = 2500$ (curve 1) and 2000 K (curve 2); $l = 0.5$ cm, $v = 25$ cm s⁻¹, and $R^* = 1$ (curve 1) and 1.5 cm (curve 2).

drop in the concentration of oxygen occurs across the sample dosing hole, from 4 to 6 orders of magnitude. Therefore, it can be seen that region II is the actual limiting factor for the ingress of oxygen into the furnace.

RESULTS AND DISCUSSION

The numerical model described above was used to obtain three-dimensional distributions of oxygen molecules within both pyrolytic graphite coated and metal-lined (tungsten and tantalum) graphite atomizers. Although all calculations were performed for Perkin-Elmer HGA-type atomizers ($R = 0.3$ cm, $L = 1.4$ cm, and $a = 0.1$ cm) the computer program can be applied to any tube geometry.

Graphite Furnaces. Figures 36 and 37 show the calculated two-dimensional distributions of normalized oxygen concentration, $n_n(r, \varphi, z)$ [the calculated concentration at the dosing hole, $n(r=R, \varphi=0, z=0)$ was taken as the normalization factor]. Figure 36 shows the distribution of oxygen in the central atomizer cross-section and Fig. 37 shows the distribution of oxygen in the longitudinal section along the vertical tube diameter. The calculations were performed for isothermal tube conditions (that is, the degree of non-isothermality $\Delta = 1$) at $T = 2300$ K. For this figure there is only one source for the ingress of oxygen (*i.e.*, the sample dosing hole, and the concentration at the tube end, n_{end} , is set equal to zero). As expected, the calculated distributions are non-uniform with a pronounced localization of the region of maximum concentration near the sample dosing hole where the source of oxygen is located. However, the extent of non-uniformity, even for a temperature as high as 2300 K, is much less than is generally

central cross-section

Figure 36. Relative distributions of oxygen molecules within the central cross-section of an isothermal graphite furnace at $T = 2300 \text{ K}$; $n_{\text{end}} = 0$.

longitudinal section

Figure 37. Relative distributions of oxygen molecules within the longitudinal section of an isothermal graphite furnace at $T = 2300$ K; $n_{\text{end}} = 0$.

accepted: the concentration of oxygen at the tube bottom of the central cross-section is only 3.2 times lower than the concentration of oxygen near the sample dosing hole. Previous considerations of oxygen in graphite furnaces assumed that the concentration of oxygen near the tube wall was much lower than at its axis [78, 80]. The reason for the relatively low degree of non-uniformity is that the rate constant for the oxidation of pyrolytic graphite is fairly low even at elevated temperatures. The discontinuity that appears along the central axis of the atomizer is an artifact of the computational network used in the modelling. This artifact appears because of the fact that the tube radius, r , goes to zero at the tube axis.

The calculated distributions can also be visualized as grey-scale images, where black represents the maximum concentration of oxygen for any given distribution and white represents an absence of oxygen. The grey-scaled images were created using the *Mathematica*[™] software program (Wolfram Research Inc.) which is designed to facilitate the presentation and visualization of mathematical results. The conditions used for the calculation of the images given below are given in Table 19. For all of the distributions presented below, the image labelled (a) represents the longitudinal section along the vertical tube diameter, and the image labelled (b) represents the distribution of the concentration integrated along the length of the tube. The location of the images labelled (c) - (e) are given in Table 19. The temperature of the atomizer for all the calculations was 2300 K.

The imaged distributions for the situation illustrated in Figs. 36 and 37 ($\Delta = 1$, $T = 2300$ K, and $n_{\text{end}} = 0$) are given in Fig. 38. Figure 38(a) shows the distribution of oxygen molecules in the longitudinal section, while Figs. 38(c) - 38(e) show cross-

Table 19. Conditions used for the calculations of the imaged distributions of oxygen in tube-type atomizers for electrothermal atomization AAS.

Figure #	Substrate	Δ	$n_{\text{end}} / n_{\text{max}}$	location of cross-section		
				(c)	(d)	(e)
38	Graphite	1	0.0	0.0 L	0.5 L	0.9 L
39	Graphite	2	0.0	0.0 L	0.5 L	0.9 L
40	Graphite	1	0.1	0.0 L	0.5 L	0.9 L
43	Tantalum	2	0.0	0.0 L	0.2 L	0.5 L
44	Tantalum	1	0.1	0.0 L	0.5 L	0.9 L
45	Tungsten	1	0.1	0.0 L	0.5 L	0.9 L

Figure 38. Imaged representation of the distributions of oxygen molecules within an isothermal graphite furnace. Other conditions are given in Table 19.

sections in: (c) the central part of the tube ($z = 0$), (d) halfway between the tube centre and the tube end ($z = L/2$), and (e) near the end of the tube ($z = 0.9 L$). It can be seen from these results that the cross-sectional distribution of oxygen in a graphite furnace is practically uniform at distances greater than $L/2$ from the tube centre [Figs. 38(d) and 38(e)]. The greatest degree of non-uniformity is in the central cross-section [Fig. 38(c)]. This leads to the fact that the gradients in the distributions integrated along the tube length [Fig. 38(b)] are more uniform than those in the central cross-section [Fig. 38(c)]. Since all measured absorbance values in electrothermal atomization AAS are integrated along the tube length, Fig. 38(b) can provide information about the integrated effect of oxygen. The integrated distribution is only slightly non-uniform and the integrated concentration decreases monotonically as the distance from the sample dosing hole is increased.

The model, as constructed, allows the influence of factors such as the furnace non-isothermality and impurities in the purge gas on the distribution of oxygen, to be investigated. Figure 39 shows the structure of the oxygen molecular cloud for the same conditions as Fig. 38 with the exception that the degree of furnace non-isothermality, Δ , was taken to be 2. With this value of Δ , the temperature of the furnace along the tube length varies from a maximum value at the centre of the tube, 2300 K, to a minimum value at the end of the tube, 1150 K, following a Gaussian distribution (see Eqn. 22a). It can be seen from Fig. 39 that the main features of the distributions are the same as in the previous case but the distributions are slightly more uniform. The reason for this is that the introduction of temperature gradients leads to a decreasing effective furnace temperature. As can be seen from the fourth boundary condition, Eqn. 21a, the non-

Figure 39. Imaged representation of the distributions of oxygen molecules within a non-isothermal graphite furnace. Other conditions are given in Table 19.

uniformity of the distributions will mainly depend on the relationship k/D : the higher the ratio the more non-uniform will be the distributions. Because the rate constant, $k(T)$, decreases faster with a decrease in temperature than the diffusion coefficient the distributions become more uniform at lower temperatures.

The influence of the presence of oxygen in the external purge gas is shown in Fig. 40. This situation is simulated by arbitrarily taking a value of $n_{\text{end}}/n_{\text{max}} = 0.1$. All other conditions in Fig. 40 are otherwise the same as those in Fig. 38. It can be seen that taking into account the additional source of oxygen leads to a more uniform distribution of oxygen within the graphite furnace but does not produce any other notable changes in the oxygen distribution.

All of the results presented above show that the distribution of oxygen within a pyrolytic graphite coated graphite tube are relatively uniform even at temperatures as high as 2300 K. Calculations performed for lower temperatures yielded even more uniform distributions. The major reason for this is that the rate constant, $k(T)$, for the oxygen - pyrolytic graphite interaction is small even at higher temperatures. As can be seen in Table 18, the rate constants for the interaction of oxygen with metal tubes are significantly greater and should yield substantially different results. The next section will deal with the interaction between oxygen and metal-tube atomizers.

Metal Tubes. The distributions of oxygen molecules are shown in the central cross-section (Fig. 41) and the longitudinal section (Fig. 42) of a tantalum-lined tube. The conditions for the calculations were similar to those used to calculate the graphite furnace distributions shown in Figs. 36 and 37 with the exception that a non-isothermal situation is presented with the degree of non-isothermality, $\Delta \approx 2$. It can be seen that the

Figure 40. Imaged representation of the distributions of oxygen molecules within an isothermal graphite furnace. Other conditions are given in Table 19.

central cross-section

Figure 41. Relative distributions of oxygen molecules within the central cross-section of a non-isothermal Ta-lined furnace at $T = 2300$ K, $n_{\text{cnd}} = 0$, $\Delta = 2$.

longitudinal section

Figure 42. Relative distributions of oxygen molecules within the longitudinal section of a non-isothermal Ta-lined furnace at $T = 2300$ K, $n_{\text{end}} = 0$, $\Lambda = 2$.

distributions in tantalum-lined furnaces show a sharp decrease in concentration in both the cross-section (Fig. 41) and the longitudinal section (Fig. 42). Indeed the concentration of oxygen near the bottom of the furnace approaches zero (Fig. 41) and the majority of the oxygen molecules are confined to a region fairly close to the sample dosing hole (Fig. 42).

The imaged distributions for this situation are presented in Fig. 43. Figure 43(a) clearly shows that the distribution of oxygen molecules inside a tantalum-lined furnace have a cloud structure that is essentially limited to the central part of the furnace. When going from the central cross-section (c) to cross-section (e) at a distance of 0.7 cm from the centre of the tube it can be seen that there is a smoothing of the concentration gradients as well as a sharp decrease in the oxygen concentration.

Figure 44 shows the structure of the oxygen molecular cloud within the tantalum-lined HGA-type furnace when the secondary source of oxygen ingress into the furnace from impurities in the argon purge gas is taken into account. It is interesting to note that in this case the molecules are located almost exclusively near their sources: there are three local maxima in oxygen concentration, two at the ends of the furnace and one in the middle of the furnace near the dosing hole, with a low concentration of oxygen between these two extremes.

The distribution of oxygen within a tungsten-lined furnace is shown in Fig. 45. All other conditions are the same as for Fig. 44. The main features of this distribution are the same as for the case of the distributions in the tantalum-lined furnace. The only difference is that the oxygen clouds extend further into the furnace than in the case of the tantalum-lined furnace because of the lower value for the rate constant, $k(T)$.

Figure 43. Imaged representation of the distributions of oxygen molecules within a non-isothermal Ta-lined furnace. Other conditions are given in Table 19.

Figure 44. Imaged representation of the distributions of oxygen molecules within an isothermal Ta-lined furnace. Other conditions are given in Table 19.

Figure 45. Imaged representation of the distributions of oxygen molecules within an isothermal W - lined furnace. Other conditions are given in Table 19.

The results presented for the distributions of oxygen molecules within metal tubes show extremely non-uniform distributions. These are a direct consequence of the relatively high values of their rate constants for heterogeneous oxidation (see Table 18).

Estimation of the total number of free oxygen molecules. The mathematical model described above has allowed the three-dimensional results for a wide range of conditions to be calculated. However, these calculations are only possible with the assistance of a computer. Nevertheless, for simplified cases some useful estimations can be made directly. The estimation of the total number of free oxygen molecules because of their ingress through the sample dosing hole is given below. The assumptions that are made are: 1) the oxygen molecules are distributed uniformly along a length L^* within a tube-type atomizer and 2) all ingressing molecules disappear by heterogeneous reaction at the atomizer walls. Using these assumptions the following balance equation can be written:

$$J_{O_2} = n_{O_2} 2\pi R L^* k(T) \quad (36)$$

where the right-hand side of the equation gives the total removal of oxygen molecules because of their heterogeneous reaction with the entire inner surface area of the furnace, $2\pi R L^*$. Realizing that, with a uniform distribution of oxygen molecules, the total number of molecules is given by $N_t = \pi R^2 L^* n_{O_2}$, the above equation can be presented as:

$$N_t = J_{O_2} \frac{R}{2k(T)} \quad (37)$$

It can be seen that the total number of oxygen molecules is proportional to both the flux of the molecules and the radius of the tube and is inversely proportional to the rate

constant for the heterogeneous reaction. Using the previously calculated value for the flux of oxygen based on the experimental results of Sturgeon and Falk [87] ($J_{O_2} \approx 9.3 \times 10^{15} \text{ [molecules s}^{-1}\text{]}$) in addition to their experimental conditions ($T = 2100 \text{ K}$, $k(T) = 10.06 \text{ cm s}^{-1}$), Eqn. 25 gives $N_t \approx 1.4 \times 10^{14}$ molecules. With the assumption that these molecules are distributed uniformly over the entire furnace volume ($V = 0.19 \text{ cm}^3$) an estimation of the partial pressure of oxygen under these conditions can be obtained: $p_{O_2} (T = 2100 \text{ K}) \approx 5 \times 10^{-5} \text{ atm}$. This value can serve as a rough approximation of the p_{O_2} in pyrolytic graphite coated graphite furnaces under typical operating conditions. Although the value obtained is much higher than is generally accepted, it is in fact a direct consequence of experimental results [87]. An interesting feature of Eqn. 37 is that there are two factors that are temperature dependent, J_{O_2} and $k(T)$. Both of these factors increase with an increase in temperature (see Eqns. 27 and 32). Therefore, it is possible for the total number of oxygen molecules to increase with an increase in temperature. In order to analyze this point in more detail it is necessary to have better information about relationship between the inside atomizer temperature, which determines $k(T_3)$, and the temperature in the dosing hole, which determines the value of the diffusion coefficient for the ingress flux, $J(T_2)$. This information is not available at present.

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PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

CONCLUSIONS

The results obtained for pyrolytic graphite coated graphite furnaces show that: 1) the oxygen concentration is much higher; and 2) the distribution of the concentration much more uniform, than is generally accepted. In contrast to the distributions of oxygen calculated for graphite furnaces, those in metal tubes are strongly non-uniform and, when the ingress of oxygen through both the sample dosing hole and through the tube ends is accounted for, the molecular cloud consists of three independent structures. These structures are confined to the tube ends and the tube centre. An expression that allows the estimation of the total number, N_t , of oxygen molecules within a tube atomizer resulting from their ingress at a rate of J [molecules s^{-1}] through the sample dosing hole is obtained: $N_t = JR / (2k(T))$, where R is the tube radius and $k(T)$ is the temperature dependent rate constant for heterogeneous reactions with the tube wall. Using this equation an estimation of the oxygen partial pressure within a Perkin-Elmer HGA-type graphite furnace of $\sim 5 \times 10^{-5}$ atm at $T = 2100K$ was obtained. It is shown that, under typical operating conditions for Perkin-Elmer HGA-type atomizers, $J \sim 10^{14} - 10^{16}$ molecules s^{-1} . A protection coefficient to the ingress of oxygen through the sample dosing hole is introduced and it is shown that the flow of the external argon purge gas reduces the diffusional ingress of oxygen by a factor of $10^2 - 10^3$.

SUGGESTIONS FOR FUTURE RESEARCH

As a result of the research reported in this thesis, certain areas have been identified as requiring further investigation. In the development of the techniques for the atomization of solution residues by cathodic sputtering in a glow discharge, it was only possible to use test solutions containing one element in an aqueous solution. Any significant excess of acid, salt or another element leads to a matrix interference. A technique that is designed to minimize these interferences, radio-frequency cathodic sputtering in a glow discharge for atomic absorption spectrometry, is being developed in this laboratory. In the area of fundamental investigations of cathodic sputtering in a glow discharge, investigations have been initiated to measure the concentration gradients that exist within the cathodic sputtering atomizer. These measurements will be made using the charge-coupled device (CCD) imaging system that was introduced in Chapter 4. Preliminary investigations [105] have shown that the concentration gradients that exist can be considerable, and the measured distributions of analyte atoms are dependent on all three of the experimental conditions: applied power, argon flow rate, and argon pressure.

The use of the CCD imaging system is in its infancy and future applications of this technique are unlimited. One of the first areas that requires investigation is the atomization of those elements whose analysis line are below 280 nm. The SSF system of Gilmutdinov *et al.* [18, 19] cannot be used at these shorter wavelengths because the film that is used does not have a response in this region. The CCD camera on the other hand can respond down to 180 nm. However, this is just a future application of the CCD imaging system in its present state of development. What is more interesting is to

speculate on the future development of this technique. At present, the limitation of this technique is that it only provides images that are integrated along the length of the atomizer. However, there are indications that the concentration gradients along the length of the atomizer are greater than the concentration gradients across the atomizer [76, 77]. Therefore, a system that can measure the three-dimensional distribution of atoms in the analysis volume is required. Other workers [71, 106] have been able to reconstruct three-dimensional maps of spectroscopic emission from two-dimensional images that were taken at several different viewing angles. This approach cannot be applied to imaging of electrothermal atomizers where there is only one viewing angle available. The approach that appears to have the best chance of success is to image the signal transmitted by coherent forward scattering. The coherent forward scattering technique only produces a signal when resonant radiation interacts with the analyte atom in the presence of a magnetic field. By using a thin, flat magnetic field that is perpendicular to the optical axis, and by scanning this magnetic field along the length of the graphite tube, previous workers [76] have been able to measure the longitudinal distribution of analyte atoms. Combining the CCD-imaging technique with coherent forward scattering will allow two-dimensional images to be recorded for a given cross-section of the graphite furnace. These cross-sections can then be combined to give a three-dimensional map of the analyte atom distribution within the atomizer.

In Chapter 5 it was stated that the computer model of the oxygen distribution in tube atomizers was a first step in the attempt to describe fully the distribution of atomic and molecular species in these atomizers. A synopsis of the complete plan for modelling these distributions is given below. The complete model has been broken down into three

independent programs. These programs are outlined in order of their increasing complexity (and correspondingly their increasing uncertainty).

Part I - Oxygen. This model predicts the distribution of oxygen in a tube atomizer that is at its final temperature. There are two sources of oxygen that are considered: 1) the sample injection port, and 2) impurities in the argon sheath gas. Loss of oxygen from the atomizer is by diffusion out the ends and by reaction at the tube walls. The distribution of oxygen is completely defined by four variable parameters: 1) the diffusion coefficient (oxygen in argon), 2) and 3) the furnace temperature and degree of isothermality, Δ , and 4) the tube wall (*e.g.*, graphite) + oxygen rate constant:

All four of the above parameters are known so the predictions based on them are not subject to large uncertainties. The results of this model have been reported in this thesis.

Part II - Molecules. This model predicts the time-dependent distribution of metal oxides within a tube atomizer. Only one source of metal oxide is considered, the thermal dissociation of the initial sample. The metal oxides that are formed can be lost either by diffusion out the tube ends or by reaction at the tube walls. For this model the number of parameters needed to define the calculated distributions has increased to seven. These seven variable parameters are: 1) the sample spot size, 2) the supply function, 3), 4) and 5) the maximum furnace temperature, heating rate and degree of non-isothermality, Δ , 6) the diffusion coefficient (MeO_x in argon), and 7) the tube wall (*e.g.*, graphite) + MeO_x heterogeneous reduction rate constant:

Five of these seven parameters, the sample spot size, the diffusion coefficient, furnace temperature, heating rate and Δ , are known. The remaining two parameters, the supply function and the rate constant, require intelligent guesses. Fortunately, these guesses can be refined by the CCD-imaging results for molecular distributions. The model, with its supply and loss of metal oxide as outlined above, fits the interpretation of the distributions of aluminium oxide as presented in Chapter 4. A preliminary attempt to correlate the results of this model with the measured distributions is shown in Fig. 46. The two contour maps on the right-hand side are absorbance contour maps of aluminium oxide molecular distributions taken from Fig. 27. The two contour maps on the left-hand side are preliminary results of the computer modelling. It can be seen in Fig. 46 that the model predicts qualitatively the same features of the vaporization process that have been measured using the CCD-imaging system. However, there are several problems that are evident. For example, in order for this model to be dynamic (as opposed to the static oxygen model) it must incorporate a fourth dimension - time. Since the philosophy behind the construction of these models was to be able to do all calculations in a reasonable time on a personal computer, the incorporation of time into the model means that the increments in r , φ , and z must be larger. This leads to the problem that is evident in the centre of the contour maps which is, as $r \rightarrow 0$ there can be no solution. While the preliminary results have shown that the basis of the model is correct, its construction still needs improvement.

Part III - Analyte. This model predicts the time-dependent distribution of the analyte

(a)

(iii)

(b)

(v)

Figure 46. Preliminary correlation between the results of the computer modelling for: (a) the initial stages of atomization, and (b) after the absorbance maximum, and the results of the CCD-imaging taken from Fig. 26.

within a tube atomizer and requires the combined results of the previous two models. The source of analyte is the heterogeneous reduction of the analyte oxide at the tube wall. This requires the knowledge of the three dimensional distribution of the analyte oxide in the gas phase as predicted by Part II. Loss of the analyte atoms from the analysis volume is either by diffusion out the tube ends or by oxidation in the gas phase. The loss by homogeneous oxidation requires the knowledge of the three dimensional distribution of oxygen in the gas phase as predicted by Part I. With the increasing complexity of the problem the number of parameters needed to define the calculated distributions has now increased to eleven. These eleven variable parameters are: 1) -- > 9) all of the parameters from the other models (T and Δ are redundant), 10) the diffusion coefficient (Me in argon), and 11) the $\text{Me} + \text{O}_2$ rate constant:

The first nine parameters are taken from the previous models and, once the results of both of these models are acceptable, the parameters will be considered known. The diffusion coefficient is also known, however, the $\text{Me} + \text{O}_2$ rate constant requires an intelligent guess. Because of the increasing number of parameters this model is subject to the most uncertainty. Fortunately, once again, the results of the model can be correlated with the CCD-imaging results to refine our guess of the oxidation rate constant. This model is still under construction and further construction will await the finalized version of Part II.

APPENDIX

Calculation of the oxygen flux through the sample dosing hole. The ingress of oxygen into a tube furnace through the sample dosing hole is determined by diffusion of the molecules through three different regions each with its separate symmetry (Fig. 47) and diffusion equation.

Initially, the molecules must diffuse to the sample dosing orifice in the graphite cones from the surrounding atmosphere (Region I in Fig. 47). It is assumed that the environment surrounding the atomizer is at a constant temperature, T_1 . The diffusion in this region has spherical symmetry and is described by the following equation:

$$D_1 \left(\frac{d^2 n_1(r)}{dr^2} + \frac{2}{r} \frac{dn_1(r)}{dr} \right) = 0 \quad (38)$$

where D_1 is the diffusion coefficient for oxygen molecules and $n_1(r)$ is their distribution in region I. The general solution of Eqn. 38 is:

$$n_1(r) = n_0 - \frac{A}{r} \quad (39)$$

where it is assumed that at a large distance from the atomizer the oxygen concentration is constant and equal to n_0 (in a normal air environment $n_0 \approx 0.5 \times 10^{19} \text{ cm}^{-3}$), that is $n_1(r=\infty) = n_0$. The coefficient A can be determined by the boundary conditions that exist between Regions I and II.

The second step in the complete process is the diffusion of oxygen molecules through the sample dosing hole against the external flow of protective sheath gas (Region II in Fig. 47). It is assumed that this region is at a constant temperature, T_2 , and the argon sheath gas has a constant linear velocity, v . The possibility of reaction of the ingressing oxygen with the graphite cones is neglected. This means that, at any cross-

Figure 47. Model of the dosing hole area and the frame of reference used for the derivations given in the Appendix (note that the three regions have different frames of reference).

section of the cylindrical dosing hole, the distribution of oxygen molecules will be uniform and these distributions will only be dependent on the axial coordinate, x . With these assumptions the equation for the convective diffusion in region II will have the following form:

$$D_2 \frac{d^2 n_2(x)}{dx^2} + v \frac{dn_2(x)}{dx} = 0 \quad (40)$$

where D_2 is the diffusion coefficient in region II and $n_2(x)$ is the distribution of molecules in this region. The general solution of Eqn. 40 is:

$$n_2(x) = B + C \exp\left(-\frac{v}{D_2} x\right) \quad (41)$$

where x is the distance in the dosing hole from the outside edge of the dosing hole (see Fig. 47) and B and C are two coefficients that can be determined from the boundary conditions that exist between Region II and both Region I and III.

Finally, after passing through the dosing hole the molecules diffuse into the furnace volume (Region III in Fig 47) creating the ingressing flux. It is assumed that this region is at a constant temperature, T_3 , and that the cloud of molecular oxygen has a spherical symmetry with a complete absence of oxygen at a distance R^* from the dosing hole. With these assumptions the equation that describes the oxygen propagation through the furnace is:

$$D_3 \left(\frac{d^2 n_3(r)}{dr^2} + \frac{2}{r} \frac{dn_3(r)}{dr} \right) = 0 \quad (42)$$

where D_3 is the diffusion coefficient in Region III and $n_3(r)$ is the distribution of molecules in this region. The general solution of Eqn. 42 is:

$$n_3(r) = -\frac{E}{R^*} + \frac{E}{r} \quad (43)$$

where the boundary condition $n_3(r=R^*) = 0$ has been taken into account and E is a coefficient that can be determined from the boundary conditions that exist between Region II and III. In order to find the four unknown coefficients, A , B , C , and E , it is necessary to create four boundary conditions for the boundary between Region I and II and the boundary between Region II and III. The boundary conditions equate both the flux of oxygen and the concentration of oxygen at the interfaces of the three regions. These equalities for the interface of regions I and II are:

$$n_1(r=a) = n_2(x=0) \quad (44)$$

and

$$-2D_1 \frac{dn_1(r=a)}{dr} \Big|_{r=a} = D_2 \frac{dn_2(x=0)}{dx} \Big|_{x=0} + n_2(x=0) v \Big|_{x=0} \quad (45)$$

The boundary conditions at the interface of regions II and III are:

$$n_2(x=l) = n_3(r=a) \quad (46)$$

and

$$2D_3 \frac{dn_3(r=a)}{dr} \Big|_{r=a} = D_2 \frac{dn_2(x=l)}{dx} \Big|_{x=l} + n_2(x=l) v \Big|_{x=l} \quad (47)$$

By substituting the three general solutions (Eqns. 39, 41, and 43) into the boundary conditions Eqns. 44 - 47, we obtain the following equations containing the unknown coefficients, A , B , C , and E :

$$n_0 - \frac{A}{a} = B + C \quad (48)$$

$$-2D_1 \frac{A}{a^2} = \nu B \quad (49)$$

$$B + C \exp\left(-\frac{\nu}{D_2} l\right) = E \left(\frac{1}{a} - \frac{1}{R^*} \right) \quad (50)$$

$$-2D_3 \frac{E}{a^2} = \nu B \quad (51)$$

By definition the flux across the interface between Regions II and III is the flux of oxygen into the furnace. This diffusional flux is presented as follows:

$$J = -2\pi a^2 D_3 \frac{dn_3(r=a)}{dr} = 2\pi D_3 E \quad (52)$$

Solving Eqns. 48 - 51 for E and substituting E into Eqn. 52 yields:

$$J = \frac{2\pi a n_0}{\frac{1}{D_1} + \frac{1}{D_2} \frac{2l}{a} \frac{1}{p} (e^p - 1) + \frac{1}{D_3} \left(1 - \frac{a}{R^*} \right) e^p} \quad (53)$$

From the system of equations (48 - 51) the other coefficients, A, B, and C, can also be found. Substitution of these coefficients into Eqns. 39, 41, and 43 yields the total distribution of oxygen along the line "outside environment - dosing hole - furnace". The distributions obtained for typical conditions are shown in Fig. 35.

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